Electrochemical Processes Within the Slimes Layer of Lead Anodes During Betts Electrowinning

by

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Abstract

In the Betts process for lead electrorefining the noble impurities originally present in the bullion form a strong and adherent layer of slimes. Within this layer the established ionic concentration gradients can lead to secondary reactions. The following processes were analyzed from a thermodynamic perspective: (A) hydrolysis of the acid (B) precipitation of secondary products (C) reaction of noble compounds.

The nature of the concentration gradients within the slimes layer and related secondary processes was studied by using transient electrochemical techniques which include: (A) current interruption, (B) AC impedance, and (C) a variation of SACV (Small Amplitude Cyclic Voltammetry). These studies were complemented by: (A) physico-chemical data on electrolyte properties, (B) "in-situ" and "industrially recovered" slimes electrolyte compositions, (C) SEM and X-ray diffraction analysis of the slimes layer. For comparison purposes the electrochemical behaviour of "pure" Pb electrodes was also studied.

Upon current interruption the anodic overpotential decays, first abruptly, (as the uncompensated ohmic drop disappears) and then slowly (due to the presence of a back E.M.F. created by ionic concentration gradients that decay slowly). Current interruption measurements showed that: (A) concentration gradients exist across the slimes layer, (B) inner solution potentials within the slimes layer can be larger than those measured from reference electrodes located in the bulk electrolyte, (C) secondary products can shift the inner solution potential to negative values which reverse upon re-dissolution and (D) ionic diffusion is seen upon current interruption but it is complex and difficult to model due to the presence of processes that can support the passage of internal currents.

The anodic polarization components were obtained by analyzing the potential and current dependance upon application of a small amplitude sinusoidal waveform. This dependance was found to be linear in the low overpotential region (< 250mV). Thus, upon subtraction of the uncompensated ohmic drop, the remaining polarization is due to the "apparent" ohmic drop of the slimes electrolyte and to liquid junction and concentration overpotentials. These components are directly linked to the electrolysis conditions and to the slimes layer structure. Furthermore, the ratio of these components can be used to obtain the point at which the precipitation of secondary products starts. Changes in this ratio can also be related to the anodic effects caused by the presence of addition agents.
AC impedance measurements performed in the presence of a net Faradaic current showed that the impedance increases uniformly as the slimes layer thickens up to the point at which noble impurities start to react. Three electrical analogue models were used to describe the impedance spectra.

A steady-state mathematical model that predicts concentration and potential gradients across the slimes layer was developed. Only when a position dependent eddy diffusion term was incorporated in the numerical solution, were reasonable local ionic concentrations and overpotentials obtained.
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Nomenclature

\[ a_i \] molar activity coefficient of species i: \[ a_i = \gamma_i C_i \]

\[ a_{Pb^{2+}}(x) \] Activity of Pb\(^{2+}\) as a function of the distance from the slimes/electrolyte interface.

\[ a_{Pb^{2+}}(\text{bulk}) \] Activity of Pb\(^{2+}\) in the bulk electrolyte (i.e. outside the slimes/bulk electrolyte interface).

\[ b \] slope, mV (Eq. 5, Chapter 6).

\[ B_i \] Frequency independent parameter, \( [\Omega \text{ cm}^2 \text{ sec}^{-1/2}] \), (Eq. 6, Chapter 5)

\[ b_1, b_2, b_0 \] Frequency independent parameters, \( [\Omega \text{ cm}^2 \text{ sec}^{-1/2}] \), (Eq. 10, Chapter 6)

\[ b_D \] Capacity of the electrical double layer, \([\mu \text{F cm}^{-2}]\)

\[ C_{di} \] Geometrical capacitance, \([\mu \text{F cm}^{-2}]\)

\[ C^* \] Frequency independent parameter defined in Eq. 4, Chapter 5.

\[ C_{Pb^{2+}} \] Bulk Pb\(^{2+}\) concentration, \([\text{mol cm}^{-3}]\)

\[ C_{i0} \] Concentration of species i at the electrode surface (at \(x=0\)), \([\text{mol cm}^{-3}]\)

\[ C_i \] Concentration of species i, \([\text{mol cm}^{-3}]\):

Species a: Pb\(^{2+}\)  
Species b: SiF\(_6\)^{2-}  
Species c: H\(^+\)

\[ C_{w} \] Concentration of species i in the bulk electrolyte (at \(x=\infty\)), \([\text{mol cm}^{-3}]\)

\[ C_{PE1} \] Analogue parameter that represents the distributed nature of the anode/slimes and the slimes/slimes electrolyte interface

\[ C_{PE2} \] Analogue parameter that represents the presence of a distributed capacitance generated by the concentration gradients present in the slimes electrolyte.

\[ D \] Diffusion coefficient, \([\text{cm}^2 \text{ sec}^{-1}]\)

\[ D_i \] Diffusion coefficient of species i, \([\text{cm}^2 \text{ sec}^{-1}]\)

\[ D^e \] Eddy diffusion constant, \([\text{cm}^2 \text{ sec}^{-1}]\)

\[ \bar{D}_{Pb^{2+}} \] Mean diffusion coefficient for Pb\(^{2+}\) ions, \([\text{cm}^2 \text{ sec}^{-1}]\)

\[ D_i^m \] Molecular diffusion coefficient of species i, \([\text{cm}^2 \text{ sec}^{-1}]\)

\[ D_i \] Overall diffusion coefficient of species i, \([\text{cm}^2 \text{ sec}^{-1}]\) : \[ D_i = D_i^m + D^e \]

\[ e(t) \] Potential as a function of time

\[ E_{\text{control}} \] Difference in potential between the reference and working electrodes under potentiostatic control.

\[ F \] Faraday's constant, 96487 C eq\(^{-1}\)

\[ I_{corr} \] Steady-state corrosion current density, \([\text{Amp m}^{-2}]\)

\[ I_o \] Exchange current density, \([\text{Amp m}^{-2}]\)
Current density at the electrode surface, \([\text{A cm}^{-2}]\).

Superficial current density at the anode/slimes interface as a function of the electrolysis time, \([\text{A cm}^{-2}]\).

Total molar ionic strength \(I_t = 0.5(M_{12}(v_1Z_1^2 + v_2Z_2^2) + M_{23}(v_2Z_2^2 + v_3Z_3^2)) = 4\times[\text{PbSiF}_6] + 3\times[\text{H}_2\text{SiF}_6]\)

Molar ionic strength of \(\text{H}_2\text{SiF}_6\) in a \(\text{H}_2\text{SiF}_6\)-\(\text{PbSiF}_6\) mixture = \(3\times[\text{H}_2\text{SiF}_6]\)

Molar ionic strength of \(\text{PbSiF}_6\) in a \(\text{H}_2\text{SiF}_6\)-\(\text{PbSiF}_6\) mixture = \(4\times[\text{PbSiF}_6]\)

Imaginary number, \(\sqrt{-1}\)

Characteristic length of the electrode, \([\text{cm}]\)

Slope defined in Eq. 4, Chapter 5, \([\text{sec}^{-0.5}]\)

Molality, \([\text{mol of solute/Kg of solvent}]\)

Molarity, \([\text{mol/l}]\)

Water mol fraction with respect to species \(i\).

Number of electrons involved in electrode reaction.

Statistical parameters defined in Appendix 9.

Analogue parameter that represents charge transfer resistances associated with the lead dissolution processes, \([\Omega\text{cm}^2]\).

Analogue parameter related to the DC conductivity of the slimes electrolyte, \([\Omega\text{cm}^2]\).

Analogue parameter related to the DC resistance of the slimes electrolyte, \([\Omega\text{cm}^2]\).

Analogue parameter related to the charge transfer resistance associated with the lead dissolution process, \([\Omega\text{cm}^2]\).

Resistance of the electrolyte present between the reference electrode and the anode boundary layer, \([\Omega\text{cm}^2]\).

Charge transfer resistance, \([\Omega\text{cm}^2]\).

Diffusional (DC) resistance, \([\Omega\text{cm}^2]\).

Resistance of the film created by the addition agents, \([\Omega\text{cm}^2]\).

"Apparent" average resistivity of the electrolyte present across the slimes layer, \([\Omega\text{cm}^2]\).

Polarization resistance, \([\Omega\text{cm}^2]\).

"Uncompensated" ohmic resistance, \([\Omega\text{cm}^2]\).

Universal gas constant, \([8.3114 \text{ J mol}^{-1} \text{ deg}^{-1}]\)

Stoichiometric coefficient in electrode reaction

Absolute temperature, \([\text{K}]\)

Number of cations and anions into which a mole of electrolyte dissociates.

Solution composition, \([\text{wt}\% \text{H}_2\text{SiF}_6]\)

Distance from the slimes/bulk electrolyte interface at which point \(D^e\) is to be computed, \([x_i \leq x_{\text{total}}]\), \([\text{mm}]\)
\( x_{\text{total}} \) Total slimes thickness, [mm]

\( x \) Mixing fraction (Eq. 22, Chapter 7).

\( Z \) Charge number of species \( i \), [eq mol\(^{-1}\)]

\( Z(\omega) \) Impedance as a function of frequency, [\( \Omega \text{cm}^2 \)]

\( Z_0 \) Imaginary component of the impedance, [\( \Omega \text{cm}^2 \)]

\( Z_R \) Real component of the impedance, [\( \Omega \text{cm}^2 \)]

\( |Z| \) Absolute value of the impedance, [\( \Omega \text{cm}^2 \)]. \( |Z| = \sqrt{Z_R^2 + Z_0^2} \)

\( Z_{\text{a/se}} \) Faradaic impedance at the lead anode/slimes electrolyte interface.

\( Z_{\text{a/sl}} \) Electronic impedance at the lead anode/slimes interface.

\( Z_{\text{CPE}} \) Impedance of the CPE analogue element.

\( Z_{\text{ZARC}} \) Impedance of the ZARC analogue circuit.

\( Z_{\text{dc}}(t) \) Changes in DC impedance as a function of time.

\( Z_{\text{sl/be}} \) Faradaic impedance at the slimes/bulk electrolyte interface.

\( Z_{\text{sl/se}} \) Faradaic impedance at the slimes/slimes electrolyte interface.

\( Z_{\text{w,sl}} \) Warburg ionic diffusional impedance in the slimes electrolyte/bulk electrolyte interface.

\( Z_{\text{w}} \) Warburg ionic diffusional impedance throughout the slimes electrolyte.

\([M^{m}]\) Ionic concentration of ions \( M \), [M].

\([M^{m}]_b\) Ionic concentration of ions \( M \) at the slimes/bulk electrolyte interface, [M].

\([M^{m}]_e\) Ionic concentration of ions \( M \) at the anode/slimes electrolyte interface, [M].

\([M^{m}]_r\) Concentration of ions \( M \) at the anode/slimes interface with respect to their concentration at the slimes/bulk electrolyte interface (e.g. \([Pb^{+2}]_r = \frac{[Pb^{+2}]}{[Pb^{+2}]_b}\)).

\( I_t \) Total molar ionic strength = \( 4\times[PbSiF_6] + 3\times[H_2SiF_6] \)

\([H_2SiF_6]_t\) \( H_2SiF_6 \) concentration at the total molar ionic strength of \( H_2SiF_6-PbSiF_6 \) mixtures, [M].

\([PbSiF_6] + [H_2SiF_6]\) \( PbSiF_6 \) and \( H_2SiF_6 \) concentrations in the electrolyte mixtures, [M].

\([PbSiF_6]_t\) \( PbSiF_6 \) concentration at the total molar ionic strength of \( H_2SiF_6-PbSiF_6 \) mixture, [M].

\( \alpha \) and \( \beta \) Arbitrary positive constants whose value depends on the electrolysis conditions: \( \alpha \) [mm] and \( \beta \) [cm\(^2\) sec\(^{-1}\)] (Eq. 31, Chapter 7).

\( \beta_a \) Anodic Tafel slope

\( \beta_c \) Cathodic Tafel slope.

\( \delta \) Thickness of the hypothetical Nernst boundary layer, [cm]
\[ y, \text{ Individual molar activity coefficient.} \]
\[ \gamma, \text{ Mean activity coefficient} \]
\[ \Delta \Phi, \text{ Migration or "liquid junction" potential, [mV]} \]
\[ \Phi_e, \text{ Maximum value of the migration potential for a fixed slimes thickness, [mV]} \]
\[ \Phi_1, \Phi_2, \text{ Dimensionless parameters in Eqs. 4 and 5, Chapter 5.} \]
\[ \Psi_{\text{zc}}, \text{ Fractional element in CPE analogue element} \]
\[ \Lambda_{\text{mix}}, \text{ Equivalent conductivity of the } H_2\text{SiF}_6\text{-PbSiF}_6 \text{ mixtures, [cm}^2 \text{ eq}^{-1} \Omega^{-1}] \]
\[ \Lambda_{H_2\text{SiF}_6} \text{ and } \Lambda_{\text{PbSiF}_6}, \text{ Equivalent conductivity of the pure } H_2\text{SiF}_6 \text{ and PbSiF}_6 \text{ solutions at the total ionic strength of } H_2\text{SiF}_6\text{-PbSiF}_6 \text{ mixtures, [cm}^2 \text{ eq}^{-1} \Omega^{-1}] \]
\[ \lambda, \text{ Individual equivalent conductivity of ions } i, \text{ [cm}^2 \text{ eq}^{-1} \Omega^{-1}] \]
\[ \eta_{\text{ac}}, \text{ Activation overpotential, [mV]} \]
\[ \eta_{\text{u}}, \text{ "Uncompensated" ohmic drop, [mV]} \]
\[ \eta_{\text{A}}, \text{ Anodic overpotential, [mV]} \]
\[ \eta_{\text{c}}, \text{ Concentration overpotential, [mV]} \]
\[ \eta_{\text{tot}}, \text{ Total ohmic drop across the slimes layer, [mV] (Eq. 32, Chapter 7)} \]
\[ \eta_{\text{i}}, \text{ Concentration overpotential due to } Pb^{2+}, \text{ [mV] (Eq. 33, Chapter 7)} \]
\[ \eta_{\text{A}}, \text{ Steady-state anodic overpotential from the solution of the Nernst-Planck flux equations, [mV] (Eq. 34, Chapter 7)} \]
\[ \eta, \text{ Dynamic viscosity (coefficient of), [cP]} \]
\[ \kappa, \text{ Electrical conductivity, [mmho cm}^{-1}] \]
\[ \kappa (x_i), \text{ Electrical conductivity changes as a function of the distance from the anode/slimes interface, } x_i, \text{ [mmho cm}^{-1}] \]
\[ \kappa_{\text{mix}}, \text{ Electrical conductivity of } H_2\text{SiF}_6\text{-PbSiF}_6 \text{ mixtures, [mmho cm}^{-1}] \]
\[ \kappa_{\text{PbSiF}_6}, \text{ Electrical conductivity of PbSiF}_6 \text{ at the total ionic strength of } H_2\text{SiF}_6\text{-PbSiF}_6 \text{ mixtures, [mmho cm}^{-1}] \]
\[ \kappa, \text{ Bulk electrolyte electrical conductivity, [mmho cm}^{-1}] \]
\[ \mu, \text{ Absolute ionic mobility of ion } i, \text{ [cm}^2 \text{ sec}^{-1} \text{ volt}^{-1}] \]
\[ \nu, \text{ Kinematic viscosity (coefficient of), [cSt].} \]
\[ \rho_{\text{m}}, \text{ Specific electrical resistivity of the electrolyte entrapped within the slimes layer, [rad cm].} \]
\[ \rho, \text{ Solution density, [g cm}^{-3}] \]
\[ \sigma_{\text{w}}, \text{ Warburg Coefficient, [} \Omega \text{ cm}^2 \text{ sec}^{-0.5}] \]
\[ \tau, \text{ Relaxation time, [sec]} \]
\[ \tau_{\text{D}}, \text{ Dielectric relaxation time of the bulk electrolyte, [sec], } \tau_{\text{D}}=C_{\text{sp}}.R_b \]
\[ \tau_{\text{f}}, \text{ Relaxation time of the Faradaic reaction taking place upon discharge of the double layer, [sec]} \]
\( \tau_m \) \hspace{1cm} \text{Relaxation time of the diffusional processes across the hypothetical Nernst boundary layer, [sec].}

\( \tau_R \) \hspace{1cm} \text{Relaxation time required to equilibrate the charge of the electrical double layer, [sec].}

\( \omega \) \hspace{1cm} \text{Frequency, [rad sec}^{-1}\text{].}

\( \omega_{\text{min}} \) \hspace{1cm} \text{Minimum frequency at which the AC impedance was acquired (or analyzed), [rad sec}^{-1}\text{].}

\( \omega_{\text{max}} \) \hspace{1cm} \text{Maximum frequency at which the AC impedance was acquired (or analyzed), [rad sec}^{-1}\text{].}

**Abbreviations**

AAS \hspace{1cm} \text{Atomic Absorption Spectroscopy}

AC \hspace{1cm} \text{Alternating current}

BEP \hspace{1cm} \text{Betts electrorefining process}

cd \hspace{1cm} \text{Current density}

C.P.V. \hspace{1cm} \text{Cathode polarization voltage}

CPE \hspace{1cm} \text{Constant phase angle element}

DC \hspace{1cm} \text{Direct current}

E.M.F. \hspace{1cm} \text{Electromotive force}

EPMA \hspace{1cm} \text{Electron probe microanalysis.}

FFT \hspace{1cm} \text{Fast Fourier transform.}

FRA \hspace{1cm} \text{Frequency Response Analyzer}

PCR \hspace{1cm} \text{Periodic current reversal}

R.M.S. \hspace{1cm} \text{Root mean square}

SACV \hspace{1cm} \text{Small amplitude cyclic voltammetry}

SEI \hspace{1cm} \text{Solartron Electrochemical Interface}

SSM \hspace{1cm} \text{Secondary solidified material}

SEM \hspace{1cm} \text{Scanning Electron Microscopy}

SSR \hspace{1cm} \text{Solid State Relay}
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**Introduction**

The Betts process for lead electrowinning treats lead bullion containing 1-4% impurities. Antimony, arsenic, bismuth, and a variety of minor metals including silver and gold are amongst these impurities. The bullion is cast into anodes of about 1 m$^2$, weighing between 200 and 300 kg. These anodes are electrolytically corroded with the simultaneous plating of relatively pure lead (>99.99% Pb) on cathodes (pure lead starting sheets) of about the same area as the anodes. The electrolyte is typically an aqueous lead fluosilicate solution (0.2 to 0.5 M PbSiF$_6$) containing excess fluosilicic acid (0.5 to 0.8 M H$_2$SiF$_6$). The impurities are largely retained on the anode scrap as an adhering slime. Betts refining is the preferred lead refining process when bismuth must be separated from lead. Since bismuth forms a solid solution with lead at concentrations normally found in lead bullion, it is necessary for the anode slimes to adhere so that they can cement out the bismuth from the electrolyte after it has corroded with lead\(^1\).

This study was designed to obtain a fundamental understanding of the anodic processes that take place upon electrochemical dissolution of lead anodes as used in the Betts process. During the refining of lead by the Betts process, ideally, only lead would dissolve and the noble impurities would remain unreacted and attached to the anode forming a strong, adherent, and highly porous slimes layer. The extent to which this ideal operation can be achieved in practice is a complex function of the lead anode physical metallurgy and of the electrolysis conditions. This dissertation has focused on studying how the electrolysis conditions affect the behavior of typical lead anodes. The main objectives of this research were:

1) To analyze from a thermodynamic perspective, the conditions under which hydrolysis of the acid, precipitation of secondary products, and dissolution of noble compounds can take place.

2) To obtain the components of the anodic polarization and relate them with:
   a) transport processes across the slimes layer
   b) hydrolysis and secondary products precipitation
   c) noble compounds dissolution
   d) bulk electrolyte composition (including addition agents)
   e) current density.

3) To formulate a mathematical model that can be used to predict concentration and potential gradients across the slimes layer.

---

1 If bismuth does not corrode with lead it would enrich at the anode surface until lead corrosion is stopped.
The single, most important parameter to study was found to be the ionic concentration gradients in the electrolyte entrapped within the slimes layer. One of the direct effects of the presence of these concentration gradients is the precipitation of secondary products within the slimes layer. The characterization of these secondary products and their effect on the dissolution of noble compounds was studied by several methods. Among these, transient DC (direct current) and AC (alternating current) electrochemical techniques were used to find the extent to which precipitation of secondary products and entrapped electrolyte concentration gradients affect the refining cycle. The electrolyte composition within the slimes and the accompanying potential gradient were obtained by incorporating tap holes in typical lead anodes. The study and characterization of this entrapped electrolyte required the use of several analytical procedures, including titrimetric analysis and atomic absorption spectroscopy. The characterization of the physico-chemical properties of this entrapped electrolyte was achieved by measuring the electrical conductivity, viscosity, and density of synthetically prepared solutions whose compositions approximated those of inner electrolytes as found from anode tap holes or calculated from theory. In addition to this, sampling of the slimes layer and characterization of the contained secondary products was an important part of this work. Scanning electron microscopy and X-ray diffraction techniques were employed to detect the phases and elements in the slimes layer.

A mathematical model based on the Nernst-Planck flux equations was developed to describe the establishment of concentration gradients within the slimes layer. This model predicts these gradients when combined with relationships between concentrations and fundamental solution properties (i.e. activities, mobilities, diffusion coefficients). The full application of this model will occur only when more experimental data on these fundamental properties become available.

To explain the presence of secondary products and their stability range from a thermodynamic perspective, computer generated Eh-pH diagrams were drawn.
Chapter 1 Literature Review

I Introduction

This chapter deals mainly with the Betts electrorefining process for lead, as described in the literature. In this process lead bullion is purified by transferring most of the lead from a soluble anode to a cathode through a lead-containing electrolyte while leaving behind impurities in an adherent anode slime. The electrochemistry of this process involves the properties of anode slimes and of entrained electrolyte. Thus, the processes of anodic corrosion of lead and transport of lead ions through the entrained electrolyte are essential to the understanding of the Betts process. In this chapter, the physical metallurgy of lead anodes, which affects the slimes adherence is also discussed.

II Metallurgy of Lead

Lead is an ancient metal. It was used by the Romans for components of their water distribution systems, and for that purpose it had to be malleable and ductile [1]. The ancients made lead of acceptable purity probably by smelting lead ores under conditions that prevented arsenic, antimony, and other hardening elements from reducing to the metallic phase. This could be accomplished in most cases by producing high lead slags such as those still produced in fire assaying. In those days it was necessary to avoid excessive copper in the ore, but arsenic, antimony, bismuth, nickel, iron, etc. were reliably held in the slag by maintaining the high oxidizing conditions of lead silicate based slags. Lead recoveries were low - not better than 85% from the highest grade hand picked galena ore. When high lead recoveries were found to be obtainable by coke-based blast furnace reduction, lead so produced was too hard, usually because of its copper, antimony, and arsenic content. The function of lead refining became both a softening process and a method of recovering silver and gold [2].

Nowadays the extraction process can be conveniently portrayed in the two-step flowsheet shown in Fig. 1. The first step involves bullion production from the sulphide concentrate and the second step the refining of bullion to the final product.

The conventional route for bullion production requires sintering of the concentrate to produce a lead oxide containing product, which is then reduced in a blast furnace with metallurgical coke to produce lead bullion. The KIVCET
and QSL processes represent two relatively recent commercial developments [3] that replace both the sintering-blast furnace combination with a single furnace that treats concentrates, and reduce both the costs of lead smelting and the environmental impact.

The KIVCET [4] process replaces the sintering/blast furnace operations with a flash smelting step. In this process, lead sulphide is oxidized to lead bullion and sulphur dioxide in a stream of oxygen. In a second step, the bullion and slag flow under a weir to an electrically heated settling hearth where coke breeze or coal is added to reduce the residual lead oxide in the slag and produce a final bullion (for refining) as well as a low-lead slag.

![Fig. 1 Flowsheet for Lead Extraction from Sulphidic Concentrates.](image)

The QSL [5] process consists of a long, horizontal, tubular, brick-lined converter in which lead concentrates are pelletized and injected near one end into a bath containing lead bullion, lead oxide-containing slag, and lead sulphide matte. Oxygen is blown into the bath in the feed injection (and lead-bullion discharge) zone where it ultimately oxidizes sulphide sulphur to sulphur dioxide gas. Slag is tapped from the far end of the reactor after passing through a zone where reducing coal-air mixtures are injected through tuyeres to lower its lead oxide content.
The refining of bullion is carried out by either a pyrometallurgical route or a combined pyrometallurgical/electrometallurgical route. Comparisons between these two routes show that the pyrometallurgical route is usually used when ores with low Bi content are treated [7,8]. The generalized pyrometallurgical flowsheet is shown in Fig. 2. This process consists of a series of steps which capitalize on a complex series of phase relationships to extract all the impurities contained in the lead bullion down to very low levels. Reviews on the chemistry and technology of these refining steps are available in the literature [4,6,9-11].

The combined pyrometallurgical/electrometallurgical route is shown in Fig. 3. Here, copper dressing is performed to remove the bulk of the copper as a combination of matte and arsenide - antimonide for further treatment, thus allowing for the removal of some arsenic and antimony. Arsenic and antimony are sometimes reduced further as sodium arsenate - antimonate dross by oxidizing in the presence of caustic soda, because their levels in bullion must be controlled to produce suitable anodes for successful electrorefining practice.

1 Fig. 2 was taken as is from the literature and does not contain inputs required for material balances.
Electrorefining is carried out in either a fluosilicic, fluoboric or sulphamic acid electrolyte and produces a commercial lead cathode product and an anode with an adhering slime [12]. The purity of the produced lead is usually higher than 99.99% [13]. The slimes, representing only 2 to 4% of the anode weight, are treated by a variety of processes to recover silver, copper, antimony, gold, bismuth, and sometimes tin and indium [14-21].

Processes that entirely avoid smelting (and its attendant gas and dust treatment systems and associated environmental risks), utilizing hydrometallurgical/ electrometallurgical flowsheets, have also been proposed to replace the current technology [23]. These include (a) the U.S. Bureau of Mines ferric chloride leach process [24] which recovers lead via the molten salt electrolysis of PbCl₂, (b) the Minemet Recherche ferric chloride leach process [25] which recovers lead from chloride leach solutions using aqueous electrolysis and (c) the U.S. Bureau of Mines process [26] for leaching lead concentrates in waste fluosilicic

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1 Nitric acid media are not suitable because, in the presence of free acid, nitrate is reduced (to nitric oxide gas) at the cathode, preferentially to plating of lead. At higher pH, where the nitrate ion is much more inert to reduction, the electrical conductivity of the electrolyte is much too low for an economic practice.
acid with an oxidant (hydrogen peroxide or lead peroxide) followed by aqueous electrolysis from the fluosilicic acid leach solution. All of these processes have been piloted, but none has been commercialized.

III Plant Practice in Lead Electrorefining

A detailed description of the Betts Electrorefining Process (BEP) can be found in Betts' book [27] and numerous patents [28-32]. The fundamentals of the process described there remain applicable to all the plants which electrorefine lead nowadays.

The BEP process is used in Canada [33-36], China [22,37,38], East Germany [39], Italy [40-42], Japan [43-51], Peru [52-54], Rumania [55,56], Russia [57-59], U.S.A. [60] and West Germany [61-63]. The average annual production of lead by BEP is approximately 1,000,000 tons. Since the production of refined lead in the non-socialist countries (for which good figures are available) is close to 4,700,000 tons per year [64], it can be assumed that up to about 20% of the world lead production is refined by the BEP. Two variations of the BEP, the sulphamic acid and the fluoboric acid processes are operated in Italy [41] and in West Germany [61] respectively.

The Betts Electrorefining Process normally utilizes a fluosilicic acid (H₂SiF₆) electrolyte containing lead fluosilicate to electrorefine impure lead anodes into pure lead cathodes. The fluoborate and the sulphamate processes are identical to the fluosilicate process except for the substitution of the electrolyte. Fluoboric acid has not been used extensively due to its relatively high cost. HBF₄ is a stable acid with a good electrolytic conductivity and a high solubility of the lead salt. It is also used in lead plating baths [65-67], lead fluoborate-fluoboric acid rechargeable batteries and in the recovery of lead from spent batteries [68-72].

The sulphamic acid process has two main limitations when compared to the fluosilicic acid process [40,58,73]: firstly, sulphamic acid decomposes rapidly at current densities larger than 100 Amp/m² resulting in high reagent replacement cost; secondly, the free acid is a crystalline solid of limited solubility, and limited ionization in aqueous solution, leading to a low conductivity of sulphamic acid solutions (at most, half of the conductivity of equivalent fluosilicic acid solutions). This results in larger power costs in refining. The significant advantage of the

1 Commercialization of any new lead processes faces a lack of need for plant expansion in this industry and so must be justified on the basis of conversion or replacement of existing capacity.
sulphamic acid process is that it is the most efficient process for the removal of tin from impure lead (Sn remains in the slimes) [74-77]. Plants that use the fluosilicic process remove Sn prior to electrolysis by using the Harris process [78]. When anodes containing significant Sn concentrations are refined by the Betts process, tin dissolves with lead at the anode and co-deposits at the cathode. The lead-tin alloy may be sold, or some post treatment of the cathodes is necessary to remove Sn [79].

The wide use of $\text{H}_2\text{SiF}_6$ in lead electrorefining is due to its low cost. Fluosilicic acid is produced as a by-product of the treatment of phosphate rock in fertilizer manufacture [80]. Fluorides and silica contained in phosphate rock form fluosilicate and are separated from the fertilizer product. Fluosilicic acid is also produced as a by-product during the dissolution of apatite with sulphuric acid [54,80]. During the electrorefining operation, fluosilicic acid is consumed by entrapment in the anode slimes and by volatilization from the surface of the electrolyte. The acid develops significant vapour pressures through volatile decomposition products according to the reaction,

$$H_2\text{SiF}_6 \rightarrow 2\text{HF}(g) + \text{SiF}_4(g)$$

SiF$_4$ and HF are both corrosive and toxic and are removed from the tankhouse atmosphere by adequate ventilation.

Table 1 shows some of the operating parameters of various lead electrorefining plants. The wide variation in electrolysis conditions seen in this table does not seem to have a strong influence on the final quality of the refined lead. For example, lead concentrations in the electrolyte can be varied between 30 and 270 g/l without affecting seriously the refined lead quality. The electrolyte recirculation rates are also varied widely, with no apparent correlation to other operating parameters. Extremely high electrolyte velocities might improve mass transfer across electrode boundary layers, but can also nullify the additive effects, worsening the deposit quality and causing short circuits [81].

Table 1 also shows that the current densities employed in the Betts process fall in the range of 120 to 230 Amp/m$^2$. Higher current densities have been achieved through the use of galvanodynamic techniques such as current modulation and periodic current reversal (PCR). The current modulation technique consists of decreasing the current density (e.g. from 220 to 160 Amp/m$^2$) in small steps [33,87]. Each constant current density step is determined on the
basis of an anode overpotential value which increases as the slimes layer thickens and decreases when the current density is reduced. The upper limit for the anode overpotential is usually determined by Bi dissolution from the anode. Fig. 4 shows the current density program that can be applied to the electrorefining circuit without reaching the critical overpotential value for Bi dissolution. The higher average current density possible with current modulation reflects in a shorter electrorefining cycle and higher refinery production.

Periodic current reversal (PCR) in lead electrorefining is widely employed in China [38]. PCR involves frequent short reversals of the electrolysis current direction [88]. This reduces the concentration polarization in the slimes layer and levels the cathodic deposit by selectively dissolving projections. High current efficiencies, good cathode quality, low electrolyte losses, low energy consumption and a decrease in the number of short circuits have been reported through the use of PCR [22]. A 16% increase in free acid was found in the slimes layer due to PCR. [22]
### TABLE 1. Betts lead electrorefining in the world

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb, g/l</td>
<td>236-270</td>
<td>75</td>
<td>90-100</td>
<td>74</td>
</tr>
<tr>
<td>Total H₂SO₄, g/l</td>
<td>52-61</td>
<td>135</td>
<td>110-115</td>
<td>104-124</td>
</tr>
<tr>
<td>Free H₂SO₄, g/l</td>
<td>2-5 Bi, 0.5-2 Cu, 1-2 As, 130-200 Sn</td>
<td>147</td>
<td>400 Sb, 800 Fe, 110 As, 28 Zn, 290 Sn, 0.2 Ag</td>
<td></td>
</tr>
<tr>
<td>Others, mg/l</td>
<td>600-1100</td>
<td></td>
<td>1000</td>
<td>300-450</td>
</tr>
<tr>
<td>Additives Consumption:</td>
<td></td>
<td></td>
<td></td>
<td>200-300</td>
</tr>
<tr>
<td>Lignin Sulphonate, g/ton</td>
<td>28-43</td>
<td></td>
<td>5-7</td>
<td>32-45</td>
</tr>
<tr>
<td>Glue, g/ton</td>
<td>35-38</td>
<td></td>
<td>40-43</td>
<td>Pressure Tank with centrifugal copper pump</td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>1.6 m³/min x 20 m Head</td>
<td></td>
<td>154-172</td>
<td>18-25</td>
</tr>
<tr>
<td>Circulation Apparatus</td>
<td></td>
<td></td>
<td>154-172</td>
<td>1.5-1.7</td>
</tr>
<tr>
<td>Recirculation Rate, 1/min</td>
<td></td>
<td></td>
<td></td>
<td>1.5-1.7</td>
</tr>
<tr>
<td>Acid loss, Kg/ton</td>
<td>30</td>
<td>40</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Current:</td>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Amp/m², Cathode</td>
<td>120-140</td>
<td>147</td>
<td>185</td>
<td>154-172</td>
</tr>
<tr>
<td>Cell Voltage, V</td>
<td>0.5-0.6</td>
<td>0.47</td>
<td>0.55</td>
<td>0.68 Sb, 0.073% Cu, 0.044% Sn</td>
</tr>
<tr>
<td>Current, kw per Generator</td>
<td>15000 Amp @70V</td>
<td>5000 amp @ 50V 13000 amp @ 50V</td>
<td>95</td>
<td>0.75 Sb, 0.13% Bi, 0.05% Sn</td>
</tr>
<tr>
<td>Current Efficiency, %</td>
<td>95.6-98.7</td>
<td>93</td>
<td>175-180</td>
<td>96.30</td>
</tr>
<tr>
<td>Energy Consumption Kwh/ton Pb:</td>
<td>154-157</td>
<td>143</td>
<td>120-130</td>
<td>120-130</td>
</tr>
<tr>
<td>Electrolysis</td>
<td>17.8-20.7</td>
<td>30</td>
<td>30-40</td>
<td>30-40</td>
</tr>
<tr>
<td>Mechanical</td>
<td></td>
<td></td>
<td></td>
<td>30-40</td>
</tr>
</tbody>
</table>

### Anodes:

<table>
<thead>
<tr>
<th>Casting Technique</th>
<th>Casting Wheel, 18 Moulds</th>
<th>Vertical Casting With Water Cooling On Top Of The Mould</th>
<th>Casting Wheel With Water Cooling On Top And Bottom Of The Mold, 15 Moulds</th>
<th>Casting Wheel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>0.98% Sb, 0.5% Bi, 0.02% Cu, 0.02% Sn, 0.01% As, 67 oz/tion Ag, 0.4 oz/tion Au</td>
<td>1.25% Sb, 0.12% Bi, 0.08% Cu, 65 oz/tion Ag, 0.07 oz/tion Au</td>
<td>0.5% Sb, 0.13% Bi, 0.05% Sn</td>
<td>0.04% Sn</td>
</tr>
<tr>
<td>Length, Width, Thickness, mm³</td>
<td>1150x1000x25-39</td>
<td>1200x800x24</td>
<td>&lt;1% Cu, 0.05% Sn, 0.05% As</td>
<td></td>
</tr>
<tr>
<td>Mode of Suspension</td>
<td>Cast Lugs</td>
<td>cast lugs</td>
<td>970x740x35</td>
<td>920x820x23</td>
</tr>
<tr>
<td>Life, Days</td>
<td>8 [half cycle scrubbing]</td>
<td>7</td>
<td>30</td>
<td>26.5</td>
</tr>
<tr>
<td>Scrap, %</td>
<td>30</td>
<td>100</td>
<td>110</td>
<td>26.5</td>
</tr>
<tr>
<td>Anode Spacing, mm</td>
<td>380-440</td>
<td>250</td>
<td>280</td>
<td>20-25</td>
</tr>
<tr>
<td>Weight, Kg</td>
<td>8-10</td>
<td>10</td>
<td>10</td>
<td>95</td>
</tr>
</tbody>
</table>

### Cathodes:

<table>
<thead>
<tr>
<th>Starting Sheet</th>
<th>Production Technique</th>
<th>Thickness, mm</th>
<th>Weight, Kg</th>
<th>Life, days</th>
<th>Anode Slimes:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production Technique</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6-1.0</td>
<td>1-2.0</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-5</td>
<td>7</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Anode Slimes:

| Composition | 36.9% Sb, 17.4% Bi, 12.1% Pb, 3.1% Cu, 0.1% Sn, 0.4% As, 8.9% Ag, 0.06% Au | 45% Sb, 4% Bi, 12% Pb, 3% Cu, 7-10% Ag, 3.2 oz/tion Au, 30% H₂O |
| Removed After ? days | 4 | 7 | |
| Percentage of Anodes Removed | 2.4-3.6 | 2.9 | |
| Scrubbing Technique | Rotating Brush | |
| Tanks: | | | |
| Length, Width, Depth, cm³ | 500x130x155 | |
| Number of Anodes, cathodes | 42, 43 | |
| Construction Materials | prefabricated concrete, PVC lining | |
| Pb Annual Production, ton | 45000 | 68000 | 27000 | 54450 |
### TABLE 1. Betts lead electorefining in the world (continuation)

<table>
<thead>
<tr>
<th>Electrolyte:</th>
<th>Cominco, Canada [a]</th>
<th>“Albert Funk”, East Germany [a]</th>
<th>Cerro del Pasco, Peru [b]</th>
<th>Kamioka, Japan [c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb, g/l</td>
<td>75 (60-80)</td>
<td>30-50</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Total H₂SO₄, g/l</td>
<td>141</td>
<td></td>
<td>120</td>
<td>130</td>
</tr>
<tr>
<td>Free H₂SO₄, g/l</td>
<td>90 (50-100)</td>
<td></td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Others, mg/l</td>
<td>8 Bi, 85 Sb, 4000 SiO₂, 1.6 Cu, 12 Sn, 5 As</td>
<td>600 Hf, 5 Sb, 0.5 Bi, 0 SiO₂, solids</td>
<td>1 Bi, 150 Sb</td>
<td></td>
</tr>
<tr>
<td>Additives Consumption:</td>
<td>170 (Aloin)</td>
<td>600</td>
<td>550 (Calcium)</td>
<td>180</td>
</tr>
<tr>
<td>Aloe, g/ton</td>
<td>250 (Calcium)</td>
<td></td>
<td>550</td>
<td>600</td>
</tr>
<tr>
<td>Lignin Sulphonate, g/ton</td>
<td></td>
<td>Centrifugal Pumps</td>
<td>Voltz Pump 18.5 kW x 2</td>
<td></td>
</tr>
<tr>
<td>Glue, g/ton</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Others, g/ton</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature, °C</td>
<td>40 [38-43]</td>
<td>35</td>
<td>40</td>
<td>35-45</td>
</tr>
<tr>
<td>Circulation Apparatus</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Centrifugal Pumps</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recirculation Rate, 1/min</td>
<td>27 (27-45)</td>
<td>15 (32% pure)</td>
<td>12</td>
<td>40</td>
</tr>
<tr>
<td>Current:</td>
<td></td>
<td></td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Amp/m³, Cathode</td>
<td>230 (max)</td>
<td>185</td>
<td>156</td>
<td>135</td>
</tr>
<tr>
<td>Cell Voltage, V</td>
<td>3-5</td>
<td>0.45</td>
<td>0.5-0.6</td>
<td>0.55</td>
</tr>
<tr>
<td>Current, Kw per Generator</td>
<td>6300 Amp/5 day, 5400 Amp/7 day</td>
<td>150</td>
<td>Mercury Rectifier 1520 Motor generator 360</td>
<td>20000 Amp 660W</td>
</tr>
<tr>
<td>Current Efficiency, %</td>
<td>90-95</td>
<td>92</td>
<td>90</td>
<td>96</td>
</tr>
<tr>
<td>Energy Consumption Kwh/ton Pb: Electrolysis</td>
<td>168</td>
<td>195</td>
<td>143</td>
<td>165</td>
</tr>
<tr>
<td></td>
<td>Mechnical</td>
<td>50</td>
<td>35</td>
<td>130</td>
</tr>
<tr>
<td>Anodes:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Casting Technique</td>
<td>Open Mould Casting</td>
<td>Casting Wheel, 12 Mould</td>
<td>Casting Wheel Horizontal Casting With Horizontal Mould</td>
<td></td>
</tr>
<tr>
<td>Composition</td>
<td>1.2-1.4% Sb, 0.4% As, 0.15% Bi, 0.05% Cu, 100 oz/ton Ag</td>
<td>1.5% Sb, 0.15% As, 1.5% Bi, 0.05% Cu, 0.01% Sn, 0.07 oz/ton Au</td>
<td>0.4% Ag, 0.3% Bi, 0.1% Cu, 0.6% As, 0.6% Sb</td>
<td></td>
</tr>
<tr>
<td>Length, Width, Thickness, mm³</td>
<td>864x660x30</td>
<td>730x710x25 (immersed surface)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mode of Suspension</td>
<td>Lugs Designed Into Casting</td>
<td>Susended Lugs</td>
<td>Susended Lugs</td>
<td>Shoulder Type</td>
</tr>
<tr>
<td>Life, Days</td>
<td>5</td>
<td>6</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>Scrap, %</td>
<td>25</td>
<td>40</td>
<td>49</td>
<td>45</td>
</tr>
<tr>
<td>Anode Spacing, mm</td>
<td>100</td>
<td>130</td>
<td>100</td>
<td>110</td>
</tr>
<tr>
<td>Weight, Kg</td>
<td>206</td>
<td>200</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Cathodes:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Starting, Sheet Production Technique</td>
<td>Continuous Drum Casting</td>
<td>Mechaniot production with on line casting of ribbon</td>
<td>Continuous Drum Casting</td>
<td>Direct Method Machine</td>
</tr>
<tr>
<td>Thickness, mm</td>
<td>6.3</td>
<td>60-70 (Final Weight)</td>
<td>80 (Final Weight)</td>
<td>6</td>
</tr>
<tr>
<td>Weight, Kg</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>Life, days</td>
<td>5 or 7</td>
<td></td>
<td>4</td>
<td>13</td>
</tr>
<tr>
<td>Anode Slimes:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition</td>
<td>40% Sb, 16% As, 13% Pb, 2.5% Cu, 2500 oz/ton Ag</td>
<td>15% Pb, 25% Sb, 15% Ag, 10% Bi, 5% Cu</td>
<td>28% Sb, 10% As, 24% Bi, 10% Ag, 1.2% Cu, 0.07% Sb, 0.52 %Fe, 10% Pb, 38.4% H₂O, 0.4% SiO₂</td>
<td>10% Pb, 15% Ag, 15% Bi, 1% Cu, 20% As, 20% Sb</td>
</tr>
<tr>
<td>Removed After ? days</td>
<td>5 or 7</td>
<td></td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>Percentage of Anodes Scrubbing Technique</td>
<td>Conveyed By Monorail Between Rubber Scrapers</td>
<td>Pneumatic stripping</td>
<td>Water Sprays</td>
<td>Rotating Brush</td>
</tr>
<tr>
<td>Tanks:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Length, Width, Depth, cm³</td>
<td>268x82x12</td>
<td>230x80x120 (inner size)</td>
<td>455x95x130</td>
<td>500x130x160</td>
</tr>
<tr>
<td>Number of Anodes, cathodes</td>
<td>24, 25</td>
<td>16, 17</td>
<td>40, 41</td>
<td>43, 44</td>
</tr>
<tr>
<td>Construction Materials</td>
<td>Asphalt Lined Concrete (old) Polymer Concrete (new)</td>
<td>Rubberted steel plates</td>
<td>Glue Lined Concrete</td>
<td>Vinyl Chloride Resin and Concrete</td>
</tr>
<tr>
<td>Pb Annual Production, ton</td>
<td>144000</td>
<td>15000</td>
<td>72000</td>
<td>30000</td>
</tr>
</tbody>
</table>
IV The Anodic Process

A. Introduction

The Betts process, as practiced by all refineries, depends on the formation of an adherent, porous anode slimes layer during electrolysis. The slimes layer consists of undissolved impurities which are removed mechanically from anode scrap after the anodes are withdrawn. If the slimes do not adhere to the anode during electrolysis they will settle through the solution and to some extent be mechanically entrained in the cathode deposit. There is no indication in the literature of a lead refining process in which (as in copper refining) slimes fall is encouraged. Further, the recovery of slimes from the bottom of the cell (as in copper refining) is perceived to be more costly. To form an adherent slimes layer, certain elements (mainly As, Sb, and Bi) must be controlled within a narrow composition range and/or ratio in the anode, and the anode casting process must be designed to control the rate of solidification to optimize the microstructure of the cast bullion.

B. The physical metallurgy of the lead anodes

The lead anode microstructure that is desired for optimum slimes structure during electrorefining is known as the honeycomb structure, because it consists of uniform size grains of lead surrounded by impurities on the grain boundaries (Fig. 5). As the lead grains dissolve they leave behind a skeleton of slimes which resembles a honeycomb. Any non-uniformity of the matrix will lead to non-adherence of the slimes layer, and any precipitates present in this matrix material will contribute to slimes detachment because of their extra weight.

There are four elements present in the lead anodes that seem to exert a strong influence on the anodic process: As, Sb, Bi and Ag. The interaction of these impurities with each other and with lead can be deduced from the available binary and ternary phase diagrams [89-93], which show that both intermetallic compounds and eutectic structures may be present. Three different slime forming systems have been identified and classified from studies on synthetic anodes [94].

1 During normal lead electrorefining practice some slimes do fall, and are cleaned out of the cells at very infrequent intervals (months).
The Physical Metallurgy of the Lead Anodes

Fig. 5  Lead anode microstructure. From an anode currently being used by Cominco Ltd. Chemical composition as described in Table 1. Top view, air cooled side.

1) Impurity phases of the solid solution type (SST): the Pb-Bi system.
2) Impurity phases of the precipitation type (PT): the Pb-Sb system.
3) Impurity phases of the eutectic type (ET): the Pb-As and the Pb-Ag systems.

The strength of slimes adhesion to the anode was quantified by Tanaka [94] through observations of slimes fall and slimes morphology. Tanaka summarized the results of these studies with the following relationships:

1) The greatest slimes adherence is obtained when impurity phases of the SST type are present in the anode in concentrations greater than 0.23% wt. A SST concentration lower than this critical value produced a slime that easily slides off the anode.
2) The addition of a third element to the eutectic systems increases significantly the slimes adherence.
3) Water quenching of the anodes increase slimes adhesion particularly in
the PT and ET systems. However, the very small slimes particles formed during quenching may also promote slimes detachment and mechanical entrainment in the cathodes.

The increase of slimes adhesion by water quenching relates directly to the lead anode solidification rate, which influences the growth and distribution of impurity-containing phases. Especially important are the eutectic forming systems where it is known that the solidification parameters (growth velocity, temperature gradient in the liquid and growth mechanism) and system parameters (volume fraction and impurities content) can lead to anomalous eutectic structures [95]. Such structures have been reported to occur in the following systems [95]:

- Ag-Pb and Ag-Bi: broken lamellar structure type
- Pb-Bi: complex structure type
- Pb-Sb: complex regular structure and irregular structure type.

It must be emphasized that even though the physical metallurgy of the lead anodes is of great importance to the Betts process, there remains a lack of knowledge in this area.

**C. Industrial practice**

As Table 1 shows, the range of anode impurities used in lead refining varies from plant to plant. In every refinery the anode composition is kept within narrow limits to obtain an adherent slimes layer. The need for production of anodes with homogeneous properties has led to control methods for cooling rates and casting techniques. In addition to the use of a casting wheel, straight horizontal [44-46] and vertical [47] anode casting systems are employed.

Fig. 6 shows the straight type horizontal lead anode casting system currently used in Japan. Although the vertical and horizontal casting processes were originally developed to save space (over that occupied by a casting wheel), they were carefully designed to achieve uniform cooling rates during the casting of the

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1 A broken lamellar structure consists of a near regular array of "broken" plates and occurs in systems that contain less than 10% of the faceting phase [95]. The complex structure consists of an array of plates that are regular over small areas around a well defined spine [95].
anodes. Such new techniques for anode casting as well as for optimizing heat treatment have been patented by Japanese companies [96], but no information was found that would indicate the nature of changes in microstructure resulting from these newer techniques.

D. Slimes electrochemical behavior

The slimes layer formed in the BEP undergoes structural and chemical changes during its growth. As the slimes layer thickens, the different phases and compounds present react with the entrained electrolyte creating secondary products. The $E_h$ - pH diagram for the PbSiF$_6$-H$_2$SiF$_6$ system [101] indicates that both lead fluoride and silica can precipitate at higher pH values. This has been related to the effect of electrolysis parameters on secondary processes (such as these precipitations) that take place within the slimes layer during electrolysis [97-100]. The transport processes within the slimes layer in the context of these secondary reactions have also been the subject of several studies [102-108].

A simple physical model to study the role of the slimes layer during anodic dissolution rate in electrorefining systems was developed by Reznichenko et al. [109]. In this model, the slimes layer was represented by a silver gauze diaphragm (representing the noble impurity) electrically connected to the anode (a highly pure base metal) and placed at a (variable) distance from the anode corresponding to the slimes - electrolyte interface. The distance between the anode and the gauze was varied to simulate the effect of an increasing ohmic drop between the anode and the slimes layer. During electrolysis, concentration gradients normally
present in a slimes layer were replaced by a simple concentration difference between the solutions on the two sides of the gauze, and this was related to a modified Nernst equation:

\[
\ln \left( \frac{[Me_2]}{[Me_1]} \right) = \left( E_1^o - E_2^o + \frac{RT}{n_i F} \ln \left( \frac{[Me_1]}{[Me_2]} \right) \right) \frac{n_2 F}{RT} 
\]

where:
- \([Me_1], n_1\) = concentration and valence of base metal
- \([Me_2], n_2\) = concentration and valence of noble metal
- \(\Delta \phi\) = ohmic drop between the base metal and the noble metal gauze
- \(E_1^o\) = rest potential of the metal to be refined
- \(E_2^o\) = rest potential of the noble metal

Equation 1 shows that the larger the ohmic drop the larger the equilibrium concentration of ions of the noble metal and the larger its dissolution rate. Although this model oversimplifies the different phenomena taking place within a slimes layer, it provides an insight as to the effect of ohmic drop buildup in the slimes layer and the dissolution rate of noble impurities normally left in the slimes. Reznichenko et al. [109] applied their model to the study of the Cu-Ag system in which they found a logarithmic relationship between the dissolution rate of noble impurities and the ohmic drop potential.

Early research on the behavior of BEP slimes has focused on relating the anodic overpotential to the cathode purity [110,111]. Among the impurities most closely followed in the cathodic deposit is Bi [112,113]. Even though the BEP has a large selectivity for the removal of Bi, it has been found that towards the end of the electrorefining cycle such selectivity can be lost. It seems that the buildup of concentration gradients and the precipitation of secondary products within the slimes layer can initiate steep increases or discontinuities in the anodic overpotential at a certain slimes thickness. This would produce a large increase in the rate of dissolution of such impurities, and subsequently in the deposition of impurities in the cathodic deposit. Fig. 7 shows how Bi contamination in the cathode increases with anodic overpotentials above a critical value (about 200 mV). This has been recognized as a general behaviour for bismuth in lead refining by the BEP [33,87,110,111]. On the other hand, the use of periodic current reversal (PCR) [39,98] has been found to increase the minimum anodic overpotential at which noble impurities start to dissolve.
Table 1 shows that the slimes layer weight is only 1 to 4% of the original anode weight; yet, the slimes occupy the whole of the original anode volume. This indicates that the porosity of the slimes layer exceeds 92% and may be as high as 98% (taking into account a density for slimes phases of about half that of the bullion). Concentration gradients in the electrolyte confined within this highly porous layer and the slimes electrochemistry are closely linked.

Wenzel et al. [97,114,115] measured the change in composition of the electrolyte contained in the slimes layer as a function of time and of slimes thickness. Fig. 8 shows the sampling method used by Wenzel, utilizing sampling wells at different distances from the anode surface. Small amounts of electrolyte were withdrawn through these wells at carefully selected times (to avoid perturbing appreciably the system).

According to their results, using a range of anode compositions (Bi from 0 to 1.74% and Sb from 0.45 to 3.01%), the more the amount of secondary solidified material (SSM) present in the anode, the steeper the pH and the Pb$^{+2}$ concentration gradient throughout the slimes layer. Also they found that the thicker the slimes layer the steeper the concentration gradients. Fig. 9 shows these changes in concentration for two different anode compositions. Wenzel et al. proposed that
due to the pH increase several reactions may occur: SiF$_6^{-2}$ decomposition to SiF$_4$ and F$^-$ (pH > 3); precipitation of Sb$_2$O$_3$ (pH > 4.9) and precipitation of PbO (pH > 7).

Table 2 shows the results of chemical and diffraction analysis, which seems to indicate the presence of these secondary compounds within the slimes layer. From an analysis of the concentration of noble impurities in the entrapped electrolyte, Wenzel et al. were able to conclude that when the SSM exceeded 5%, as determined from the Pb-Bi-Sb ternary diagram, permissible impurities in the anode were too high to obtain an acceptable impurity level in the refined lead.

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1 Note that since slimes oxidize rapidly in air, the analysis may indicate oxide phases where metallic phases were present in the in-situ slimes.
Fig. 9 Changes with electrolysis time of the relative concentrations of Pb$^{2+}$ and H$^+$ within the slimes layer with respect to their bulk values [97,115].

Bulk electrolyte composition: [PbSiF$_4$] = 0.4 M, [H$_2$SiF$_6$]$_{bulk}$ = 0.6 M, T= 35 °C, I = 200 Amp/m$^2$, Stationary Electrodes. Vertical Axis: Pb$^{2+}$ and H$^+$ concentration ratio between the electrolyte sampled within the slimes layer and the bulk electrolyte.

(a) Anode with 0.46% Sb and 0.24% Bi (≡ 1.73% SSM) (b) Anode with 0.92% Sb and 0.24% Bi (≡ 3.80% SSM)

Note: No extrapolation of the inner electrolyte concentrations at zero slimes thickness done here.

### Table 2 Chemical Composition and X-ray Diffraction Analysis of the Lead Anode Slimes [97]

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Anode Composition %wt,(rest Pb)</th>
<th>Slimes Chemical Analysis %wt</th>
<th>X-ray Diffraction Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pb</td>
<td>Sb</td>
<td>Bi</td>
</tr>
<tr>
<td>1</td>
<td>56.98</td>
<td>7.62</td>
<td>3.95</td>
</tr>
<tr>
<td>2</td>
<td>58.02</td>
<td>9.40</td>
<td>4.28</td>
</tr>
<tr>
<td>3</td>
<td>56.57</td>
<td>6.81</td>
<td>5.55</td>
</tr>
<tr>
<td>4</td>
<td>53.77</td>
<td>9.37</td>
<td>9.20</td>
</tr>
</tbody>
</table>
Wenzel's X-ray diffraction analysis on the slimes products agree with the findings of Isawa et al. [116,117], who studied the slimes composition of synthetic and industrial lead anodes and found the presence of the following compounds:

- Metallic Bi: In the Pb-Bi, Pb-Bi-As, Pb-Bi-Sb, and Pb-Bi-As-Ag systems
- Metallic As: In the Pb-As, Pb-Bi-As, and Pb-Bi-As-Ag systems
- Metallic Ag: In the Pb-Ag and Pb-Bi-As-Ag systems

Also the presence of the Bi-Sb solid solution, of the $\varepsilon$ and $\varepsilon'$ phases of the Ag-Sb system, and of water soluble As and Sb (identified as $\text{As}_2\text{O}_3$ and of $\text{Sb}_2\text{O}_3$) was found in some of the above mentioned systems and in the slimes obtained from industrial anodes [116,117].

One compound that has been difficult to characterize is $\text{Ag}_3\text{Sb}$ [94], whose presence has been detected in both synthetic and industrial lead anodes. The morphology of this compound has been found to be a function of the anode cooling rate and of the electrolysis conditions.

The electrolyte used in lead electrorefining contains impurities whose concentration ranges from a few ppm and several g/l, and have their origin in the anode from which they are dissolved (i.e. Cu$^{+2}$, Sn$^{+2}$) or from the acid manufacturing process (i.e. phosphorus species). Their steady state concentrations in the electrolyte depend on the electrolysis parameters and slimes thickness. They can affect both the anodic and cathodic processes through changes in fundamental electrochemical parameters such as the exchange current density ($i_0$), the symmetry factor ($\alpha$), and the electrical double layer capacity ($C_d$)\(^1\). Measurement of these parameters usually involve transient electrochemical techniques, such as polarization scans, current interruptions, and AC impedance studies.

Miyashita et al. [118-123] have studied extensively the influence of minor impurities and addition agents in the electrolyte used in lead refining. These studies focused on the determination of the fundamental electrochemical

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1 The term *electrical double layer* is used to describe the arrangement of charges and oriented dipoles constituting the interphase region at the boundary of an electrolyte [144, P.630]

The *exchange current density*, $i_0$, is a measure of the rate of equilibrium potential and sensitivity to interference [145, P.10]

The *symmetry factor*, $\alpha$, determines what fraction of the electrical energy resulting from the displacement of the potential from the equilibrium value affects the rate of electrochemical transformation [144, P.923]
parameters ($i_0$, e.d.l., and $\alpha$) as a function of Sn$^{2+}$, Fe$^{3+}$, Zn$^{2+}$ and glue, using a single current step transient method [118]. He found that under an oxygen atmosphere the presence of the above ionic species increased the anodic overpotential value. Thus, they may inhibit the dissolution of some noble species including lead.

When noble impurities present in the lead anodes transfer to the electrolyte they can be redeposited by cementing on less noble elements. While such redeposition is obscured during anodic dissolution, it can be inferred from corrosion measurements in the absence of a current. For example, the weight loss rate for a lead sample in the presence of dissolved bismuth has been observed in the HBF$_4$-Pb(BF$_4$)$_2$ system [66]. Fig. 10 shows how Bi concentrations as low as 2 mM enhance the corrosion rate of lead.

During the dissolution of the lead anodes in the BEP, bismuth and other noble impurities accumulate in the proximity of the slimes/bulk electrolyte interface as well as in the bulk electrolyte [39,124]. Since these noble impurities will deposit on the cathode at their limiting mass transfer rate, the permitted

![Fig. 10 Lead specific weight loss (corrosion) as a function of the immersion time in a 2 M Pb(BF$_4$)$_2$-1 M HBF$_4$ solution in the presence of 0, 2, 5, and 10 mM of Bi$^{3+}$ [66].](image)
electrolyte concentration is related to cathode purity specifications (0.12 mM of bismuth will typically lead to 10 ppm Bi in the cathode[124]). They can be removed by one of two methods:

a) Continuous cementation [125,126] through a column filled with lead particles (Fig. 11).

b) Electrodeposition in a separate electrolysis circuit [124]. The purified electrolyte is then sent to the main electrolyte stream. This method is being used in Japan [43].

The majority of plants that electrorefine lead do not purify their electrolyte, but rather operate under conditions where the dissolution of noble impurities from the anode is limited to tolerable levels.

![Continuous Purification of Electrolyte via Purification Column](image)

**V The Cathodic Process**

**A. Additives control and electrochemistry**

In the absence of additives, lead deposits with a very small overpotential, and tends to form rough, porous deposits or dendrites that result in short circuits. To obtain deposits that are flat, smooth, and free from projections, special reagents are added to the electrolyte. These "addition agents" increase the cathodic overpotential (actually called "inhibition"), and change the kinetic parameters ($i_0$, $\alpha$, and e.d.l.) under comparable electrolysis conditions [120-123].
Polarization measurements have been used for controlling and monitoring the concentration of additives in lead electrorefining circuits \([81,127-129]\), as well as for screening of additives in the electrolytic refining of Cu and for the testing of impurity levels in the electrowinning of Zn \([130-135]\). A polarization technique for determining lignin sulphonate in lead plating baths has also been described \([136]\). Long term studies and years of industrial practice, especially by Cominco researchers \([81,129]\) have led to a sufficient understanding of the levelling mechanisms of lignin sulphonate and aloes, to permit the use of polarization measurements for controlling the concentration of these species in the industrial electrolyte for lead refining. This additives control is achieved by keeping the cathode polarization voltage (C.P.V.) within preset limits, and adjustments are made by either new additions or by regeneration (in the case of aloes) with a thiosulphate salt \([128]\). The level of additives present at a given time is directly related to the C.P.V.

### B. Starting sheet technology

The cathode starting sheets used in the BEP are usually cast on a rotary drum casting machine. The stiffness of these sheets is increased by adding approximately 15 ppm Sb to the melt and by impressing wrinkles on the cathodes right after they are produced \([79]\). Procedures to avoid dross incorporation in the lead cathodes have also been developed \([137]\). In this section of the electrorefining process high levels of automation have been achieved \([138]\).

### C. Cell electrolysis parameter optimization

The overall electrorefining process has been studied using statistical correlations of some of the variables measurable in an operating plant \([39,54,98]\). To optimize the electrolysis parameters when the BEP is run at high current densities (≥ 200 Amp/m\(^2\)), factorial design of experiments at three levels for four variables has been used by Lange et al.\([98]\). They varied PbSiF\(_6\) and H\(_2\)SiF\(_6\) concentrations, temperature, and current density, at constant values of addition agent (glue), anode composition, cell geometry, and electrolyte recirculation. The influence of these parameters on the average anodic and cathodic polarization, on the cell voltage, and on the specific energy consumption was obtained by employing regression analysis correlations. In addition, changes in these parameters were correlated with the cathode quality and appearance as well as
with the consumption of glue. The optimum electrolysis parameters found for a current density increase (from 200 to 300 Amp/m²) were a Pb⁺² concentration of 60 g/l (down from 80 g/l), a glue addition maximum of 1500 g/ton Pb (up from 1250 g/l), a free H₂SiF₆ content of 120 g/l (no change) and an electrolyte temperature of 35 to 40°C. Under these electrolysis conditions, Lange et al. found that Sb and Bi slimes layers could be subjected to anodic polarizations as high as 280 mV without serious impairment of the cathode quality.

Optimization of the BEP through half cycle anode slimes scrubbing and cathode exchange was also investigated by Lange et al. [98]. Not only did the specific energy consumption decrease by the implementation of this procedure, but highly pure cathodes were assured by avoiding anodic overpotentials in excess of the preset limits for impurities dissolution. On the other hand, the exchange of cathodes and the half cycle scrubbing of the anodes incorporates labour increases making implementation difficult. The use of this technique is necessary when anodes containing high impurity levels (>5%) are to be treated. For example, in Russia [57], lead anodes containing as much as 15% Bi are scrubbed every 48
hours during the 6-day long anode cycle. In addition to this, cathodes are exchanged daily to avoid short circuits and to obtain a deposit of acceptable purity [57].

Lange et al. also studied the use of PCR in the BEP. Fig. 12 shows the anodic overpotential dependance on the PCR parameters. Thiet [39] found that the use of PCR decreased the anodic overpotential values. The reduction in the anodic overpotential values did not reflect in lower PCR energy consumption probably because it was offset by unproductive energy consumption during the reverse current phase of the cycle. Thiet also showed that the quality of the PCR cathode deposits was very high [39].

D. Bipolar refining of lead

Among other alternatives to optimize the lead electrorefining process, the use of a bipolar configuration looks most promising. In this configuration only the terminal electrodes are connected to the source of current. Between these electrodes a large number of bipolar electrodes can be incorporated. One side of these electrodes will corrode anodically, while pure lead will deposit on the other side. The impurities will be left behind as a slimes layer on the anodic side. The advantages of operating the BEP in a bipolar mode include PCR, C.P.V., optimum lead and free acid contents, and the use of jumbo electrodes (≈4m², possible because there are no bus-bar connections)¹. The process has been operated in a pilot plant where it proved to be superior to the parallel process [142]. The rationale for the current use of the parallel system is that a high economic investment is required for the substitution and implementation of the bipolar process. If new plants to electrorefine Pb are to be constructed in the future, very likely they will be assembled on the bipolar configuration.

¹ In the bipolar mode by-pass currents are reduced by increasing the area of the electrodes so that the ratio of bypass to electrode area in the cell decreases.
Chapter 2  Fundamentals of the Electrochemical Measurement Procedure

Early in the development of this project it was found that the form of ionic concentration gradients within the lead anode slimes layer needed to be studied. To study these concentration gradients without causing major disruptions to the system, "in-situ" experimental techniques were considered. Among these, transient electrochemical techniques appeared to be particularly advantageous and consequently were used extensively in this work. The study of the electrochemical response of typical lead anodes was complemented by measurements on the physico-chemical properties of $\text{H}_2\text{SiF}_6$-$\text{PbSiF}_6$ electrolytes. What follows in this chapter is a description of the electrochemical parameters germane to this work, and of the transient techniques that were used.

I. Components of the Anodic Overpotential

The anodic overpotential was measured by following the difference in potential between the lead anode ("working electrode") and a suitable reference electrode. A high purity lead wire located within a Luggin capillary and contacted with cell electrolyte was chosen as the reference electrode. Its use was possible because of the high reversibility of lead in the $\text{H}_2\text{SiF}_6$-$\text{PbSiF}_6$ electrolyte system. Furthermore, the amount of current that passes through the reference electrode is limited to the current drain of the meter (a few nanoamperes). The "anodic overpotential" $\eta_a$, measured by such an electrode would also be free of any junction potential between its tip and the slimes/electrolyte interface provided the bulk electrolyte is well mixed. In the present work (unless specified) all potentials are given with reference to such an electrode. The third electrode (a lead foil counter electrode) is required to complete the electrical circuit. The electrochemistry of this counter electrode is of no importance to the anodic processes. Fig. 1 shows a simplified view of this three electrode arrangement.

The anodic overpotential measured under constant current conditions increases continuously as the slimes layer thickens during the refining cycle. The build up of concentration gradients in the proximity of the anode/slimes interface increases continuously as the slimes layer thickens during the refining cycle.

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1 This "anodic overpotential" $\eta_a$, or potential difference between the anode and the reference electrode, includes an ohmic component, $\eta_{\Omega}$, and long range potential gradients as well as interfacial overpotential components.
changes the value of $\eta_A$ mainly through changes in its migration and concentration overpotential components. Additionally, an ohmic contribution is included in this $\eta_A$ measurement.

**Fig. 1 Electrochemical Cell Arrangement**

The importance of the ohmic component in electrochemical measurements is evident by the number of studies that have been conducted in order to assess its effect [1-9]. According to Vetter [10] the ohmic component is not a real overpotential because its presence does not have any influence on the rate or type of electrochemical processes under investigation. Ohmic drop or resistance polarization can be separated from migration and concentration overpotentials only in regions where the electrolyte composition is uniform as between the reference electrode tip and the slimes/electrolyte interface.

Concentration overpotential, $\eta_c$, is the Nernst potential generated due to activity differences of the electroactive ion. Its presence is primarily due to the limitation in the ionic transport of species moving from or towards the working electrode surface. When this concentration overpotential occurs in the presence of concentration gradients of non-electroactive ionic species, a migration potential
gradient\(^1\), \(\Delta \Phi\), is generated. The migration potential arises concurrently to \(\eta_e\). Thus, by subtracting the value of \(\eta_\Omega\) from the \(\eta_A\) measurement, an overpotential value consisting of \(\eta_e\) and \(\Delta \Phi\) is obtained.

An additional contribution to the anodic overpotential, the activation overpotential, \(\eta_{ac}\), is a function of the transport rate of charge carriers across the electrical double layer. The larger the hindrance for this transport process, the larger \(\eta_{ac}\) will be. By measuring the difference in potential between the working electrode and a point located very near its surface, the value of \(\eta_{ac}\) is obtained.

The presence of other contributions to \(\eta_A\) (crystallization, reaction) will not be described here, as they are unimportant for lead. Vetter \([10]\) establishes the conditions upon which these components are to be taken into consideration. We assume that the contributions of these overvoltages to \(\eta_A\) are either negligible or can be incorporated within \(\eta_{ac}\) or \(\eta_e\).

\section*{II. Transient Electrochemical Techniques}

The amount of information that non-transient electrochemical techniques are able to provide is rather limited \([11-14]\). Significant enhancements in electronics in the last 25 years have supplied the electrochemist with a wide range of transient techniques. Reviews on the use, applications, and limitations of these techniques are available \([11,15-21]\). Among these transient techniques, current interruption and AC impedance were used extensively in this work. These techniques were chosen due to their potential for resolving the \(\eta_A\) components.

\subsection*{A. Current interruption techniques}

Current interruption techniques go back as far as 1937 \([22]\). The original driving force for their implementation was to obtain the value of the uncompensated ohmic drop, \(\eta_\Omega\). Further research has demonstrated that by studying the polarization decay curves and their dependance with time, kinetic and mass transport information can be obtained \([23-30]\). When several phenomena are superimposed, interpretation of the current interruption decay curves is not straightforward. For example, Newman \([7,31]\) and other researchers \([3,27,32]\) have stressed the fact that upon current interruption, internal currents may not be

\footnote{The migration potential, \(\Phi\), can be calculated by solving the Nernst-Planck flux equations. Appendixes 1 and 2 describe how these equations can be solved. \(\Delta \Phi\) can be neglected in the presence of a substantial excess of supporting electrolyte.}
halted instantaneously. This will be the case if contained electrical double layers are not uniformly charged. The relaxation time required for the double layer to equilibrate can be estimated from the following relationship:

\[
\tau_R = \frac{L C_{dl}}{\kappa} \quad \text{...1}
\]

The discharge of the double layer can also take place through Faradaic reaction. The time constant for this reaction can be estimated using the following equation:

\[
\tau_f = \frac{R T C_{dl}}{F i_o} \quad \text{...2}
\]

The third major process that can take place upon current interruption is the relaxation of concentration gradients. The time constant for this unsteady state process can be estimated from the following relationship:

\[
\tau_m = \frac{\delta^2}{D} \quad \text{...3}
\]

Upon disappearance of the external current, \(\eta_0\) will vanish almost immediately (in \(\leq 10^2\) msec) [34]³. On the other hand, residual charge arrangements in a supposedly uniform charged electrolyte may affect the rate at which \(\eta_0\) vanishes.

Typical values for \(\tau_f\) and \(\tau_r\) are close to 0.5 msec [7]. Thus, the electrical double layer will be equilibrated and discharged in approximately 1 msec. After this time, concentration gradients will relax. The larger the time constant the longer it will take for the system to reach its open-circuit or equilibrium potential. Another process that can take place upon current interruption is the dissolution and/or re-precipitation of secondary products within the slimes layer. This process may originate one or several potential arrests [35]⁴.

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1 Double layers may not be uniformly charged if the difference in potential at the electrode/solution interface is not uniform.
2 L is the characteristic length that controls the current distribution [20,33].
3 In electrolytes of uniform composition, potential drops upon current interruption have time constants of the order of \(7 \times 10^2\) msec.
4 These potential arrests are sometimes referred as Flade potentials.
An estimation of the time required to relax the concentration gradients present within the slimes layer can be done by using Eq. 3. Assuming that the entire slimes layer can be considered as a "nearly" stagnant environment and that \( D \) is of the order of \( 10^{-5} \) cm\(^2\)/sec, we get for a 0.1 cm slimes thickness a value of \( \tau_m \) of 1000 sec. This shows that long relaxation times are required for the levelling of the concentration gradients present within the slimes layer. Thus, current interruption for short periods of time (~ 0.3 sec) during the galvanostatic dissolution of lead anodes was not expected to change the system appreciably. The information provided by analyzing short interruptions was supplemented by following, for selected cases, the decay in potential over extended periods of time (several days).

The experimental set-up (using a Wenking potentiostat) allowed the decay potential to be followed from about 0.5 msec after current was interrupted. Oscilloscope traces at shorter times after current interruption showed that the potential at time zero could be obtained by linear or exponential approximation of the decay curves in the vicinity of the current interruption. These studies resulted in a semi-quantitative picture of the transport processes taking place within the lead anode slimes layer.

It has been shown [1,36-39] that analysis of the potential decay curves obtained upon current interruption is more easily accomplished when the time-domain data\(^1\) are transferred into the frequency-domain through the use of Fourier transformations. Both analytical and numerical transformation of the time-domain generated data can be performed. Matching transformations on equivalent electrical circuits selected by trial and error must be found to interpret the data in terms of electrical components such as resistors and capacitors. The input and output signals are subjected to Fourier transformation (i.e. one-sided Laplace transformation) and a transfer function is obtained. In the case of a current interruption experiment, both potential, \( e(t) \) and current, \( i(t) \) are Fourier transformed to obtain the system impedance from their ratio. Appendix 3 shows how the response to current pulses of a simple RC circuit was analyzed in the frequency domain. Numerical Fourier transformation of some of the current interruption data generated in this work was carried out by using the Fast Fourier

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1 The time domain data refers to the potential and current transients dependance with time. When these data are Fourier transformed, the frequency spectrum of the system is obtained (time-domain ↔ frequency-domain). For a more complete description of this transformation see appendix 3.
Transform (FFT) algorithm [40-43]. The software packages used in this work incorporate this algorithm 1. Knowledge of the FFT algorithm, its application range and limitations, are required to understand the data generated. Appendix 3 reviews some of the relevant steps required for implementing the Fourier transformation.

B. AC impedance techniques

The use of AC impedance to study electrochemical systems spans over a period of more than 100 years. Kohlrausch, as early as 1854 [44] proposed its use for the determination of the electrical conductivity of electrolytes. Later, with an AC bridge, he obtained the conductivities of a large number of electrolytes [45]. Contributions by Warburg [46] and Randles [47] set the theoretical and experimental foundations from which AC impedance measurements have evolved. Nowadays, the technique is routinely used for the analysis of a wide range of electrochemical systems [48-54]. Electrical engineering theory has been heavily used by electrochemists to interpret the results, and reviews on its characteristics, advantages, limitations, and implementation can be found in the literature [14,19,48,55-57].

In a typical AC impedance experiment, a small sinusoidal signal (either voltage or current) is applied to an otherwise DC system. The AC output response is followed as the frequency of the input signal is changed. The ratio of the input and output signals is known as the transfer function [58,59]. Thus, the impedance, $Z(j\omega)$, is a transfer function. The system response can be assumed to be linear by limiting the amplitude of the input signal to a few mV (or a few mA). The possibility of obtaining an electrical analogue circuit by using AC impedance is a strong driving force for its application. Knowledge of this analogue allows the modelling and prediction of the output signal when the input is known.

The linkage between current interruption and AC impedance techniques arises through the use of the transfer function. Theoretically, upon Fourier transformation of the current interruption data, the transfer function obtained should match the one obtained by AC impedance. That this connection exists is shown in appendix 3. On the other hand, experimental artifacts make the analysis of data generated in the time-domain valid only for a very limited frequency range.

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1 Asyst® version 2.10 and Asystant® version 1.02.
In addition to this, the time span required for an AC measurement is several orders of magnitude larger than the one required for a current interruption measurement.

AC impedance is the best technique available for the determination of $\eta_0$ [64]. The resistance polarization value obtained using this technique should coincide with the value obtained from current interruption experiments [65]. Kinetic and mass transfer information can also be readily obtained using this technique [53,66-68]. On the other hand, most of the impedance theory developed so far has been focused on the study of very dilute solutions [19] and solid electrolytes [16].

**1. Aims and limitations of the AC impedance studies**

AC impedance studies are aimed at finding an electrical analogue that can be used to study how different physico-chemical (and in some cases mechanical) parameters affect the response of a system given a certain input function. A comprehensive analogue model ought to be able to incorporate as many parameters as variables are in the system. It also should predict the output of the system given the characteristics of the input function. Like any other mathematical model, an analogue model is established using assumptions which are based on prior knowledge of some of the fundamental properties of the system. A wide variety of electrical analogue circuits can match the response of the system but only a few could represent the physico-chemical process involved (without accounting for different interpretations for the same circuit). An indication that the model is appropriate is that the electrical parameters ought to change as the physical variables are altered. Thus, the main limitation of the impedance studies is a function of how ambiguous are the parameters involved in the circuit. Other limitations arise in unstable systems in which the parameters change faster than the AC measurement, decreasing the frequency in which the AC spectra can be accurately measured. The search of an electrical analogue that matches the response of the system has also been extensively pursued using DC transient techniques such as current interruption [8,69,64] and small amplitude cyclic voltammetry (SACV) [70,71]. DC and AC studies have been used concurrently to better characterize the system under study [15,72].

In the Betts process, AC impedance measurements were made across the slimes layer at preset slimes thickness. Changes in the impedance values were related to concentration gradients, precipitation of secondary products, and dissolution of noble compounds. From these studies, kinetic parameters
(exchange current densities, double layer capacities) were determined. Linearity in the system response was assumed by limiting the amplitude of the input sinewaves to very small values (less than 5 mV R.M.S. for potential controlled experiments and less than 35 Amp/m² R.M.S. for current controlled experiments). η₀ values were obtained from both AC impedance measurements and a current interruption routine built into the Solartron electrochemical interface.

The search of electrical analogues that match the response of the system and have physical meaning is strongly pursued in this thesis.
Chapter 3: Experimental Procedure

I. Electrochemical Experiments

A. Electrochemical cells

1. Beaker Cell

A 1 L wide mouth (ø=11 cm) polyethylene beaker was adapted to function as electrochemical cell (Fig. 1). This cell was used to study the anodic behavior of small working electrodes (i.e. working electrodes whose geometric area was between 1.4 and 3 cm$^2$). A Lucite tight cover was used to hold the electrodes in a fixed position and to avoid loss of water due to electrolyte evaporation. The cover had holes through which the electrical connections to the electrodes and the tubes used for electrolyte sampling were taken out of the cell. Previous to each experiment the cell was thoroughly washed several times using deionized water. After the cell was dried, the electrodes were firmly positioned in the cell. Then the electrolyte was introduced to the cell through a plastic tube. During the experiment, this tube was used to obtain bulk electrolyte samples. Electrolyte was added only at the beginning of the experiment in volumes that ranged between 320 and 400 ml. Mixing of the bulk electrolyte was by either magnetic stirring or recirculation. Electrolyte recirculation provided the best experimental reproducibility and was preferred to magnetic stirring. After the electrodes were positioned and the electrolyte introduced, the cell was covered and sealed using generous amounts of silicone rubber. Only after the silicone rubber had "dried to touch" (i.e. after approximately 2 Hrs.) was the cell immersed in the constant temperature water bath.

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1 $\text{H}_2\text{SiF}_6$ containing solutions can etch glass [1]. Thus, glass laboratory ware was avoided as much as possible.
2 Geometric areas do not consider surface rugosities.
3 Electrodes were immersed in a 10% Vol HNO$_3$ solution and washed with deionized water prior to their introduction to the cell.
4 Magnetic stirrer bar coated with Teflon (l=2.54 cm, ø=0.95 cm) spinning at low speed by using a Tek-stir magnetic stirrer model 58250-1.
5 As illustrated in Fig. 1 electrolyte was recirculated through plastic tubes located at opposite sides of the cell and at different electrolyte depths.
6 Electrolyte recirculation rates were between 5 and 6 ml/min. A Masterflex pump catalogue No. 7553-20 and Masterflex Tygon tubing catalogue No. 6409-14 were used.
7 100% silicone rubber, RTV Silastic 732.
2. Rectangular cell

Rectangular Lucite cells were used to study the electrochemical behavior of working electrodes whose exposed geometrical area ranged between 30 and 40 cm$^2$. Fig. 2 describes the dimensions and design features of this kind of cell\(^1\). A Lucite tight lid was used to cover the cell. In this lid, holes of appropriate size were drilled. Through these holes, the electrical connections to the electrodes and the tubes used for electrolyte sampling were taken out of the cell. Bulk electrolyte was recirculated\(^2\) using lateral cell inlet and outlet facilities.

---

1 Cell dimensions were modified according to the characteristics of the experiment. Fig. 2 shows the actual dimensions of the electrochemical cell employed in experiment LC2 to be discussed extensively in Chapter 4.

2 Electrolyte recirculation rates were between 5 and 6 ml/min.
Electrolyte from the top of the cell was brought to the bottom continuously. During the electrolysis of lead electrodes, electrolyte samples taken at different cell locations showed no significant concentration differences.

Fig. 2 shows the position of the two small Lucite strips used to support the anode. The presence of these strips allowed the electrolyte entrapped within the slimes layer to flow downwards. Additionally, wide Lucite strips were used to center the anode in the cell and to improve current distribution. Electrolyte volumes were fixed at the beginning of the experiment and ranged between 300 and 400 ml. When bulk electrolyte samples were withdrawn from the cell, electrolyte of the initial composition was added to the cell to maintain constant the electrolyte volume. As in the beaker cell case, after the electrodes were placed and electrolyte added, the lid was fitted to the cell and sealed afterwards using silicone rubber. Again, only after the silicone rubber had dried to touch, was the cell immersed in the constant temperature bath.
B. Electrodes

1. Working electrodes

(a) Materials

Working electrodes were produced from pure lead and from typical lead bullion anodes provided by Cominco Ltd. Typical anodes used in the Betts electrorefining process were taken from the anode refining wheel and some of its sections were sent to UBC. No particular details regarding the anodes cooling rates or about the pyrometallurgical steps previous to their casting were provided. According to Cominco, the anodes were cast under normal operating conditions and that's where the term "typical" comes from. The electrochemical studies here pursued required the anodes to form strong and adherent slimes. As was later found, this set of anodes did produce slimes which did not fall from the electrodes and remained attached to them during the dissolution stages.

Fig. 3 shows the anode sections that were cut from the anodes and sent to UBC. The anode A strip was sent in July 1986. This strip was cut in smaller pieces and from the area indicated in Fig. 3A, electrodes were produced. Sections of anode B were sent in March 1987. From anode B, electrodes were produced mainly from its center part (section B-1 shown in Fig. 3B). The working electrodes were prepared so as to study the electrochemical behavior of the

---

1 Pure lead working electrodes were made out of Tadanac ingots (Pb >99.99%)
"mould" cooled anode face and the "air" cooled anode face. Thus, electrodes were fabricated by cutting perpendicular sections of the anodes. Depending on the type of electrochemical cell employed, different electrode sizes were used.

(b) Beaker cell

Small working electrodes whose exposed geometric area ranged between 1.4 and 3 cm$^2$ were prepared as follows:

(I) Pure lead working electrodes

Electrodes were made by cutting small pieces of the pure lead ingot. These pieces were machined to form rectangular shaped electrodes. The machining marks on the electrode sides were removed by polishing the electrode using the 600 grit. The electrical contact was incorporated by soldering a Cu wire to the back of the electrode. Subsequently, the electrode was encapsulated with epoxy resin$^1$ exposing the electrode surface by polishing away the unwanted resin. The exposed surface was polished again using the 600 grit.

(II) Lead bullion working electrodes

Rectangular shaped electrodes were cut and machined out of the anode sections previously described. The electrode face to be exposed directly to the electrolyte (either the air cooled or the steel cooled face), was not machined. The deformed layer produced by the cutting and machining operations was removed by polishing$^2$. Electrical contact was made by either soldering a Cu wire to the back of the electrode or by pressure contact. The later technique was preferred due to the fact that the soldering process through heating, may affect the phases originally present in the anode. The pressure contact electrical connection consisted of manually pressing a bundle of the Cu wire strands to the back of the electrode and using acrylic tape to sustain the contact. The electrode was then mounted in epoxy resin and the unwanted resin was polished away. The exposed electrode surface was polished with the 600 grit.

(c) Rectangular cell

Medium size electrodes whose exposed geometric area ranged between 30 and 40 cm$^2$ were prepared as follows:

1 Acrylic plastic resin: Quick mount® self-setting resin
2 The deformed layer was measured metallographically and in some cases was as thick as 0.1 mm.
(I) Pure lead working electrodes

Electrodes were cut and machined out of pure lead ingots as in the beaker cell case. The machining marks were removed by polishing using the 600 grit. Electrical contact was made by using two Cu rods. These were screwed-in to the top of the electrode. One of these rods was used to carry current and the other to measure the electrode potential. The lateral electrode surfaces were covered with silicone rubber. The bottom, top, and one of the electrode faces were not coated with silicone rubber. Thus, only the bottom of the electrode and one of its sides were directly exposed to the electrolyte.

(II) Lead bullion working electrodes

Electrodes were prepared out of the anode sections in the same way pure lead anodes were produced. To sample the electrolyte present in the slimes layer, and to follow the inner slimes electrode potentials, holes were drilled in top of the anode. Though these holes, plastic tubes were inserted. These tubes were used either to extract small amounts of electrolyte or to insulate the pure lead wires. Additionally, one of these holes was used to insert a Pt wire. This wire was used to study the electrical conductivity of the slimes layer. The Pt wire did not have any insulation and during some experiments it was moved to other locations where slimes were present.

2. Reference electrodes

A pure lead wire was used to measure the difference in potential between the bulk electrolyte and the working electrode. This wire was mounted in a plastic tube (ø=2 mm). The tube was bent at one end, and a plastic tip was inserted there. Fig. 4 illustrates this Luggin-Haber reference electrode arrangement. The reference electrode tip was placed between 2 and 5 mm away from the original position of the working electrode. This distance remained constant during the

1 Size and location of the holes is provided when specific experiments in which electrolyte samples were taken and inner potentials obtained are analyzed.
2 From the inner slimes layer 100 μL of electrolyte were slowly extracted (over a period of 3-6 hours). A 100 μL Unimetrics removable needle syringe was used to withdraw the inner electrolyte samples.
3 The difference in potential between this wire and the anode was used as an indication of the slimes layer conductivity.
4 Johnson Matthey, 99.95% Pb, ø=1.0 mm.
5 Eppendorf pipette tips 5-100 μL
experiment. The tip of the reference electrode was located facing the geometrical center of the working electrode. After the cell was assembled and the bulk electrolyte had penetrated the reference electrode compartment, this was sealed by using silicone rubber. Thus, the electrolyte surrounding the lead wire had the same composition, temperature, and atmosphere as the bulk electrolyte.

![Diagram of Luggin-Haber reference electrode arrangement](image)

**Fig. 4** Detail of the Luggin-Haber reference electrode arrangement

- (A) Pure lead wire
- (B) Plastic Tube
- (C) Eppendorf plastic tip.

\[ \phi_1 = 1.3 \pm 0.2 \text{ mm}, \phi_2 = 0.5 \pm 0.2 \text{ mm} \]

In the experiments\(^1\) in which the difference in potential between the electrolyte solution present in the slimes layer\(^2\) and the working electrode was followed, pure lead wires were also used. Plastic tubes (\(\phi = 1.3 \text{ mm}\)) were inserted in the previously drilled holes up to \(\Omega 2 \text{ mm}\) away from the bottom of the holes. Then, the lead wires were inserted up to \(\Omega 2 \text{ mm}\) away from the lower end of the plastic tubes. This particular set-up was chosen to avoid prohibitive corrosion of the lead wires during the dissolution of the working electrode.

3. **Counter electrode**

Pure lead foils\(^3\) were used as counter electrodes. In the beaker cell case the lead foil surrounded the working electrode\(^4\) whereas in the experiments which

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1. This sort of experiments were only carried out using the rectangular electrochemical cell in which the size of the working electrode was large enough to incorporate these potential measuring probes.
2. The electrolyte entrapped within the slimes layer will be called "slimes electrolyte".
3. Lead foils whose lead content was greater than 99.95%
4. The working electrode was concentrically placed with respect to the counter electrode.
used the rectangular cell, the lead foil was located facing the working electrode and @42 mm away from it. In both cases, the area of the counter electrode was larger than the area of the working electrode. This was done to improve the current distribution and also to avoid formation of dendrites. When the beaker cell set-up was used, the geometric area of the counter electrode was between 10 and 15 times larger than the exposed geometric area of the working electrode. In the experiments performed using the rectangular cell, counter electrode areas were between 1.2 and 1.4 times larger than their working electrodes counterpart. In all the experiments, electrical contact was incorporated by soldering a Cu wire to the counter electrode. The place where the electrical contact was made was isolated from the electrolyte by a silicone rubber coating.

C. Electrolyte

Technical H$_2$SiF$_6$ obtained as a by-product of the treatment of phosphate rock [2] was neutralized with either PbCO$_3$ or PbO to prepare mother electrolyte solutions. The reactions that take place upon neutralization of the acid are:

\[
\begin{align*}
H_2SiF_6 + PbCO_3 & \rightarrow PbSiF_6 + H_2O + CO_2 \quad \ldots 1 \\
H_2SiF_6 + PbO & \rightarrow PbSiF_6 + H_2O \quad \ldots 2
\end{align*}
\]

Upon neutralization, several insoluble compounds precipitate. These precipitates were removed by filtering using Whatman paper #40. After this operation, a nearly transparent electrolyte solution is obtained. Depending on the acid strength of this solution, SiO$_2$·nH$_2$O colloidal particles may be observed [3-7].

1 Acid composition: 2.03 M H$_2$SiF$_6$ and 0.40 M SiO$_2$. This acid was provided by Cominco Ltd.
2 Phosphate rock is treated with H$_2$SO$_4$ to produce HF which is later contacted with SiO$_2$ to produce H$_2$SiF$_6$. The sequence of reactions that take place is [2]:

\[
Ca_{10}(PO_4)_6F_2 + 10H_2SO_4 + 20H_2O \rightarrow 10CaSO_4 \cdot 2H_2O + 6H_2PO_4 + 2HF \quad \ldots a
\]

\[
6HF + SiO_2 \Rightarrow H_2SiF_4 + 2H_2O \quad \ldots b
\]

\[
H_2SiF_6 \xrightarrow{heat} SiF_4 \uparrow +2HF \quad \ldots c
\]

\[
3SiF_4 + 2H_2O \Rightarrow H_2SiF_6 + SiO_2 \quad \ldots d
\]

3 Depending on the extent of the neutralization of the acid, a mixture of lead oxides and fluorides in addition to silica compounds can precipitate.
4 The presence of colloidal SiO$_2$·nH$_2$O in this system has been reported in the literature [3-7].

[41]
A titrimetric analysis routine was set up to analyze the electrolyte for $\text{H}_2\text{SiF}_6$, $\text{SiO}_2$, HF, and $\text{PbSiF}_6$. In this routine, Pb is analyzed via complexometric titration with $\text{EDTA}$ \textit{[8,9]}. $\text{H}_2\text{SiF}_6$, $\text{SiO}_2$, and HF (if present) are determined by titration with $\text{LiOH}$. Details of this procedure are provided in Appendix 4.

To obtain electrolytes of the set compositions, the mother electrolyte solutions were diluted with $\text{H}_2\text{SiF}_6$ and deionized water \textsuperscript{1}.

Additives were added to the electrolyte in selected experiments. The additives used were aloes \textsuperscript{2} and calcium lignin sulphonate \textsuperscript{3}. These additives were added from a mother solution at the beginning of the experiment. Precipitates formed due to the additives addition were removed by filtering the electrolyte prior to its introduction to the electrochemical cell.

The electrolyte samples withdrawn from the slimes layer were analyzed by using Atomic Absorption Spectroscopy (AAS) \textsuperscript{4} and specific ion electroanalytical techniques. In these samples, Pb was determined via AAS using the absorption line at 283.3 nm.

In the Sb determination via AAS, matrix effects can affect the analysis \textsuperscript{[10]}. Thus, Sb standard solutions were prepared by adding known amounts of $\text{PbSiF}_6$ and $\text{H}_2\text{SiF}_6$ so as to match the lead and acid content of the samples. The absorption line at 231.1 nm was used to determine Sb via AAS. The total Si content \textsuperscript{5} of the entrapped electrolyte was also determined via AAS. Si was determined using the absorption line at 251.6 nm and a nitrous oxide - acetylene flame. Three different standard solutions were prepared as follows:

a) From a 1000 ppm Si solution prepared by dissolving 5.056 g of Na metasilicate ($\text{Na}_2\text{SiO}_3$.$9\text{H}_2\text{O}$) in 300 ml of deionized water, adding sufficient HCl to bring the pH to about 5 and diluting up to 500 ml using deionized water.

b) From $\text{H}_2\text{SiF}_6$ technical solutions diluted so as to obtain standard solutions with less than 1000 ppm Si.

c) From $\text{PbSiF}_6$-$\text{H}_2\text{SiF}_6$ solutions diluted so as to obtain standard solutions with less than 1000 ppm Si.

\textsuperscript{1} Deionized water with electrical conductivity lower than 12 $\mu$mhos/cm.
\textsuperscript{2} Resin from the leaves of certain species of aloes plant native to South Africa.
\textsuperscript{3} Organic additive obtained as a by-product from wood pulping operations.
\textsuperscript{4} Perkin Elmer Atomic absorption Spectrophotometer model 303.
\textsuperscript{5} The total Si content corresponds to the total amount of Si present in the electrolyte as $\text{H}_2\text{SiF}_6$, $\text{PbSiF}_6$, and $\text{SiO}_2$. 

The total amount of fluorine ions present in the entrapped electrolyte was estimated by using an ion sensitive electrode. Standards were prepared by using NaF solutions. Additionally, calibration curves were obtained using H$_2$SiF$_6$ and PbSiF$_6$H$_2$SiF$_6$ standards. Gran’s plot and standard addition techniques were incorporated in these measurements [11,12].

**D. Temperature control**

The electrochemical cells previously described were immersed in a constant temperature water bath. This bath had a volume of 9 L and was covered with styroform. The bath was stirred using magnetic bars and/or air sparging. The bath temperature was controlled by using a YSI model 71 temperature controller. A thermistor probe was used to monitor the bath temperature and immersion heaters were used to maintain it. This experimental set-up allowed temperature control within ±1.5 °C of the set point.

After the bath had reached the set temperature, the assembled electrochemical cell was introduced and at least 3 hours were allowed for the cell to reach thermal equilibrium before the electrochemical experiment began.

**E. Instrumentation**

The electrochemical instrumentation involved the use of a variety of electronic equipment. A Wenking potentiostat was used in the first half of this work and a Solartron Electrochemical Interface together with a Solartron Frequency response analyzer were used in the second half. The improvements in the electronics of the Solartron devices enable complex experiments to be performed. What follows is a description of the different electrochemical arrangements used. Also, computer control of the electrochemical experiments and data acquisition will be explained.

**I. Wenking potentiostat**

A Wenking potentiostat model 70 HV1/90 was connected to an IBM XT personal computer. A Data Translation board DT 2805 was installed in one of the computer slots. This card allowed the computer to interact with the potentiostat and with the electrochemical cell. A Data Translation DT707 screw

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1 An Orion Fluoride electrode model 94-09 together with a double junction reference electrode Orion model 90-02 filled with 1M NaNO$_3$ in the outer chamber was used in these measurements.
2 Thermistor probe YSI model 402.
3 Vycor immersion heaters with 100 to 500W of power.
terminal panel was used to address the DT2805 board. This panel acts as an extension of the DT2805 card and simplifies the process of computer interfacing. All the electrical connections are done in the DT707 terminal panel which sends and receives information from and to the DT2805 board. Besides from this terminal panel, a control panel was also used to link the potentiostat, computer, and electrochemical cell connections.

Fig. 5 shows a simplified view as to how the computer interfacing process was carried out. The flow of digital and analogue data from the computer to the system under study and vice versa was controlled by using specialized software. A number of programs were written to control the digital and analogue operations performed by the DT2805 board. The complexity of these programs varied depending on the characteristics of the experiment to be conducted. A storage oscilloscope was used to test the performance of these programs and to follow the response of the system when required. A digital voltmeter was also used to check the computer measurements.

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1 Asystant® menu-driven software version 1.02, and Asyst® command-driven software version 2.10.
2 Tektronix analogue oscilloscope model 5115
3 Beckman 31/2 digit multimeter model TECH 300.
Fig. 6  Detail of the connections required to interrupt the current and to follow the cell response

(A) Three terminal cell
(B) Four terminal cell
The Wenking potentiostat was used either as a potentiostat or as a galvanostat. Potentiostatic operation was converted to galvanostatic by connecting a resistor of suitable power rating between the working and reference electrode terminals\(^1\). It was in this configuration that most of the experiments were conducted. During galvanostatic operation, current was interrupted by short-circuiting the internal battery that controls the flow of current to the cell. This was done by using a mercury wetted relay\(^2\) activated by the computer at preset times. The connections required to interrupt the current and to follow the cell response are shown in Fig. 6. As Fig. 6 shows, the current going through the cell and the difference in potential between the working and the reference electrodes were continuously logged. Figs. 6A and 6B differ only in the number of connections made to the working electrode. When two connections are used (Fig 6B), one of them is used for conveying current and the other is used for measuring potential. Experiments in which large amounts of current are involved or when contact resistances are to be avoided call for this particular electrode arrangement.

Calibration of the routines used for interrupting the current was done by using "dummy" cell electrical circuits. Appendix 5 provides a description of these measurements. The algorithm used in the computer programs to perform the current interruptions is also described in Appendix 5. By doing these calibration runs, it was found that the Wenking potentiostat halts the flow of current to the cell almost immediately (within 10 \(\mu\)sec\(^3\)). On the other hand, after the short circuit was opened it was found that the current did not immediately recover its previous value. The rise time of this process was of the order of milliseconds and was dependent of the current going through the cell (e.g. see Fig. 7). In addition, due to hardware and software limitations, the data acquisition system was able to follow the decay in potential only within 1 msec after current interruption\(^4\). Subsequent points were sampled at various acquisition rates. This resulted in the current interruption routine being able to resolve decays whose time

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1 As shown in Fig. 6, the reference terminal of the Wenking potentiostat is no longer used for connecting the reference electrode of the electrochemical cell.

2 Mercury wetted relay Elect-trol model 31511051.

3 Value obtained from oscilloscope readings.

4 Depending on the complexity of the data acquisition program, the interval of time between current interruption and the first set of data points sampled was between 0.14 msec and 1.0 msec. Oscilloscope readings were used to verify these measurements.
constants were larger than 10 msec. As the time constant of the diffusion processes under study were several orders of magnitude larger than 10 msec, this instrumental constraint was not critical.

![Graph of current step resulting from halting the flow of current to the electrochemical cell using the Wenking potentiostat. Current was halted within ~10 μsec.](image)

2. **Solartron electrochemical interface and frequency response analyzer**

(a) **Generalities:**

A 1286 Solartron Electrochemical Interface (SEI) and a 1250 Frequency Response Analyzer (FRA) were connected to an IBM XT personal computer by using the IEEE-488 interface built into these instruments. To link these instruments to the computer, an IEEE compatible board\(^1\) was installed in one of its slots. This board enables the computer to act as a "controller" of the flow of information. All the electrical connections of the electrochemical cell were attached directly to the SEI front panel.

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\(^{1}\) Scientific Solutions IEEE 488 LM board.
Programming of the IEEE-488 interface is simpler than programming of the Data translation interface previously described. All analogue to digital conversions are done directly in the IEEE apparatus. This results in all the data communications being digital. IEEE instruments are controlled by a series of pre-established commands. As these commands are executed they send information to the control device (in this case the computer). This information instructs the control device with respect to the status of the instrument.

The SEI is a complex and powerful instrument that can be used as a stand alone electrochemical device. In its simplest configuration, it can function either as a potentiostat or as a galvanostat. By pressing a button in its control panel (or by sending a command from the computer) switching between these two operating modes can easily be incorporated. Among other features, the SEI offers several ways of obtaining the value of the uncompensated ohmic drop $\text{IR}_0$. Among these, the SEI has built in a procedure ("sampled" $\text{IR}_0$ compensation) which allows the potential to be sampled a few microseconds before and after current is interrupted. However, this $\text{IR}_0$ drop compensation routine operates only under potentiostatic conditions. When galvanostatic experiments are performed, this limitation can be circumvented by switching from galvanostatic to potentiostatic operation, interrupting the current, and switching back to galvanostatic control. Under computer control the whole process takes @5 sec.

The FRA is also a complex instrument. One of its fundamental functions is to generate waveforms. Sinusoidal, triangular, or square waves in the frequency range between 10 $\mu$Hz and 65.5 Khz can be generated by this device. The frequency and amplitude of these waveforms can easily be modified. Another of the FRA main functions is to analyze the gain and phase characteristics of sinusoidal waveforms. The system transfer function can be obtained by analyzing concurrently two sinusoidal signals. This is obtained by using two channels for simultaneous measurements at any two points in the system.

(b) Description of the experimental set-up

Both DC and AC experiments were carried out using the SEI together with the FRA. Fig. 8 describes the electrical connections that were used in these experiments. Furthermore, Appendix 6 illustrates the implementation of the

1 This uncompensated ohmic drop $\text{IR}_0$ is equivalent to $\tau_0$, described in Chapter 2.
technique using dummy circuits to simulate the response of electrochemical cells. The experimental data generated using these dummy circuits was used to calibrate the electrochemical set-up.

![Diagram of Connections from the Electrochemical Cell to the Solartron Electrochemical Interface.](image)

The dissolution of pure lead and of typical lead anodes was studied using the beaker electrochemical cell previously described. In these studies, all leads were shielded to avoid pick-up noise. During the galvanostatic and potentiostatic experiments current was interrupted using the "sampled" IR compensation routine built into the SEI. In these measurements, only the value of the uncompensated resistance was obtained.

The AC impedance of pure lead and of typical lead anodes was measured under a variety of experimental conditions. Impedance measurements were made under rest potential conditions, in the absence and in the presence of a slimes layer, and in the absence and presence of DC current. All the AC impedance spectra were obtained using sampling rates and integration times set to 200 cycles per frequency followed by a 5 sec break. The SEI bandwidth

---

1 The difference in potential between the working and reference electrodes and the current flowing to the cell are continuously recorded by the SEI. During the AC experiments, the SEI removes the DC component (if present) from the potential and current waveforms before sending them to the FRA. The fundamental frequency of these waveforms was used to obtain the impedance of the system.

2 Integration times were reduced by using the auto-integration routine built-in the FRA. A long integration cycle was chosen (1% error with 90% confidence)
type chosen for experiments under potentiostatic control was the type E (maximum bandwidth 24kHz) and for experiments under galvanostatic control the type B (bandwidth >100KHz).

II. Electrolyte Physico-Chemical Properties

A. pH measurements

The pH of $\text{H}_2\text{SiF}_6$ containing solutions was measured using a liquid membrane pH electrode$^1$ and a double junction reference electrode$^2$. Measurements were made at room temperature. In these measurements, no attempts were made to correct for liquid junction potentials. pH measurements were also performed using pH sensitive paper.

B. Electrical conductivity

The electrical conductivity of $\text{H}_2\text{SiF}_6$-$\text{PbSiF}_6$ electrolytes was measured using a Radiometer conductivity meter model CDM2 and a YSI conductivity cell$^3$ model 3417. A Digital voltmeter was connected to the conductivity meter to assist in the reading of the conductivity measurements. The electrical conductivity of individual solutions$^4$ was measured by immersing the samples in a water bath whose temperature was controlled to within 0.2°C. Two thermocouples$^5$ were used to monitor the bath temperature at different positions in the water bath. The thermocouples were connected to a computer which was used as a temperature control device. Temperature was maintained within the set limits by using heating elements controlled by the computer via solid state relays (SSR)$^6$.

C. Kinematic viscosity

Kinematic viscosity of $\text{H}_2\text{SiF}_6$-$\text{PbSiF}_6$ solutions was measured using Cannon-Fenske routine viscometers for transparent liquids. The viscometers were...

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1 Orion pH electrode model 93-01.
2 Orion double junction reference electrode model 90-02. The inner filling solution used in this electrode (Orion 90-00-02) matches the characteristics of the standard KCl calomel electrode. In the outer chamber a 1 M NaNO$_3$ solution was used.
3 Cell constant = 1.05. Cell constant was obtained by measuring the electrical conductivity of a NaCl saturated solution and of a 0.100 M KCl solution at different temperatures.
4 Sample volumes vary between 25 and 30 ml.
5 Thermocouples type E Chromel(+) - Constantan(-). A 0°C reference junction was used during the temperature measurements.
6 Omega DC controlled solid state relay (SSR) model SSR 240 D10. Control voltage 2-32 Vdc.
immersed in a constant temperature water bath\(^1\) and calibrated using deionized water. Temperature was controlled within 0.2°C. From 5 to 12 viscosity measurements\(^2\) were made until average flow times\(^3\) readings were within 0.20 sec.

**D. Density**

The density of \(\text{H}_2\text{SiF}_6\)-\(\text{PbSiF}_6\) solutions was measured using 25 mL Bingham-Type pycnometers. Pycnometers were calibrated by measuring the density of deionized water. Measurements were made at room temperature. From 3 to 5 density measurements were made until the obtained mean density values were within 0.2%.

\(^1\) Cylindrical water bath with @2L volume.
\(^2\) Viscosity measurements were made using 10 ml sample volumes.
\(^3\) Flow times measured by using a digital stopwatch. Parallax errors were diminished by using a magnifying glass.
Chapter 4 Electrorefining of Lead in a Small-Scale Electrorefining Cell: A Case Study

I. Introduction

During the electrorefining of lead by the Betts electrorefining process, ionic concentration gradients become established within the slimes layer due to the restriction that the slimes layer presents to the movement of ions. Additionally, the presence of the electric field created by the passage of current contributes to the formation of concentration gradients within this layer.

The Betts electrorefining process is carried out under nearly galvanostatic conditions. Under these conditions, a constant flux of lead ions is generated at the anode/slimes interface. These ions are driven towards the cathode by diffusion, migration, and convection. In the absence of a slimes layer, mixing of electrolytes removes the migration and diffusion restrictions. Thus, if pure lead were to be dissolved, the concentration gradients generated would be present only within 100 to 1000 μm of the anode/bulk electrolyte interface where mixing disappears. On the other hand, during the refining of lead bullion, the slimes layer generates an environment in which ionic concentration gradients can be present over distances larger than 10 mm. These concentration gradients contribute to gradients in electrode potential applied to slimes filaments, and thereby affect the dissolution of noble impurities. Primarily, this gradient arises due to the larger concentration of lead ions in the vicinity of the anode interface with respect to their concentration in the bulk electrolyte. Lead ions move out of the slimes layer mainly by diffusion and migration. As lead ions are released, their positive charge must be neutralized to achieve local electroneutrality. This leads to reverse movement of SiF$_6^{-2}$ and repulsion of H$^+$ from the anode/slimes interface. Electrical neutrality has to be observed throughout the slimes layer and this dictates a strong relationship between the SiF$_6^{-2}$, H$^+$, and Pb$^{2+}$ concentration gradients.

Given the previous relationships, the slimes layer will have a large average concentration of Pb$^{2+}$ and SiF$_6^{-2}$ ions and a small average concentration of H$^+$ ions with respect to their bulk electrolyte values. Moreover, there will be gradients of their concentrations throughout the slimes depending on the slimes thickness and the current density. The interrelationship between the diffusion coefficients, ionic mobilities, and activity coefficients of the above ions plays a significant role.
in the shape of these concentration gradients. In addition, migration will promote the movement of anions from the bulk electrolyte towards the anode interface and would act in the opposite direction for cations. Diffusion will carry Pb^{2+} out of the slimes layer and SiF_{6}^{2-} and H^{+} towards it. Convection will affect the movement of all the ions and depending on the electrode size, it can affect significantly the shape of the concentration gradients.

The establishment of ionic concentration gradients within the slimes layer can shift secondary equilibria that can lead to both new solutes and precipitates such as fluoride and oxyfluoride ions, hydrated silica, and lead fluorides. The precipitates can create further hindrances (in addition of those caused by anode impurity filaments) to the convection of electrolyte and to the diffusion and migration of solutes.

The stability of the slimes layer and its adherence to the anode surface is a complex function of the lead anode physical metallurgy and of the electrolysis conditions. Upon passage of current, lead is selectively removed from the bullion and a metallic structure of noble impurities is left behind. This structure is established as a "slimes layer". The success of the Betts process relies on this structure remaining unreacted during the electrorefining cycle. By limiting the potential difference across the slimes layer to less than 200 mV, this condition is practically fulfilled. On the other hand, the complex chemistry of this layer and the presence of ionic concentration gradients within it, can affect the extent to which this potential gradient can be observed. If, due to the presence of large concentration gradients, secondary products precipitate, the slimes layer can detach. Under these conditions, the noble compounds harbored in the slimes layer may no longer remain unreacted, and depending on shifts in electrode potentials, noble impurities can be transferred to the electrolyte, then to the cathode.

In this chapter, a study of the dissolution of a typical lead anode under galvanostatic conditions is presented. The establishment of concentration gradients within the slimes layer, the precipitation of noble compounds, and the physical metallurgy of the lead anode and the produced slimes layer are reviewed in this case study. Current interruption techniques were used to find the link between the above mentioned phenomena.
II. Presentation of Results

The study of the dissolution of a typical lead anode under galvanostatic conditions was done by using the rectangular electrochemical cell described in Fig. 3.2.

Fig. 1 Lead anode top view.

The location of the holes in which the inner reference electrodes A, B, and C were inserted, is indicated in this diagram. The position of the well used to extract electrolyte samples from the slimes electrolyte is also shown.

Fig. 1 is a top view of the lead anode showing the locations where the potential sensing probes were incorporated as well as the point from which electrolyte samples from the inner slimes electrolyte were withdrawn. Particular characteristics of this experiment are provided in Table 1. Current interruption at preset slimes thickness was implemented by using the circuit described in Figs. 3.5 and 3.6.

Experiment LC2 was carried out in three stages which are described in the following paragraphs:

**Stage I:** Galvanostatic dissolution during 300 Hrs. During this stage, current flow to the cell was halted for 138 msec every 3 Hrs.

**Stage II:** Long current interruption for 190 Hrs

**Stage III:** Further galvanostatic dissolution for 30 min., during which current was halted every 10 min for 1.8 sec.
During these stages, electrolyte samples were taken from the bulk electrolyte and from the inner slimes solution at preset times. After the completion of stage III, current was halted and the corroded anode was left standing in the cell for 48 Hrs. After this time, the electrolyte was slowly drained and a dilute \( \text{H}_2\text{SiF}_6 \) solution (pH = 1.5) was used to displace the concentrated solution in the slimes layer. Afterwards, the corroded anode was removed and dried in a vacuum oven at low temperature \( (t < 40^\circ \text{C}) \). Slimes samples for observation in the SEM were prepared by using a low viscosity resin and a vacuum imbibition technique \[1,2\]. Unsupported samples of the same slimes were analyzed by X-ray diffraction.

<table>
<thead>
<tr>
<th>Table 1 Characteristics of Experiment LC2</th>
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<tr>
<td><strong>Anode Composition</strong></td>
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<tr>
<td><strong>Anode Dimensions</strong></td>
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<td><strong>Cathode</strong></td>
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<td><strong>Reference Electrodes:</strong></td>
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<td><strong>Initial Bulk Electrolyte Composition</strong></td>
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<td><strong>Additives Concentration</strong></td>
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<td><strong>Electrolyte Volume</strong></td>
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<td><strong>Electrolyte Temperature</strong></td>
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<td><strong>Electrolyte Recirculation Rate</strong></td>
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<tr>
<td><strong>Current Density during stages I and III (from geometric surface area)</strong></td>
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<tr>
<td><strong>Stage I Current Interruption Length and Frequency</strong></td>
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<tr>
<td><strong>Stage III Current Interruption Length and Frequency</strong></td>
</tr>
<tr>
<td><strong>Instrumentation</strong></td>
</tr>
</tbody>
</table>

1 Spurr low-viscosity embedding media, \( \eta = 60 \text{ cP} \)

2 In the imbibition technique, penetration of the epoxy resin is encouraged by extracting the air within the sample using a pressure difference (i.e. a vacuum).
A. Anodic overpotential measurements

1. Stage I

The anodic overpotential response of electrode LC2 under galvanostatic conditions is shown in Fig. 2. As can be seen from all four reference electrodes, $\eta_A$ increases quasi linearly as the slimes layer thickens. At the same time, $\eta_A$ measured by the inner reference electrode A shows that steep excursions in the potential of the solution inside the slimes layer also can be present, although, they do not seem to affect the $\eta_A$ value measured by the outer reference electrode. The relatively uniform slope of these measurements suggests that the same reaction and the same ions are being seen by all the reference electrodes.

The anodic overpotential response of the outer and inner reference electrodes to current interruptions are shown in Fig. 3. Details of the $\eta_A$ behavior of the inner reference electrodes A, B, and C are provided in Figs. 4 and 5. In these figures current interruptions 43 to 47 are not shown as oscilloscope readings taken during that time interval required detachment of the current interruption triggering device on the data acquisition board.

---

1 Measurements on the slimes electrical conductivity were made by following the difference in potential between a bare Pt wire inserted in the slimes layer and the lead anode. In these measurements, it was found that the difference in potential between the Pt wire and the lead anode was negligible. The Pt wire and the anode appeared to be short-circuited indicating the high electrical conductivity of the slimes filaments.

2 Oscilloscope readings were consistent with computer measurements.
Fig. 2 Anodic overpotential (uncorrected for $\eta_0$) changes as a function of the slimes layer thickness.

Stage I in Table 1.

Position of the reference electrodes:
**Outer**: Located in the bulk electrolyte, $\pm$5mm away from the slimes/electrolyte interface
**Inner A, B, and C**: Located within the lead anode at $\pm$3, 6, and 8.5 mm away from the slimes/electrolyte interface
Fig. 3 Outer and inner A, B, and C reference electrodes anodic overpotential response to current interruptions (during an otherwise galvanostatic experiment).

Abscissa values reflect current interruption number. Current interruption measurements were made every 3 Hrs. (i.e. every 0.138 mm slimes). The first current interruption was made in the absence of slimes and the 100th current interruption was made at a 13.8 mm slimes thickness.
Fig. 4 Detail of the $\eta_A$ response of the inner A reference electrode to current interruptions (during the whole electrorefining cycle). Fig. (B) is the same data presented in (A) with an expanded vertical scale.

Fig. 5 Detail of the $\eta_A$ response of the inner B (Fig. A) and inner C (Fig. B) reference electrodes to current interruptions (during the whole electrorefining cycle).
The response of the outer reference electrode to current interruption is shown in Fig. 6 for different slimes thickness. Upon current interruption, the $\eta_A$ value first drops abruptly, then decays slowly. The abrupt overpotential decay is nearly equal to the so-called uncompensated ohmic drop, $\eta_\Omega$. Furthermore, upon application of current back to the cell, it can be seen that, the thicker the slimes layer, the longer it takes to attain the $\eta_A$ value observed prior to current interruption (Fig. 6).
Fig. 7 Changes in the value of the uncompensated ohmic drop, \( \eta_{in} \), as a function of the slimes thickness.

From the \( \eta_{in} \) response of the outer reference electrode to current interruptions.

As shown in Fig. 7, \( \eta_{in} \) remains between 14 and 16 mV during the whole experiment. Only during the first interruption of current (at zero slimes thickness) does a larger potential drop appear. The decrease in this value results from changes in the electrolyte concentration in the near proximity of the slimes/electrolyte interface. Within a few milliseconds, steady state is attained and \( \eta_{in} \) no longer changes. Upon interruption of current, the concentration gradients present within the slimes layer begin to relax towards equilibrium. \( H^+ \) moves from the bulk electrolyte towards the slimes layer and \( Pb^{2+} \) and \( SiF_6^{2-} \) move in the opposite direction. This process is currentless and will cause interaction between the diffusion and migration fluxes so that the potential gradient decays in the same way as the concentration gradients.

The response of the inner reference electrode A to current interruptions is different than that observed by the outer reference electrode. Depending on the slimes thickness, \( \eta_A \) measured by this electrode can show a random behavior (see Fig. 4A). Thus, for example Figs. 8A and 8F show that upon current interruption \( \eta_A \) jumps towards higher values rather than decreasing. There is no unambiguous explanation for such jumps. The other curves in Fig. 8 show that
upon current interruption $\eta_A$ decays linearly. The amplitude of this decay is smaller than that shown by the outer reference electrode at similar slimes thickness (see Fig. 3). Additionally, there is no initial steep decay in $\eta_A$ upon current interruption. This is an indication that between this electrode and the lead anode the inner slimes electrolyte does not have a uniform composition.

**Fig. 8** Detail of the $\eta_A$ response to current interruptions measured by the **inner A** reference electrode (at different slimes layer thickness).

**X axis:** Time, msec  
**Y axis:** Anodic overpotential, mV
The inner reference electrode B response to current interruptions is shown in Fig. 9. Upon interruption of current, a very small decrease in $\eta_A$ takes place (see also Fig. 5A). This electrode is very close to the lead anode/slimes interface and the concentration of Pb$^{2+}$ in its vicinity is expected to be very high. As this interface moves away from this reference electrode, the region over which concentration gradients span grows and so decays in $\eta_A$ of larger amplitude can take place upon current interruption (see Fig. 5A).

**Fig. 9** Detail of the $\eta_A$ response to current interruptions measured by the inner B reference electrode (at different slimes layer thickness).

<table>
<thead>
<tr>
<th>X axis: Time, msec</th>
<th>Y axis: Anodic overpotential, mV</th>
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<tbody>
<tr>
<td>23</td>
<td>22</td>
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<tr>
<td>19</td>
<td>26</td>
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<tr>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>11</td>
<td>34</td>
</tr>
<tr>
<td>7.6</td>
<td>38</td>
</tr>
<tr>
<td>3.8</td>
<td>42</td>
</tr>
<tr>
<td>7.5 mm</td>
<td></td>
</tr>
<tr>
<td>3.8</td>
<td>54</td>
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<tr>
<td>60</td>
<td>70</td>
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<tr>
<td>120</td>
<td>74</td>
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<tr>
<td>240</td>
<td></td>
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<td>300</td>
<td>80</td>
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<td>180</td>
<td>120</td>
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<td>240</td>
<td>180</td>
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<tr>
<td>300</td>
<td>240</td>
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<tr>
<td>74.</td>
<td>120</td>
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<tr>
<td>70.</td>
<td>240</td>
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<tr>
<td>66.</td>
<td>300</td>
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<td>62.</td>
<td>180</td>
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<tr>
<td>58.</td>
<td>120</td>
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<td>54.</td>
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<td>50.</td>
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<tr>
<td>48.</td>
<td>240</td>
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<tr>
<td>44.</td>
<td>300</td>
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<tr>
<td>12.3 mm</td>
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<tr>
<td>9.8</td>
<td>54</td>
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<tr>
<td>16.3</td>
<td>74</td>
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<tr>
<td>10.2 mm</td>
<td></td>
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<tr>
<td>9.8</td>
<td>54</td>
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<tr>
<td>16.3</td>
<td>74</td>
</tr>
<tr>
<td>13.7 mm</td>
<td></td>
</tr>
<tr>
<td>10.2 mm</td>
<td></td>
</tr>
<tr>
<td>13.7 mm</td>
<td></td>
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</tbody>
</table>

The response of the inner reference electrode C to current interruption is depicted in Fig. 10. This electrode does not show any significant decrease in its $\eta_A$ value upon current interruption (see Fig. 5B). Furthermore, the amplitude of the potential decay shown by this electrode is the smallest among all the other

---

1 The reference electrode potential is related to the lead ion concentration. Knowledge of the activity coefficients of the various species that are in the vicinity of these electrodes is required to estimate these ionic concentrations.
reference electrodes (see Figs. 3 and 5B). The presence of a highly concentrated Pb\(^{2+}\) region between this electrode and the anode/slimes layer interface can account for this behavior.

![Graph](image)

Fig. 10 Detail of the \(\eta_A\) response to current interruptions measured by the **inner C** reference electrode (at different slimes layer thickness).

**X axis:** Time, msec  **Y axis:** Anodic overpotential, mV

A plot of the anodic overpotential values obtained right after current interruptions for the four reference electrodes is shown in Fig. 11. By comparison with Fig. 2, the correlation between the \(\eta_A\) curves becomes more evident. Fig. 11 shows that the activities of the lead ions at fixed positions change as the anode/slimes interface moves, reflecting variations in the inner slimes electrolyte composition. Furthermore, the lines for the various reference electrodes are almost parallel, indicating a near steady-state in the solution gradients between any two reference electrodes.
Fig. 11 Anodic overpotential (corrected for $\eta_0$) changes as a function of the slimes layer thickness.

Stage I in Table 1.

Position of the reference electrodes:

**Outer**: Located in the bulk electrolyte, $\approx 5\text{mm}$ away from the slimes/electrolyte interface

**Inner A, B, and C**: Located within the lead anode at $\approx 3$, $6$, and $8.5\text{mm}$ away from the slimes/electrolyte interface

2. **Stage II**

After forming a 13.8 mm thick slimes layer, current was interrupted for 190 Hrs and the lead anode polarization was followed as a function of time. By
interrupting the current for an extended period of time, the concentration gradients present within the slimes layer are expected to disappear. Changes in these concentration gradients are reflected in the polarization values which decrease as a function of time.

Stage II in Table 1. After anodic dissolution up to a 13.8 mm thick layer of slimes (Fig. 2) current was halted for 190 Hrs and the polarization was followed as a function of time.

The arrows indicate the polarization values prior to current interruption. Details of the polarization decay in the first milliseconds after current interruption can be seen in Figs. 6H, 8H, 9D, and 10D.

Fig. 12 shows how the difference in potential between the reference electrodes and the lead anode decays during current interruption. The outer and inner A reference electrode polarizations decay to values close to zero within a few hours. On the other hand, the potential difference measured by inner reference electrodes B and C is negative. Furthermore, after a certain time has elapsed, the polarization displayed by these electrodes jumps to near zero values. The closer the reference electrode is to the anode/slimes interface, the longer it takes for this polarization jump to occur. This rise in potential difference is
attributed to dissolution of precipitated products that result from changes in electrolyte composition in the inner slimes layer. Mixed electrochemical processes that can support internal currents in the absence of an external current, such as the reduction of an oxidized ion, also can account for the negative polarization values displayed by these electrodes.

3. Stage III

After allowing the concentration gradients present within the slimes layer to relax during the long current interruption, current was applied back to the cell during 30 min (Fig. 13).

Fig. 13 Changes in the value of the anodic overpotential (uncorrected for \( \eta_{\text{OA}} \)) as a function of the electrolysis time.

Stage III in Table 1. After interrupting the current for 190 Hrs (Fig. 13), current was applied back to the cell and the \( \eta_{\text{A}} \) values shown in this plot were obtained.

---

1 Among these mixed electrochemical processes are: (a) local concentration cells (b) cementation reactions (c) Re-dissolution of \( \text{PbF}_2 \): \( \text{PbF}_2 + 2e^- = \text{Pb}^{2+} + 2F^- \)
Current interruptions were applied at different electrolysis times as indicated by the arrows shown in each plot:

(1) 0.01 min (2) 10 min (3) 20 min (4) 30 min

Each plot indicates the overpotential response measured by a different reference electrode:

(A) Outer (B) Inner A (C) Inner B (D) Inner C

**Fig. 14** Anodic overpotential response upon current interruption (Stage III Table 1)
Fig. 13 shows how the anodic overpotential values increased during the application of current back to the cell. Concentration gradients within the slimes layer become established very rapidly: In 30 min only ≈0.02 mm of slimes were formed yet the $\eta_a$ values increased by more than 40 mV. This shows that the slimes layer does hinder appreciably the flow of ions. Current interruptions during 1.8 sec were applied during this stage to study the characteristics of these concentration gradients (Fig. 14). At time zero no significant decay in potential is observed upon current interruption in any of the reference electrodes. As concentration gradients become established, larger overpotential drops can be observed upon current interruption.

B. Analytical chemistry

1. Bulk electrolyte concentrations

The changes in composition in the bulk electrolyte during Stage I are shown in Fig. 15. A continuous depletion of Pb$^{+2}$ in the bulk electrolyte is seen to take place during the formation of the slimes layer. As the current efficiency for the refining process was close to 100%, this depletion can only be associated with Pb$^{+2}$ concentration enrichment in the electrolyte within the slimes layer. Concurrently to the Pb$^{+2}$ depletion, there is a continuous, yet small increase in acid concentration which is related to H$^+$ depletion within the slimes layer. No major changes in the bulk electrolyte concentration of hydrolyzed SiO$_2$ were detected during this stage.

The changes in the bulk electrolyte composition during Stage II are shown in Fig. 16. Upon current interruption, there is an increase in the Pb$^{+2}$ bulk electrolyte composition, and a decrease in the acid concentration. Once current is interrupted, Pb$^{+2}$ and SiF$_6^{-2}$ diffuse out of the slimes layer while H$^+$ diffuses in.

---

1 In the same period of time, the outer anodic overpotential rose by less than 2 mV in the absence of the slimes layer (Fig. 2), as compared to a 65 mV rise in the presence of a 13.8 mm thick layer of slimes (Fig. 11).

2 Material balances indicated that the slimes electrolyte can have average [PbSiF$_6$] higher than 1 M while [H$_2$SiF$_6$] can be lower than 0.5 M.

3 SiO$_2$ as determined by titration via the LiF-LiOH technique described in Appendix 4 is merely a composite of all dissolved species containing at least 1 oxygen atom. The general formula Si$_x$(OH)$_y$F$_z$ with 1 ≤ y ≤ 4, and $\frac{z}{x}$ ≤ 6 accounts for the existence of these species.
Fig. 15 Changes in composition of the bulk electrolyte as a function of the slimes layer thickness.

Stage I in Table 1.
At preset electrolysis times bulk electrolyte samples were withdrawn from the bulk electrolyte and analyzed for the species shown in this plot.

From chemical analysis data

Fig. 16 Changes in the bulk electrolyte composition as a function of the current interruption time.

Stage II in Table 1.
From chemical analysis data
2. Inner slimes electrolyte concentrations.

Some information about local ionic concentrations within the slimes layer was obtained by withdrawing small amounts of electrolyte (≈100 μl) from a fixed point located ≈3mm away from the slimes/electrolyte interface (as shown in Fig. 1). 

![Graph showing changes in the local composition of the slimes electrolyte as a function of the movement (from the sampling point) of the anode/slimes interface.](image)

**Fig. 17** Changes in the local composition of the slimes electrolyte as a function of the movement (from the sampling point) of the anode/slimes interface.

Stage I in Table 1.
From a fixed point located ~3 mm away from the slimes/bulk electrolyte interface (Fig. 1) electrolyte samples were withdrawn at preset times and analyzed for the species shown in the plot. 

*From chemical analysis data*

Fig. 17 shows the changes in the composition of the inner slimes electrolyte during stage I as the anode/slimes interface moves away from the sampling point. As can be seen, Pb\(^{2+}\) concentrations at this point are not as high as the average values predicted from mass balance computations. Furthermore, the acid balance is also somewhat larger than expected. However, Pb\(^{2+}\) concentrations were found to be between 3 and 6 times larger than the corresponding bulk electrolyte values. Differences between mass balances and local compositions may be due to presence of precipitates and also to the fact that sampling was made only at one point within the slimes layer. Fig. 17 also shows that negative changes in the acid concentration accompany positive PbSiF\(_6\) variations. This indicates that SiF\(_6^{2-}\) exerts an influence in the transport processes within the slimes layer. The SiO\(_2\) concentrations shown in Fig. 17 indicate that large amounts of these species are contained in the inner slimes electrolyte.
Analysis of ionic species of noble impurities in this electrolyte showed that AsO\(^+\) was present in concentrations of ~0.17 mM whereas [BiO\(^+\)] was lower than 0.01 mM. Additionally, [SbO\(^+\)] in the entrapped electrolyte was of the order of 0.2 mM. Furthermore, no major changes in the concentration of these noble species were detected during the refining cycle. These small amounts of noble impurities in the inner electrolyte indicate that they do not react significantly at the corresponding overpotential levels shown in Fig. 12.

![Graph A](image1.png) ![Graph B](image2.png)

**Fig. 1** Changes in the local concentration of the total Si and F present in the slimes electrolyte as a function of the movement (from the sampling point) of the anode/slimes interface

Stage I in Table 1. Electrolyte samples taken from a fixed point located ~3 mm away from the slimes/bulk electrolyte interface were analyzed for total Si and F using three different analytical techniques.

**(A)** Changes in the total concentration of Si-bearing species
**(B)** Changes in the total concentration of F-bearing species

From chemical analysis data

---

1 Analysis of the cathode at the end of stage III confirmed that impurities dissolution was not significant. Cathode impurities concentrations were: 0.0003% Cu, 0.0010% Sb, 0.0016% Bi, <0.0003% Sn, <0.0001% Ag, and <0.0001% Tl.
Inner slimes electrolyte concentrations.

Stage II in Table 1. From a fixed point located ~3 mm away from the slimes/bulk electrolyte interface electrolyte samples were withdrawn at preset times and analyzed for the species shown in the plot.

From chemical analysis data

Fig. 19 Changes in the local composition of the slimes electrolyte as a function of the current interruption time.

Chemical analysis of total Si and F in the inner slimes electrolyte during stage I are provided in Fig. 18. Si and F total concentrations decrease as the slimes layer thickens. Changes in the local composition of the slimes electrolyte are unexpected under steady state anode dissolution conditions. Time dependent processes such as changes in convection due to movement of the anode/slimes interface and/or gradual precipitation of secondary compounds can account for the Si and F decrease at a fixed point such as observed in Fig. 18.

Changes in the composition of the inner slimes electrolyte during stage II are depicted in Fig. 19. Although no major changes in Pb\(^{2+}\) concentration are observed during the long current interruption, a significant enhancement in the acid concentration is observed. Also, a sudden decrease in [SbO\(^+\)] concentration seems to occur just a few hours after current interruption. As expected, the total Si and F concentrations increase during the current interruption stage (see Fig. 20). Thus, as concentration gradients disappear, the driving force for convection decreases continuously and redissolution of precipitates can take place.
Fig. 20 Changes in the local concentration of the total Si and F present in the slimes electrolyte as a function of the current interruption time.

Stage II in Table 1. Electrolyte samples taken from a fixed point located ~3 mm away from the slimes/bulk electrolyte interface were analyzed for total Si and F using three different analytical techniques. Total Silica and total fluorine were calculated by adding the concentrations of all the Si and F-bearing species.

(A) Changes in the total concentration of Si-bearing species
(B) Changes in the total concentration of F-bearing species

From chemical analysis data

C. Characterization of the slimes layer

As described in the previous section, the total concentration of noble impurities present in the cathodic deposit was lower than 30 ppm. Thus, no significant dissolution of noble phases and compounds present in the original lead anode should take place. The relationship between the phases and compounds present in the uncorroded lead anode and those found in the slimes layer was studied by using metallographic techniques. Electron probe microanalysis (EPMA) of these samples was done by using energy dispersive spectrometry. Additionally, X-ray diffraction was used to study the distribution and presence of these phases and compounds within the slimes layer.
1. Metallography of the starting lead anode

Fig. 21 shows the section of the lead anode used in the metallographic analysis, and the observation points chosen to correspond to locations where the slimes layer structure was later studied.

![Diagram of anode section](image)

Fig. 21 Section of the lead anode and of the slimes layer studied metallographically.

The observation points in the uncorroded specimen were chosen to correspond to matching locations in the slimes layer.

Fig. 22 shows the microstructure of the lead anode ("air" face, location #1 in Fig. 21)\(^1\). A variation of the so-called "honeycomb" structure can be observed in Fig. 22. As found from EPMA\(^2\), the inner grains in this microstructure have a large concentration of lead-rich phases, whereas the grain boundaries are somewhat depleted in lead and can contain large concentrations of noble elements (Sb, As, Bi, Ag). EPMA performed in this sample (Fig. 22C) shows significant variations in elemental concentrations along the grains and the grain boundaries.

---

1 This sample was prepared by polishing up to 600 grit followed by 5 μm alumina. Afterwards, the sample was chemically etched with a polishing-etching solution of the following composition: 20 ml CH\(_3\)COOH (concentrated), 42 ml H\(_2\)O\(_2\) (30%), 40 ml HNO\(_3\) (concentrated), and 70 ml of glycerine [6-8].

2 EPMA in etched samples is not recommended as irregular absorption of x-rays resulting from topography affects the analysis. Thus, the electron probe microanalysis shown in Fig. 22C only indicates qualitative changes in concentrations.
Fig. 22 Lead anode microstuctures. Anode "A", Air cooled face. All micrographs correspond to the same observation point( point #1 Fig. 21).

Secondary Electron Images

Specimen was polished up to grit 600 and subsequently chemically polished/etched

<table>
<thead>
<tr>
<th>EPMA Fig. C, %wt</th>
<th>Cu</th>
<th>As</th>
<th>Ag</th>
<th>Sb</th>
<th>Pb</th>
<th>Bi</th>
</tr>
</thead>
<tbody>
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</tr>
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<td>7</td>
<td>0</td>
<td>9</td>
<td>2</td>
<td>3</td>
<td>83</td>
<td>2</td>
</tr>
</tbody>
</table>
The changes in the anode microstructure at different parts of the lead anode can be seen in Figs. 23 and 24 (locations #2 and #3 respectively of Fig. 21). EPMA \(^2\) performed on this sample shows that there is less Pb in the grain boundaries than inside the grains. Furthermore, Bi seems to be present with lead throughout the whole microstructure. This analysis also shows a eutectic phase that is rich in As and Sb (points 6 and 7) whereas Sb and Ag-rich phases can be observed in the proximities of the grain boundaries (points 8 and 9) and in some cases within the grains. The precipitates within the grains have a random composition. Most of these precipitates are Pb-rich compounds. Additionally, Cu-As compounds (not identified in Fig. 23) can also be seen inside the grains. The microstructures compared in Fig. 24, show the continuity of the honeycomb structure throughout the sample.

---

1 These samples were not etched. They were prepared by polishing up to 600 grit followed by using 0.5 µm alumina. Backscattered electrons were used to reveal the anode microstructure.

2 As these samples were not etched, relative changes in the probe microanalysis are significant and represent semi-quantitative changes in the elemental composition of the samples.
Fig. 23 Lead anode microstructures. Anode "A". All micrographs correspond to the same observation point (point #2 Fig. 21).

Backscattered Electron Images
Specimen was polished up to grit 600 followed by using 0.5 μm alumina (sample was not etched or chemically polished).

<table>
<thead>
<tr>
<th>Point</th>
<th>Cu</th>
<th>As</th>
<th>Ag</th>
<th>Sb</th>
<th>Pb</th>
<th>Bi</th>
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<td>0</td>
<td>1</td>
<td>87</td>
<td>5</td>
</tr>
</tbody>
</table>
Fig. 24 Lead anode microstructures. Micrographs correspond to different observation points (A) and (B) Observation point #2 Fig. 21 (C) and (D) Observation point #3 Fig. 21

Backscattered Electron Images
Specimens were polished up to grit 600 followed by using 0.5 μm alumina (samples were not etched or chemically polished)
2. Analysis of the slimes layer phases and compounds

(a) SEM analysis

The slimes microstructure\(^1\) \(\approx\) 2 mm away from the slimes/bulk electrolyte interface is shown in Fig. 25\(^2\). The Pb-rich phases inside the grains have dissolved and the noble phases are left behind. The dissolution of the Pb-rich phases near the grain boundaries can be seen in Fig. 26. EPMA showed that large concentrations of noble elements are present along the former grain boundaries and that there are gradients in their concentrations (e.g. compare points 1 and 2). Additionally, noble compounds and various segregates were detected in these microstructures (see points 3 and 4). Fig. 26C shows the form of the precipitates of noble phases originally present inside the lead anode grains which report to the slimes layer.

The slimes layer microstructure\(^1\) \(\approx\) 12 mm away from the slimes/bulk electrolyte interface is shown in Fig. 27. Evidence for the presence of Si-rich compounds is the major difference between this microstructure and the microstructures shown in Figs. 25 and 27. As can be seen in Fig. 28, Si surrounds the former grain boundaries and appears randomly throughout the structure. Si is expected to result from the hydrolysis of SiF\(_6\)^{-2} which should be more severe near the anode/slimes interface.

\(^1\) Total slimes thickness \(\approx\) 13.8 mm.

\(^2\) Samples were mounted using a vacuum imbibition technique and a low viscosity resin. Careful polishing using the 0.5\(\mu\)m cloth grit was used to remove the excess of resin. Samples were coated with graphite previous to their observation in the SEM.
Fig. 25 Microstructure of the slimes layer @2mm away from the slimes/electrolyte interface (position #2 Fig. 21)
Backscattered Electron Image
Fig. 26 Detail of the microstructure of the slimes layer @2mm away from the slimes/electrolyte interface (position #2 Fig. 21)

Backscattered Electron Images

<table>
<thead>
<tr>
<th>EPMA Fig. C, %wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point</td>
</tr>
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<td>-------</td>
</tr>
<tr>
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</tr>
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<td>2</td>
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<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
</tbody>
</table>
Fig. 27  Microstructure of the slimes layer @12mm away from the slimes/electrolyte interface (position #3 Fig. 21)
Backscattered Electron Image
**Fig. 28** Detail of the microstructure of the slimes layer @12mm away from the slimes/electrolyte interface (position 3 Fig. 21)

*Backscattered Electron Images*

<table>
<thead>
<tr>
<th>EPMA Fig. C, %wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
</tbody>
</table>
Table 1 shows the results of the X-ray diffraction analysis of unsupported slimes samples. 

<table>
<thead>
<tr>
<th></th>
<th>Outer Slimes (≥2 mm from the slimes-electrolyte interface)</th>
<th>Inner Slimes (≥12 mm from the slimes-electrolyte interface)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbF₂</td>
<td>X</td>
<td>XXX</td>
</tr>
<tr>
<td>SiO₂</td>
<td>X</td>
<td>XX</td>
</tr>
<tr>
<td>Sb₂O₃</td>
<td>X</td>
<td>XXX</td>
</tr>
<tr>
<td>Sb₂O₄</td>
<td>X</td>
<td>XX</td>
</tr>
<tr>
<td>Bi</td>
<td>X</td>
<td>XX</td>
</tr>
<tr>
<td>Sb</td>
<td>X</td>
<td>XX</td>
</tr>
<tr>
<td>PbO (yellow)</td>
<td>.</td>
<td>-</td>
</tr>
<tr>
<td>Ag₃Sb</td>
<td>.</td>
<td>XX</td>
</tr>
<tr>
<td>Cu₃Sb</td>
<td>.</td>
<td>XX</td>
</tr>
<tr>
<td>As₂O₃</td>
<td>-</td>
<td>X</td>
</tr>
<tr>
<td>PbSiO₃</td>
<td>.</td>
<td>.</td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>X</td>
<td>XX</td>
</tr>
</tbody>
</table>

Phase presence is dubious
- Phase detected in very small concentrations
X Phase detected in low concentrations
XX Phase detected in medium concentrations
XXX Phase detected in large concentrations

The presence of PbF₂ in these samples and its relative larger concentration in the inner slimes is a supplementary indication to the presence of Si detected by EPMA that hydrolysis of SiF₆²⁻ takes place.

The presence of metallic Bi, and Sb, together with some of their oxides was as expected from electron probe microanalysis. The presence of intermetallic compounds (i.e. Ag₃Sb and Cu₃Sb) was also expected from these analysis.

---

1 With multiple phases present there were overlapping peaks that caused problems with positive, unambiguous identification.
2 The presence of oxides can be the result of oxidation of the slimes after they were dried.
Chapter 5 Anodic and Rest Potential Behavior of Pure Lead in $\text{H}_2\text{SiF}_6$-$\text{PbSiF}_6$ Electrolytes

I. Overview of Pure Lead Dissolution in $\text{H}_2\text{SiF}_6$-$\text{PbSiF}_6$ Electrolytes Under Galvanostatic Conditions

In this chapter the dissolution of a pure lead electrode is discussed in terms of DC and AC electrochemical measurements. A qualitative analysis of the controlling mechanisms for lead dissolution is presented. The different components of the anodic overpotential are related to phenomena taking place in the electrode boundary layer. In the case of pure lead, there are no complications due to the presence of slimes.

A. Anodic overpotential in the absence of large concentration gradients in the anode boundary layer

During the galvanostatic dissolution of the lead bullion anode described in Chapter 4, the value of the uncompensated ohmic resistance, $\eta_0$, remained nearly constant during the whole electrorefining cycle (Fig. 4.7). In this case, the presence of large ionic concentration gradients within the slimes layer results in a counter E.M.F. that is responsible for the failure of the anodic overpotential to decay to zero upon current interruption. When pure lead is dissolved, $\eta_0$ increases continuously with time as seen in Fig. 1, as a result of the progressive ohmic resistance created by the movement of the anode/electrolyte interface. Increases in $\eta_0$ reflect changes in the distance between the reference electrode and the anode/electrolyte interface which directly affect the $R_s$ value. Under these conditions, $\eta_0$ appears to be the only source of potential between the lead anode and the reference electrode. By subtracting the calculated ohmic resistance from the $\eta_A$ measurements, the extent to which concentration gradients become established in the anode boundary layer can be studied. As Fig. 1A shows, the corrected anodic overpotential value remains constant during the dissolution of lead, indicating a constant thickness of the boundary layer across which concentration gradients persist. Concentration overpotential can be considered to be the only source of potential under these circumstances, as lead dissolution

---

1 As explained in Chapters 2 and 4, $R_s$ [$\Omega\text{cm}^2$] is the specific resistance of the electrolyte and is related to $\eta_0$ by the following relationship: $\eta_0=IR_s$. 

[86]
Anodic overpotential in the absence of large concentration gradients in the anode boundary layer occurs nearly reversibly ($\eta_{ac}=0$ mV). The small magnitude of the generated concentration overpotential indicates that large concentration gradients are not established.

![Diagram](image-url)

**Fig. 1** Potential difference between a fixed reference electrode and a corroding anode in the absence of addition agents.

Experimental conditions: Galvanostatic Experiment, Current Density= 200 Amp m$^{-2}$, Electrode Area 1.50 cm$^2$, $[\text{PbSiF}_6]=1.31$ M, $[\text{H}_2\text{SiF}_6]=0.30$ M, $T=40\pm1.5^\circ$C, bulk electrolyte electrical conductivity $\kappa=220$ mmhos cm$^{-1}$. Beaker electrochemical cell, electrolyte volume $\approx300$ml, stationary electrolyte. Wenking potentiostat-Data Translation Board-IBM XT computer.

(A) $\eta_{ac}$ variation during the dissolution of pure lead
(B) $\eta_{ac}$ changes obtained by interrupting the current at preset times.

---

1 $\eta_{ac}$ determination was done by using AC impedance techniques described in section III.
2 In the case shown in Fig. 1 concentration gradients in the Nernst boundary layer span over a region between 100 and 1000 $\mu$m thick. By comparison, during the refining of impure lead, concentration gradients are present throughout the whole slimes layer (i.e. the Nernst boundary layer spans over several mm).
B. Correlation between the anodic overpotential and the presence of addition agents.

During the refining of lead, addition agents (i.e. aloes and lignin sulphonate) are normally used to modify cathodic reactions. The presence of addition agents can also affect anodic reactions through complex adsorption mechanisms [1]. In general, the $\eta_A$ values observed during the galvanostatic dissolution of pure lead were found to increase in the presence of addition agents in the bulk electrolyte. Moreover, when an excess of these additives is added to the electrolyte, to the extent that suspended material is visible, they collect on the anode and promote very large overpotential values. This behavior is shown in Fig. 2A where it can be seen that in a few hours $\eta_A$ rises from 0 to $\approx$1000 mV. In this case, current interruption measurements indicate that $\eta_\Omega$ accounts for most of the overpotential values (Fig. 2B). In the presence of purely resistive films in the anode surface, $\eta_\Omega$ can be described by the following equation:

$$\eta_\Omega = IR_s = I(R_b + R_{film})$$

$R_b$ was found to be equal to 1.4 $\Omega$cm$^2$ from the ohmic drop value obtained a few seconds after the electrolysis began. Any extra increases in $\eta_\Omega$ are due to the presence of $R_{film}$. The $\eta_\Omega$ produced by this film along with its resistance are plotted in Fig. 2B. It seems as if the addition agents form or generate a highly resistive film that may be counter productive to the refining process. Furthermore, the presence of this film favours the development of concentration gradients in the anode/electrolyte interface. Thus, the $\eta_A$ values obtained upon current interruption increase continuously with time (see inset Fig. 2A) indicating that the stagnant zone at the anode surface is thickening.

1 See section II.b.
2 Visual observation of the anode after the refining process showed that a yellowish film adhered to the anode surface. Such a film was visible only when the amount of undissolved addition agents was large. In electrolyte solutions where the electrolyte was filtered prior to its introduction to the cell, the addition agent film was not visible at naked eye.

The amount of suspended solids produced by excess additives (aloes and lignin sulphonate) seem to increase with increasing lead concentrations in the electrolyte. Techniques for increasing the dissolution of these and other additives are reported in the literature [2].
Fig. 2 Overpotential changes during the galvanostatic dissolution of pure lead (in the presence of excess quantities of addition agents)

Experimental conditions: Current Density = 180 Amp m\(^{-2}\), Electrode Area 31.0 cm\(^2\), \([\text{PbSiF}_6]\)=1.31 M, \([\text{H}_2\text{SiF}_6]\)=0.30 M, 2 g l\(^{-1}\) aloe and 4 g l\(^{-1}\) lignin sulphonate (suspended material was visible), T=40±1.5°C. Rectangular electrochemical cell, electrolyte volume 320ml, bulk electrolyte recirculation rate 6 ml min\(^{-1}\). Wenking potentiostat-Data Translation Board-IBM XT computer.

(A) \(\eta_a\) increases as a function of the electrolysis time

(B) Changes in the \(\eta_a\) and \(R_{\text{film}}\), as a function of the electrolysis time. Left axis: \(\eta_a\) due to the presence of a colloidal film of "undissolved" addition agent (\(\eta_{a, \text{film}}\)). Right axis: \(R_{\text{film}}\) obtained from the following relationship: \(R_{\text{film}} = \frac{\eta_{a, \text{film}}}{I}\)

C. Correlation between the anodic overpotential and the presence of secondary products that precipitate on the anode surface

Increases in the anodic overpotential values as a result of changes in its ohmic component also can be due to the precipitation of nearly insoluble salts such as PbF\(_2\) and SiO\(_2\). The precipitation of these salts can be observed if sufficiently large concentration gradients in the anode boundary layer become established. The presence of these compounds in the anode surface would hinder the movement of ions and induce even larger concentration gradients as well as increase \(\eta_a\). If the concentration gradients are large enough, even the highly
Establishment of Ionic Concentration Gradients in the Anode Boundary Layer and their Relationship to the Anodic Overpotential

In the previous section it was shown that during the dissolution of pure lead, $\eta_A$ increases almost exclusively due to changes in its ohmic component. By subtracting $\eta_Q$ from $\eta_A$, the activation and concentration overpotentials can be

1 The maximum solubility of pure PbSiF$_6$.4H$_2$O at 40 °C is 5 M (see Appendix 7).
Establishment of Ionic Concentration Gradients in the Anode Boundary Layer and their Relationship to the Anodic Overpotential

The division of the anodic overpotential in its ohmic, activation, and concentration components was attempted by studying the anodic response of pure lead to current steps. Prior to the experiment ~0.5 mm of the exposed surface of the working electrode was removed by anodic dissolution at low current density. This aided in obtaining reproducible results. Variation in $\eta_A$ as a result of the presence of addition agents was studied using the same cell and electrodes. The thickness of the hydrodynamic boundary layer was not controlled, yet, by fixing the recirculation rate of the bulk electrolyte, reproducible results were obtained.

Fig. 4 Current step function used to study the establishment of concentration gradients in the anode boundary layer. The transient period for both current rise and fall was smaller than 10 μsec. The time $t_2$ marks the onset of the current interruption.

Fig. 4 shows the characteristics of the current steps used to study the anodic behavior of pure lead. After the application of each current step, current was

1 As described in Chapter 2, concentration overpotential, $\eta_c$, develops due to the establishment of concentration gradients in the anode boundary layer and is a function of the current density and the hydrodynamic conditions. Activation overpotential, $\eta_a$, develops due to the transport hindrance that the charge carriers find during their movement across the Helmholtz electrical double layer. $\eta_a$ can be determined accurately in the absence of concentration gradients and only when it is controlling the reaction rate.

2 The experiment started by analyzing the $\eta_A$ changes using an additives-free electrolyte. Subsequently, this electrolyte was slowly substituted with an electrolyte of matching composition but containing addition agents.

3 The hydrodynamic conditions in the vicinity of the anode/electrolyte interface are more nearly a product of convection than of electrolyte recirculation. However, electrolyte recirculation assured uniform electrolyte composition between the reference electrode and the anode/electrolyte interface.
interrupted and the decay potential was followed until it reached its former rest potential value (≤0 mV). Then, the current density was increased and the next current step was applied.

A. In the absence of addition agents in the bulk electrolyte

Fig. 5 shows the changes in $\eta_A$ due to the application of the current steps. Right after current is applied there is an abrupt change in $\eta_A$ \(^1\). This steep overpotential change arises due to the presence of the $\eta_\Omega$ \(^2\) and can be described by the following relationship (see also Fig. 6):

$$\eta_A \text{ (immediately after application of current)} = IR_s = \eta_\Omega$$  \(^2\)

---

1. The first $\eta_A$ reading was taken 100 msec after the application of the current step. Oscilloscope measurements at shorter times indicated that the $\eta_A$ value at time zero could be obtained by extrapolation of the measured data.

2. $\eta_\Omega$ prior to and during the application of the current step was determined by using AC impedance techniques (see Section III). In addition the ohmic drop compensation routine built-in the electrochemical interface was used to obtain $\eta_\Omega$ (see Appendix 6).
The $R_g$ value obtained from the slope of the plot shown in Fig. 6, was nearly equal to the $R_g$ value obtained prior to the application of the current steps. The activation overpotential, if present, would be observable by a non-zero intercept or as a curvature near the origin. Evidently, activation overpotential is not controlling the dissolution of the lead anode.

The $\eta_A$ values compensated for the initial $\eta_0$ (Fig. 6) are presented in Fig. 7. The overpotential obtained immediately after application of current is very close to zero (which implies that $\eta_{ac}=0$ mV) \(^1\). Subsequent increases in the anodic overpotential are due to changes in the concentration of ionic species within the anode boundary layer \(^2\). Thus, increases in $\eta_A$ are nearly equal to changes in its $\eta_c$ component.

---

1 As described by Eq. 2, at time $t=0$, $\eta_c=0$. Thus, the overvoltage at $t=0$ becomes equal to the initial value of the activation overpotential \(3, p. 356\).

2 As the anode dissolves, an extra increment to $\eta_0$ can also be present in these measurements. $\eta_A$ changes can be neglected during the first seconds after the application of current.
In the absence of addition agents in the bulk electrolyte

Each Curve corresponds to the \( \eta_A \) response to a different current density step from lower to higher current densities.

**Fig. 7** Anodic overpotential response (corrected for initial \( \eta_A \)) of a pure lead electrode to the current steps described in Fig. 4.

From the \( \eta_A \) data shown in Fig. 5 the \( \eta_A \) values shown in Fig. 6 were subtracted.

Each curve corresponds to the \( \eta_A \) values obtained at different current densities, as follows (from bottom to top): 10, 50, 100, 150, 206, 250, 300, 500, 800, 1000, 1400, and 1600 Amp m².

The anodic overpotential response during the first seconds after the application of the current step was modelled by using the analytical solution of Fick's diffusion equation under unsteady state conditions. To solve this equation the following assumptions were used:

1) Absence of Migration
2) Absence of Convection
3) Unit Activity coefficients
4) Dissolution of lead is not controlled by kinetics (\( \eta_{ac}=0 \)).
5) Linear semi-infinite conditions

Description of the boundary conditions required to solve this equation are provided in Appendix 8 along with its analytical solution. From this solution, the following relationship between the concentration overpotential and the square root of time should be observed if the dissolution process is dominated by diffusion:

\[
\exp \left[ \frac{\eta_c(0,t_1)nF}{RT} \right] = 1 + \frac{2I}{nFC_{pb}^2} \frac{t_1}{\pi D_{pb}^{1/2}}
\]

...3

By defining:
In the absence of addition agents in the bulk electrolyte

\[ \Phi_i = \exp\left[ \frac{\eta_c(0,t_i)nF}{RT} \right] \]

\[ m_D = \frac{2I}{nFC_{Pb^{2+}}^i \sqrt{nD_{Pb^{2+}}}^i} \]

Eq. 3 can be expressed as a linear equation:

\[ \Phi_i = m_D \sqrt{t_i} + b_D \]

Thus, by plotting \( \Phi_i \) vs. \( \sqrt{t_i} \), a straight line with slope, \( m_D \), and intercept, \( b_D \), should be obtained.

By using the data shown in Fig. 7, and assuming that \( \eta_c(0,t_i) = \eta_A \), the plots shown in Fig. 8 were obtained. In this figure, a linear relationship between \( \Phi_i \) and the square root of time is limited to times smaller than 1 sec. From curve fitting these data to Eq. 4, the data shown in Table 1 were obtained. Correlation coefficients close to 1 were obtained in almost the whole range of current densities studied. The average diffusion coefficient, \( D_{Pb^{2+}} \), agrees with the values reported in the literature. This diffusion coefficient, while dominated by the movement of Pb\(^{2+}\), also includes the effects of other ions (SiF\(_6^{2-}\) and H\(^+\) among others). Changes in the transference number of the lead ions will take place when concentration gradients are fully developed and this will affect the absolute value of this coefficient. The presence of these concentration gradients is observable in the analyzed data, as departures from linearity and as changes in the value of the intercept \( b_D \) from unity.

The agreement between the solution of Fick's equation and the results of the current step experiments confirms that in the absence of addition agents, the lead dissolution process is controlled by diffusion.

---

1 As seen in Fig. 8, the larger the applied current density the smaller the linear region between the square root of time and \( \Phi_i \).
2 Diffusion coefficients for lead in HClO\(_4\)-Pb(ClO\(_4\))\(_2\) electrolytes at 25 °C reported in the literature are:
\[ D_{Pb^{2+}} = 9.4 \times 10^{-6} \text{ cm}^2/\text{sec} \] [1]; \[ D_{Pb^{2+}} = 4.8 \times 10^{-6} \text{ cm}^2/\text{sec} \] [4].
3 The solution of Fick's second law presented in Appendix 8 implies that the transference number of lead is zero. Any departures from this transference number will affect the obtained diffusion coefficient.
4 Notice also that \( b_D \) decreases as the current density increases.
In the absence of addition agents in the bulk electrolyte.

Fig. 8 Changes in $\Phi$, as a function of the square root of time, $\sqrt{t_1}$.

From the data presented in Fig. 7.

Each curve corresponds to the $\Phi$ values obtained at different current densities, as follows (from bottom to top): 10, 50, 100, 150, 200, 250, 300, 500, 800, 1000, 1400, and 1600 Amp m\(^{-2}\).

Table 1 Results of the analysis of the concentration overpotential increases during the first second after application of the current steps. *Fick's Second Law approximation.*

<table>
<thead>
<tr>
<th>Current Density, Amp-m(^{-2})</th>
<th>Fitting Parameters of Eq. 4</th>
<th>Regression Coefficient, $r^2$</th>
<th>$D_{PB}^{*2}$ cm(^2)-sec(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.00</td>
<td>0.0371</td>
<td>0.927</td>
</tr>
<tr>
<td>100</td>
<td>0.99</td>
<td>0.0720</td>
<td>0.979</td>
</tr>
<tr>
<td>150</td>
<td>0.99</td>
<td>0.1127</td>
<td>0.983</td>
</tr>
<tr>
<td>250</td>
<td>0.97</td>
<td>0.1614</td>
<td>0.951</td>
</tr>
<tr>
<td>300</td>
<td>0.97</td>
<td>0.1946</td>
<td>0.951</td>
</tr>
<tr>
<td>400</td>
<td>0.96</td>
<td>0.2775</td>
<td>0.957</td>
</tr>
<tr>
<td>500</td>
<td>0.95</td>
<td>0.3624</td>
<td>0.963</td>
</tr>
<tr>
<td>800</td>
<td>0.91</td>
<td>0.5672</td>
<td>0.951</td>
</tr>
<tr>
<td>1000</td>
<td>0.89</td>
<td>0.8205</td>
<td>0.964</td>
</tr>
<tr>
<td>1398</td>
<td>0.83</td>
<td>1.1494</td>
<td>0.959</td>
</tr>
<tr>
<td>1598</td>
<td>0.80</td>
<td>1.1921</td>
<td>0.940</td>
</tr>
</tbody>
</table>

$D_{PB}^{*2} = 5.3 \pm 0.8 \times 10^6$
If concentration overpotential is the only source of potential (after subtracting \( \eta_0 \)) its presence will be observed after interrupting the current. This can be seen in Fig. 9 which shows the decay in the anodic overpotential corrected for ohmic drop obtained after interrupting the current\(^1\).

![Diagram of anodic overpotential decay](image)

By solving Fick's equation under current interruption conditions (see Appendix 8), the following linear relationship should be observed:

\[
\Phi_2 = m_b \left( \sqrt{t_1} - \sqrt{t_2} \right) + b_b
\]

where:

\[
\Phi_2 = \exp \left[ \frac{\eta_a(0, t) n F}{RT} \right]
\]

with \( m_b \) and \( b_b \) as defined by Eq. 4.

Eq. 5 is applicable only when \( t_1 \) is very small (less than 1 sec) because convection will stop the thickening of the anode boundary layer. Fick's second law could not be used to analyze the \( \eta_a \) response upon current interruption.

---

\(^1\) \( \eta_0 \) was measured prior to the interruption of current by measuring the impedance at high frequencies and by using the current interruption routine built into the SEI. Upon current interruption, the observed ohmic drop coincided with that obtained in these measurements.
because the boundary conditions are not known precisely. Nevertheless, what the data in Fig. 9 show is that, upon current interruption, concentration gradients relax and this relaxation can be followed by monitoring the anodic overpotential dependance with time.

**B. In the presence of addition agents in the bulk electrolyte**

If addition agents are added to the bulk electrolyte, the $\eta_A$ response changes (Fig. 10). Upon subtracting the initial $\eta_A$ value from the $\eta_A$ readings, the remaining overpotential was positive (Fig. 11). This $\eta_A$ value decreased during the first milliseconds after the application of current. After this initial decrease, changes in $\eta_A$ were a function of the applied current density. In any case, $\eta_A$ increased only up to the point at which convection stops the thickening of the boundary layer.

![Figure 10](image.png)

The differences in the $\eta_A$ and $\eta_0$ values at the beginning of the application of the current steps where consistent throughout the range of current densities studied (see Figs. 12 and 13). Such differences are the result of the presence of an adsorbed film of addition agents in the electrode interface. Such a film extends...
In the presence of addition agents in the bulk electrolyte

18.8 r-

688.

M

Fig. 11 Anodic overpotential response (corrected for initial $\eta_0$) of a pure lead electrode to the current steps described in Fig. 4

From the $\eta_A$ data shown in Fig. 10 the $\eta_{IA}$ values shown in Fig. 12 were subtracted. Each curve corresponds to the $\eta_A$ values obtained at different current densities (in Amp m$^2$) as shown to the left of every curve. For the different current densities applied, $\eta_A$ values at $t=0$ were as follows:

<table>
<thead>
<tr>
<th>Current density, Amp m$^2$</th>
<th>50</th>
<th>150</th>
<th>250</th>
<th>406</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_A$ corrected for $\eta_0$ (at $t=0$), mV</td>
<td>10</td>
<td>8.2</td>
<td>9.6</td>
<td>11.5</td>
<td>9.1</td>
</tr>
</tbody>
</table>

(A) Long range variation of the $\eta_A$ response (corrected for initial $\eta_0$). $\eta_A$ increases up to the point at which convection stops the thickening of the boundary layer.

(B) Detail of the $\eta_A$ increases.

the region where concentration gradients can be found. Upon passage of current, concentration gradients become established, changing the resistance of the film and the kinetics for lead dissolution. The non-zero intercept of the anodic overpotential curves indicates that inhibition is present as a result of this adsorbed film. On account of the synergistic effect between addition agents, activation overpotential, and concentration overpotential, no simple analysis of the $\eta_A$ transients can be performed. Yet, the $\eta_A$ response indicates clearly that the addition agents affect the anodic reaction for lead in such a way that $\eta_{Iac}$ can no longer be considered to be zero.
In the presence of addition agents in the bulk electrolyte

Fig. 12 Comparison between the anodic overpotential value obtained right after application of current (*) and the uncompensated ohmic drop obtained from the high frequency intercept of the impedance spectrum (O).

$\eta_A$ values derived from the data presented in Fig. 10. $\eta_A$ values obtained from the high frequency AC measurements under rest potential conditions ($\eta_A = IR_s$).
In the presence of addition agents in the bulk electrolyte

Fig. 13 Changes in the anodic overpotential upon application of a current step.

From the data presented in Fig. 10. Applied current density: 400 Amp m\(^2\).

Upon application of current \(\eta_A\) increases from 0 to 96 mV and decreases slowly afterwards. From AC measurements under rest potential conditions an \(R_v\) value of 2.09 \(\Omega\)cm\(^2\) was found. Thus, \(\eta_n=2.09\Omega\)cm\(^2\) \* 40 mAmp cm\(^{-2}\) = 83.6 mV.

The inset plot shows the changes in \(\eta_A\) (mV) as a function of time (sec) after correcting the anodic overpotential for \(\eta_n\).

Finally, the ohmic drop measured by either fast current interruption or high frequency AC impedance measurements predicted \(\eta_A\) values which were slightly larger than measured (Fig. 14). The difference between these values is partially due to the presence of a film resistance, \(R_{film}\) (so-called "film inhibition").
Fig. 14 Changes in the anodic overpotential as a function of the current interruption time.

Experimental conditions as described in Fig. 10. After applying current (I=400 Amp m²) for 320 sec (t₁-t₂=320 sec) current was halted and the overpotential decay was followed as a function of time. Upon current interruption \( \eta_A \) decreases abruptly (from 105 to 12 mV). From AC measurements prior to the interruption of current an \( R_e \) value of 2.17 \( \Omega \)cm² was found. Thus, \( \eta_0=2.17\Omega \text{cm}^2 \times 40 \text{ mAmp cm}^{-2} = 86.8 \text{ mV} \). The inset plot shows the changes in \( \eta_A \) (mV) as a function of time (sec) after subtracting \( \eta_A \) from the first \( \eta_A \) reading.

III. AC Impedance

A. Introduction

In the previous section, DC (direct current) transient techniques were used to study the dissolution of pure lead and its relationship to the components of the anodic overpotential. In this section, a complementary study using AC techniques is presented \(^1\).

---

1 For a description of the implementation of the AC techniques see Appendix 6.
In the absence of a net DC current, application of an AC voltage at low frequencies ($\omega<10^3$ rad/sec) generates sinusoidal concentration gradients whose amplitudes decrease exponentially from the electrode surface towards the bulk electrolyte [5,6]. These concentration gradients cause a characteristic AC energy absorption. As the AC frequency is increased (up to $10^5$ rad/sec), ionic diffusion cannot keep up with the change in direction and so energy absorption disappears to be replaced by a phase angle characteristic of a capacitor which represents processes in the vicinity of the electrical double layer. At extremely high frequencies (larger than $10^5$ rad/sec) only the movements of ions and dipoles in solution, representing dielectric properties, can keep up with changing potentials [7,8]. This phenomenon is rarely seen because such high frequency measurements in liquid electrolytes are experimentally difficult or inaccessible.

AC impedance studies in the presence of a net Faradaic current are analogous to the impedance studies in the absence of a net DC bias provided the electrochemical processes under investigation behave linearly. If conditions at the electrode/electrolyte interface change due to the passage of current, they will be reflected in the AC impedance spectrum. For example, nonlinearities in the response of the system can produce a net rectification current and a rectified voltage. The presence of these nonlinearities and their effect on the related electrochemical processes have been studied by using Faradaic Rectification Techniques [6,9]. In highly reversible systems where diffusion controls the dissolution process (such as lead dissolution in $\text{H}_2\text{SiF}_6$-$\text{PbSiF}_6$ electrolytes), AC studies in the presence of a DC current can provide a better insight as to the extent to which concentration gradients become established in the anode boundary layer. Also, information on the effects produced by the presence of addition agents can be derived from AC studies.

B. Impedance spectra obtained in an electrolyte without addition agents

The AC behaviour of pure lead under rest potential conditions (i.e. in the absence of a net Faradaic DC current) is shown in Fig. 15 2. The straight line

---

1 The bulk electrolyte has a uniform composition and its properties are a function of its geometrical capacitance $C_g$ and bulk resistance $R_b$. From these values, the dielectric relaxation time of the bulk electrolyte, $\tau_D$, can be obtained ($\tau_D=R_bC_g$) [7].

2 A sinusoidal current waveform with an amplitude of $21.3$ Amp/m² R.M.S. was swept from lower to higher frequencies while the impedance was measured at every frequency. Application of DC currents of the same order of magnitude of the amplitude of the AC waveform (see Fig. 7) resulted in overpotentials lower than 5 mV.
obtained indicates that diffusion in the electrode boundary layer is the only mechanism controlling the dissolution/deposition of Pb\(^{2+}\). At high frequencies, the interception of the impedance curve with the \(Z_r\) axis is equal to the value of the uncompensated ohmic resistance, \(R_g\)\(^1\). When this value was subtracted from the impedance curve, a 45° straight line was observed in the impedance diagram (Fig. 16)\(^2\).

**Fig. 15** Impedance diagram of pure lead under rest potential conditions (in the absence of addition agents)

Experimental conditions: electrode area 2.34 cm\(^2\), \([\text{PbSiF}_6]=0.35\) M, \([\text{H}_2\text{SiF}_6]=0.84\) M, \([\text{SiO}_2]=0.13\) M, \(T=40\pm1.5^\circ\)C, beaker electrochemical cell, electrolyte volume \(\approx 300\) ml, bulk electrolyte recirculation rate \(\approx 6\) ml min\(^{-1}\), Solartron Electrochemical Interface-IEEE Card-IBM XT computer.

Impedance curve obtained under galvanostatic control, AC waveform amplitude 21.3 Amp m\(^{-2}\) R.M.S.

A total of 65 experimental points are plotted. Some of the frequencies (in rad sec\(^{-1}\)) at which these points were sampled are indicated in the diagram.

From the high frequency intercept of this plot with the \(Z_r\) axis, the \(R_g\) value can be obtained (\(R_g=1.40\) \(\Omega\)cm\(^{-2}\)).

---

1 For a fixed distance between the reference and the working electrodes, this value was very reproducible (variations were less than 0.5%). These \(R_g\) values were used to obtain \(\eta_0\) prior to the application of the current steps (see section II.b).

2 Impedance diagrams in which the real part of the impedance is the abscissa, \(Z_r\), and the negative of the imaginary part of the impedance is the ordinate, \(-Z_i\), are also known as Argand plots. In an Argand plot the AC frequencies at which the impedance was measured are also shown.
Impedance spectra obtained in an electrolyte without addition agents

Some frequencies (in rad sec\(^{-1}\)) are shown for both the experimental (solid line) and the regressed data (dotted line). The impedance curve was fitted to a CPE element \(Z_{CPE} = B_i(j\omega)^{-\Psi_{ZC}}\) from which the following values were obtained: \(B_i = 0.139 \ \Omega \text{cm}^2 \text{sec}^{-\Psi_{ZC}}\) and \(\Psi_{ZC} = 0.50\).

Quality of Fit Parameters (65 experimental points were fitted to the CPE analogue):
\[
\begin{align*}
r^2 &= 0.951, \quad \text{Ly}^2 = 2.19 \times 10^3 \ \Omega \text{cm}^4 \\
r^2_3 &= 0.962, \quad \text{Ly}_3^2 = 1.70 \times 10^3 \ \Omega^2 \text{cm}^4 \\
r^2_{\text{ee}} &= 0.958, \quad \text{Ly}_{\text{ee}}^2 = 3.75 \times 10^3 \ \Omega^4 \text{cm}^4
\end{align*}
\]

To model the diffusion processes that take place in the electrode boundary layer, distributed elements have been used [8][9][10]. Among these distributed elements, the Constant Phase Angle Element (CPE) has been used extensively [7]. The impedance of the CPE element can be described by the following equation:

\[
Z_{CPE} = B_i(j\omega)^{-\Psi_{ZC}}
\]

When the fractional exponent, \(\Psi_{ZC}\), approaches a value of 0.5, the CPE element describes a semi-infinite diffusional process. Under these conditions the

---

1 All real electrical analogue elements are distributed in space, i.e. their absolute value changes with position due to their finite size. Diffusion processes are distributed over the electrode boundary layer, and constitute a classical example of a distributed element [8].

2 A **distributed element** is a component in an analogue model that represents properties of the system distributed over macro distances, such as ionic concentration gradients across the Nernst diffusion layer.
Impedance spectra obtained in an electrolyte without addition agents

The impedance of the CPE element is equal to the so-called Warburg impedance [7,10,11]. The Warburg impedance for the semi-infinite diffusion case is defined as [7,8,12]:

\[ Z_{w,\infty} = \sigma_w(j\omega)^{0.5} \]...

When \( \Psi_{zc} = 0.5 \) the Warburg coefficient can be obtained from the \( B_1 \) value (\( B_1 = \sigma_w \)). Thus, \( Z_{w,\infty} \) is a subset of the generalized CPE response. For the \( \text{Pb}/\text{Pb}^{2+} \) equilibrium reaction \( \sigma_w \) is given by the following equation:

\[
\sigma_{w,\infty} = \frac{RT}{(nF)^2} \frac{\delta}{C_{p_{b^{2+}}} D_{p_{b^{2+}}}} \left( \frac{D_{p_{b^{2+}}}}{\delta^2} \right)^{0.5} \frac{RT}{(nF)^2} \frac{1}{C_{p_{b^{2+}}} \sqrt{D_{p_{b^{2+}}}}} \]...

When \( \Psi_{zc} \) is different than 0.5 a generalized representation of the Warburg coefficient [13-15] can be obtained from the following equation:

\[
B_1 = \frac{RT}{(nF)^2} \frac{\delta}{C_{p_{b^{2+}}} D_{p_{b^{2+}}}} \left( \frac{D_{p_{b^{2+}}}}{\delta^2} \right)^{\Psi_{zc}} \frac{RT}{(nF)^2} \frac{\delta^{1-2\Psi_{zc}}}{C_{p_{b^{2+}}} D_{p_{b^{2+}}}^{1-\Psi_{zc}}} \]...

The impedance curve shown in Fig. 16 was curve fitted to Eq. 6 from which the following values were obtained: \( B_1 = 0.139 \, \Omega \, cm^2 \, sec^{\Psi_{zc}} \) and \( \Psi_{zc} = 0.5 \). When these values were incorporated in Eq. 8, \( D_{p_{b^{2+}}} \) was found to be equal to \( 2.1 \times 10^{-6} \, cm^2/\text{sec} \). For different experiments this number varied by as much as one order of magnitude. Nevertheless, it was always observed that diffusion was the only controlling mechanism for lead dissolution/precipitation. Activation polarization if present would have been observed in the Argand diagram as an arc from which

---

1 Warburg studied the establishment of concentration gradients in the electrode boundary layer upon application of an AC voltage. By solving Fick's second law under AC conditions, Warburg found that a square root frequency dependance of the impedance should be observed if the process was controlled by diffusion. This square root dependance is equivalent to observing a 45° relationship between the real and the imaginary components of the impedance (or a \( \Psi_{zc} \) value of 0.5). The assumptions under which Warburg solved Fick's second law are similar to those described in the previous section to solve the DC transient case: presence of a supporting electrolyte, unit activity coefficients, absence of convection. Any departures from these conditions will be reflected in departures from the predicted theory.

2 Notice that Warburg impedance is strictly valid only when \( \Psi_{zc} = 0.5 \). Unfortunately, in the study of diffusion processes by AC techniques, \( \Psi_{zc} \) values of 0.5 are the exception rather than the rule [13]. By introducing a generalized form of the Warburg impedance the physical meaning of each of the involved parameters may change. For example, variations in the \( \Psi_{zc} \) value have been related to the presence of irregularities in the electrode surface at the micrometer level. Also, \( D_{p_{b^{2+}}} \) no longer represents an absolute diffusional coefficient but rather an integral value related to all the ionic species present across the diffusion layer.

3 Lack of well-defined hydrodynamic conditions could be attributed to this large variation in the observed diffusion coefficients. As can be seen in Eq. 9 when \( \Psi_{zc} \) departs from 0.5 it is not possible to obtain the diffusion coefficient unless the thickness of the Nernst boundary layer is known.
the exchange current density, $i_0$, and the double layer capacitance, $C_d$, could have been obtained (to obtain the so-called Randles circuit [16]). Evidently, for lead dissolution in the absence of addition agents $\eta_{ac}\to 0$ (i.e. $i_0\to \infty$).

<table>
<thead>
<tr>
<th>Current Density, Amp/m²</th>
<th>0</th>
<th>0</th>
<th>100</th>
<th>150</th>
<th>150</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$, $\Omega cm^2 sec^{-y_{ac}}$</td>
<td>0.139</td>
<td>0.139</td>
<td>0.074</td>
<td>0.066</td>
<td>0.070</td>
<td>0.056</td>
</tr>
<tr>
<td>$\Psi_{zc}$</td>
<td>0.50</td>
<td>0.50</td>
<td>0.43</td>
<td>0.43</td>
<td>0.43</td>
<td>0.43</td>
</tr>
</tbody>
</table>

AC impedance curves obtained ~2000 sec after the application of the set current density. The amplitude of the applied AC waveform was set to 21.3 Amp/m² R.M.S. The experimental impedance curves were fitted to Eq. 6 using between 60 and 66 points. Regression coefficients and residuals for the regression curves were [$1<\omega<2000$ rad/sec]:

- $r^2_\omega>0.96$ with $|y_\omega|^2<10^{-3}\Omega^2 cm^4$
- $r^2_\omega>0.95$ with $|y_\omega|^2<10^{-4}\Omega^2 cm^4$

AC impedance curves obtained while a net anodic DC current was applied were similar to those observed under rest potential conditions (Fig. 17). Upon application of current the AC impedance decreases with respect to the impedance.
observed in the absence of a net DC current. Straight lines with slopes close to 39° were obtained (i.e. $\Psi_{zc} \sim 0.43$) while the $B_1$ values were between 0.07 and 0.05 $\Omega \text{cm}^2 \text{sec}^{-1}$ and appear to change with current density (see Table 2).

C. Impedance spectra obtained in electrolytes containing addition agents

Addition agents are known to affect the electrochemistry of lead fundamentally through changes in its kinetic parameters [1,17,18]. The "levelling" phenomenon found in electrodeposits and attributed to additives is partially due to a re-distribution of current from changes in the inhibition intensity [19,20].

![Impedance diagram of pure lead under rest potential conditions (in the presence of addition agents)](image)

**Fig. 18** Impedance diagram of pure lead under rest potential conditions (in the presence of addition agents)

Experimental conditions: electrode area 2.34 cm$^2$, [PbSiF$_6$]=0.37 M, [H$_2$SiFe]=0.82 M, [SiO$_2$]=0.13 M, T=40±1.5°C, $\equiv 2 \text{ g l}^{-1}$ aloe and $\equiv 4 \text{ g l}^{-1}$ lignin sulphonate, beaker electrochemical cell, electrolyte volume $\equiv 310$ml, bulk electrolyte recirculation rate $\equiv 6$ ml min$^{-1}$. Solartron Electrochemical Interface-IEEE Card-IBM XT computer. Impedance curve obtained under galvanostatic control. AC waveform amplitude 21.3 Amp m$^{-2}$ R.M.S.

A total of 130 experimental points were obtained. Some of the frequencies (in rad sec$^{-1}$) at which these points were sampled are indicated in the diagram ($R_z=1.74 \Omega \text{cm}^2$).

1 "Inhibition intensity" in Winand's terms [19,20] includes activation overvoltage as well as other polarizations caused by addition agents.
The impedance spectrum obtained when addition agents are present in the
bulk electrolyte is shown in Fig. 18. There are big differences between this
spectrum and that obtained in the absence of addition agents (compare Figs. 15
and 18). The presence of two well-defined arcs can be seen in Fig. 18. The arc
observed at large frequencies ($\omega>4000$ rad/sec) is related to the charge transfer
for the Pb/Pb$^{2+}$ reaction ($i_\Pi$, $C_{dl}$) whereas the arc which spans over frequencies
smaller than 4000 rad/sec is associated with the presence of an adsorbed layer
of addition agents that affect the movement of ions from/towards the electrode
surface (and the region where concentration gradients can be present) ¹. The $R_s$
value was not affected by the presence of the addition agents.

![Impedance spectrum](image)

**Fig. 19** Impedance diagrams of pure lead under rest potential conditions obtained at two
different amplitudes of the applied AC waveform (in the presence of addition agents)

Experimental conditions: as described in Fig. 18.
The AC amplitude values shown in the plot refer to their R.M.S. value

A total of 130 experimental points were obtained. Some of the frequencies (in rad sec⁻¹) at
which these points were sampled are indicated in the diagram.
$R_s$ was subtracted from both impedance curves.

¹ This low frequency arc was only observed after a small Faradaic current was applied (less than 50
Amp/m² for 400 sec), after which, it was always present in the impedance curves obtained under rest
potential conditions.
Impedance spectra obtained in electrolytes containing addition agents

Under rest potential conditions, a decrease in the amplitude of the applied AC waveform produced a decrease in the size of the low frequency arc while the high frequency arc remained virtually unchanged (Fig. 19). It appears as if by decreasing the amplitude of the AC waveform, the size of the region where concentration gradients are present expands resulting in apparent increases in the impedance.

Fig. 20 Analogue circuits used to model the high frequency response of the impedance curve shown in Fig. 15.

The analogue shown in (B) is obtained when $Z_{\text{CPE}} \rightarrow 0$. This will happen at high frequencies or small values of the $B_1$ parameter.

(A) Analogue used to represent the high frequency region of the impedance spectrum:

$$Z(j\omega) = R_s + \frac{R_a + B_1(j\omega)^{-\alpha}}{1 + R_a C_d(j\omega) + C_d B_1(j\omega)^{1-\alpha}}$$

(B) Analogue used to represent processes taking place in the electrical double layer:

$$Z(j\omega) = R_s + \frac{R_a}{1 + R_a C_d(j\omega)}$$
Analysis of the impedance spectrum obtained at high frequencies ($\omega>500$ rad/sec) was done by using the electrical analogue shown in Fig. 20. In this circuit, $R_{ct}$ represents the charge transfer resistance which is related to $i_o$ through the following equation [21]:

$$R_{ct} = \left( \frac{\partial\eta}{\partial i} \right)_{i \to 0} = \frac{RT}{nF i_0} \quad \cdots 10$$

The impedance of the analogue circuit shown in Fig. 20A can be described as follows $^2$:

$$Z(j\omega) = R_s + \frac{R_{ct} + B_1(j\omega)^{-\psi_{zc}}}{1 + R_{ct}C_{di}(j\omega) + C_{di}B_1(j\omega)^{1-\psi_{zc}}} \quad \cdots 11$$

The CPE included in the analogue shown in Fig. 20A is used only to subtract the high frequency part of the arc observed at low frequencies from the charge transfer arc. This CPE is not intended to represent any particular process but only to subtract the higher frequency data.

The values of the analogue elements obtained from the curve fitting process are as follows (Fig. 21): $R_{ct}=1.665$ $\Omega$cm$^2$ ($\pm$5%), $C_{di}=20.6$ $\mu$F/cm$^2$ ($\pm$3%), $B_1=149.25$ $\Omega$ cm$^2$ sec$^{-\psi_{zc}}$ ($\pm$5%), and $\psi_{zc}=0.74$($\pm$2%). From the $R_{ct}$ value $i_o$ was found to be equal to 82 Amp/m$^2$ ($\pm$5%). For the same electrode these values were reproduced within 15%. On the other hand, small changes in the bulk electrolyte composition, electrolyte temperature, bulk electrolyte recirculation rate, and electrode roughness appreciably affected the $i_o$ and $C_{di}$ values. In any case, for a fixed electrolyte composition, $i_o$ values were not smaller than 70 Amp/m$^2$ ($70<i_o<500$ Amp/m$^2$) whereas $C_{di}$ values were between 18 and 30 $\mu$F/cm$^2$. Since in the absence of addition agents a charge transfer arc was not found ($i_o \to \infty$), it is concluded that the presence of the addition agents affects significantly the kinetics for the Pb/Pb$^{2+}$ equilibrium reaction. The decrease in the $i_o$ values as a result of the presence of addition agents can be attributed to: (A) changes in the

---

1 The Stern-Geary equation has also been used to relate the steady-state corrosion current density, $i_{corr}$, and the polarization resistance, $R_p$ [25]:

$$i_{corr} = \left[ \frac{\beta_s\beta_r}{2.303(\beta_s+\beta_r)} \right] \left( \frac{1}{R_p} \right)$$

2 Analytical representation of the impedance was obtained by using the Laplace plane techniques described in Appendix 3.
Impedance spectra obtained in electrolytes containing addition agents

Fig. 21 High frequency section of the impedance diagram shown in Fig. 18.

Impedance curve was fitted to the electrical analogue shown in Fig. 20A ($R_\text{s}$ was computed from the high frequency intercept of the impedance curve with the $Z_\text{s}$ axis).

From the curve fitting process, the following values were obtained: $B_1 = 149.250 \ \Omega \text{cm}^2 \text{sec}^{-1}$, $\Psi_\text{zc} = 0.741$, $R_\text{ct} = 1.655 \Omega \text{cm}^2$, $C_\text{dl} = 20.6 \mu \text{F cm}^2$.

Some frequencies (in rad sec$^{-1}$) are shown for both the experimental (solid line) and the regressed data (dotted line).

Quality of Fit Parameters (51 experimental points were fitted to obtain the values of 4 parameters):
$r_\text{x}^2 = 0.973$, $|y_\text{x}|^2 = 2.49 \times 10^{-1} \Omega^2 \text{cm}^4$
$r_\text{y}^2 = 0.941$, $|y_\text{y}|^2 = 6.16 \times 10^{-2} \Omega^2 \text{cm}^4$
$r_\text{abs}^2 = 0.985$, $|y_\text{abs}|^2 = 1.16 \times 10^{-1} \Omega^2 \text{cm}^4$

electrochemically active surface area and (B) variations in the current distribution in the anode vicinity. An effective decrease in the $i_0$ value (considering that the electrochemically active surface area is the same in the cases presented in Figs. 16 and 21) would mean that the kinetics for lead dissolution and deposition have become "less" reversible.
The AC arc observed at \( \omega < 4000 \) rad/sec is more difficult to model by an electrical analogue. Its presence is associated with a bounded concentration region created by addition agents, some of which adsorb on the electrode surface changing the \( i_e \) and \( C_{dl} \) values. The "spikes" observed during the application of the current steps (see Section II.b) are undoubtedly associated with the phenomena displayed by the AC impedance curves.

**Fig. 22** Impedance diagrams of pure lead obtained in the presence and in the absence of a net Faradaic current (in the presence of addition agents)

Experimental conditions: As described in Fig. 18.
The AC amplitude was the same in both cases (21.3 Amp m\(^2\) R.M.S)

\( R_s \) was subtracted from both impedance curves.

In the presence of a net anodic current, the impedance decreases significantly (Fig. 22). As the current density increases, the size of the arc observed at high frequencies decreases while the low frequency arc does not change to the same extent (Fig. 23). Eventually, at high current densities (cd \( > 200 \) Amp/m\(^2\)) the high frequency arc vanishes and only one arc related to diffusion in the anode boundary layer is observed. Thus, it appears as if during the anodic dissolution of lead the polarization created by the addition agents decreases as the current density
Impedance spectra obtained in electrolytes containing addition agents increases. The decrease in the size of the low frequency arc may be the result of a defined boundary layer whose size has compacted due to the presence of a fixed electric field created by the passage of a net Faradaic current.

Fig. 23 Detail of the impedance diagrams obtained in the presence of a net Faradaic current (in the presence of addition agents)

Experimental conditions: As described in Fig. 18. The AC amplitude was the same in both cases (21.3 Amp m⁻² R.M.S)

Rₐ was subtracted from both impedance curves.

1 The exchange current density is also a function of the concentration of the electroactive ion in the electrode surface [22-24].

2 Notice how the radius of the high frequency arc obtained in the presence of a net Faradaic current (Rₑ~0.08 Ωcm², Fig. 23) is at least 20 times smaller than under rest potential conditions (Rₑ~1.5 Ωcm², Fig. 21). The term "apparent" charge transfer resistance decreases until at high current densities Rₑ~0. The "apparent" charge transfer resistance refers to the Rₑ values that may be observable upon passage of a net Faradaic current when studying irreversible systems using AC techniques.

3 Notice that addition agents are also dispersed by the anodic process because: (A) the interface is retreating, and (B) there is a flux of Pb⁺² in the opposite direction. Thus, decreases in the size of the low frequency arc as the current density increases can be due to a depletion of addition agents in the anode boundary layer.
Chapter 6 Electrochemical Behavior of Lead bullion Electrodes in the Presence of Slimes

I. Introduction

In the previous Chapter it was shown that in the absence of addition agents in the bulk electrolyte, the Pb/Pb$^{2+}$ system behaves nearly reversibly (i.e. Pb$\rightleftharpoons$Pb$^{2+}$+2e$^{-}$ with $i_{0} \to \infty$). The presence of addition agents in the bulk electrolyte decreases the reversibility of the system through small increases in the activation overpotential. Moreover, the addition agents were found to enhance the concentration gradients at the electrode/solution interface through the formation of specifically and/or electrostatically absorbed films. This Chapter deals with the establishment of concentration gradients within the slimes layer and their relationship to the anodic overpotential observed in the presence and in the absence of a net Faradaic current.

All experiments shown in this Chapter were performed at T=40±1.5°C, using the beaker electrochemical cell (Fig. 3.1) and the Solartron equipment (Fig. 3.8). Data acquisition and control of the experiment were performed using an IBM XT personal computer via the IEEE interface (Fig. 3.7). Electrodes were prepared from the same anode $^{1}$ (anode A, Fig. 3.3) as described in section 3.1.B. Electrolyte was recirculated continuously at 6 ml/min (cell volumes varied between 300 and 320 ml). The geometrical area of the electrodes $^{2}$ was used to compute the current density and the impedance per unit area. In experiments in which addition agents were added to the electrolyte, any insoluble precipitates were removed prior to the introduction of the electrolyte to the cell. The assumed concentration of addition agents prior to the filtering operation was 2 g/l aloe and 4 g/l lignin sulphonate. The compositions of the electrolytes used in the various experiments presented in this Chapter are shown in Table 1.

---

1 Anode composition: 0.01% Sn, 0.02% Cu, 0.14% Bi, 0.25% As, 1.12% Sb, 81 oz/ton Ag.
2 The geometrical area of the electrodes was 1.44±0.02 cm$^{2}$. 

[115]
Table 1 Characteristics of the experiments presented in chapter 6

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Electrode Face</th>
<th>Addition Agents</th>
<th>$[\text{PbSiF}_6]$ mol/l</th>
<th>$[\text{H}_2\text{SiF}_6]$ mol/l</th>
<th>$[\text{SiOJ}$ mol/l</th>
<th>Bulk electrolyte Conductivity, $\kappa$, at $T=40^\circ\text{C}$, mmhos/cm</th>
<th>Characteristics of the experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA2</td>
<td>mould</td>
<td>yes</td>
<td>0.27</td>
<td>0.69</td>
<td>0.14</td>
<td>300</td>
<td>Galvanostatic dissolution at I=200 Amp/m²</td>
</tr>
<tr>
<td>CA4</td>
<td>mould</td>
<td>yes</td>
<td>0.45</td>
<td>0.77</td>
<td>0.14</td>
<td>315</td>
<td>Potentiostatic dissolution at $E_{\text{control}}=220$ mV</td>
</tr>
<tr>
<td>CA5</td>
<td>mould</td>
<td>yes</td>
<td>0.45</td>
<td>0.76</td>
<td>0.14</td>
<td>315</td>
<td>Galvanostatic dissolution at I=800 Amp/m²</td>
</tr>
<tr>
<td>CA6</td>
<td>mould</td>
<td>yes</td>
<td>0.45</td>
<td>0.73</td>
<td>0.14</td>
<td>320</td>
<td>Galvanostatic dissolution at I=200 Amp/m²</td>
</tr>
<tr>
<td>CC1</td>
<td>air</td>
<td>no</td>
<td>0.35</td>
<td>0.84</td>
<td>0.09</td>
<td>345</td>
<td>Galvanostatic dissolution at I=200 Amp/m²</td>
</tr>
<tr>
<td>CC2</td>
<td>air</td>
<td>no</td>
<td>0.36</td>
<td>0.83</td>
<td>0.09</td>
<td>345</td>
<td>Galvanostatic experiment.</td>
</tr>
</tbody>
</table>

In the presence of a net Faradaic current the impedance spectra were obtained under galvanostatic control except in Exp. CA4 in which the curves were obtained under potentiostatic control. Under current interruption conditions all the impedance spectra were obtained under Galvanostatic control.

The AC impedance was obtained in a wide frequency range ($0.063<\omega<4\times10^5$ rad/sec) under either potentiostatic or galvanostatic control. The amplitude of the applied AC waveform was set to 5 mV R.M.S. and 35 Amp/m² R.M.S. respectively. In either case, 20 data points were obtained per decade of frequency swept. All impedance spectra are reported with respect to the time at which the AC measurement started. Typical AC measurement times are shown in Table 2.

---

1 Under galvanostatic conditions application of AC frequencies in excess of $3\times10^4$ rad/sec often resulted in phase shifts produced by the Solartron Electrochemical Interface due to bandwidth limitations. On the other hand, under potentiostatic control, frequencies as high as $4\times10^4$ rad/sec could be applied without observing phase shifts. A phase shift is a displacement of the capacitative component of the impedance curve towards negative values [1-3].

2 For example if $0.063<\omega<6300$ there are $\log_{2.033}=6$ decades of frequency swept and the impedance is measured at $6\times20=120$ discrete points.

[116]
### Table 2  Average times required to measure the AC impedance spectrum

<table>
<thead>
<tr>
<th>Frequency Range</th>
<th>Time, Hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{\text{min}}$, rad/sec</td>
<td>$\omega_{\text{max}}$, rad/sec</td>
</tr>
<tr>
<td>0.063</td>
<td>408407</td>
</tr>
<tr>
<td>0.63</td>
<td>408407</td>
</tr>
<tr>
<td>6.3</td>
<td>408407</td>
</tr>
</tbody>
</table>

### II. AC Impedance Characterization of the Starting Working Electrodes.

Prior to the anodic dissolution of lead bullion electrodes their impedance was obtained under rest potential conditions. Table 3 summarizes the characteristics of the obtained spectra. The differences between the various spectra are explained in the next paragraphs.

### Table 3  Summary of the values of the electrical analogue parameters obtained under rest potential conditions

<table>
<thead>
<tr>
<th>Experiment and Sweep Number</th>
<th>Addition Agents</th>
<th>Pot/Gal Control</th>
<th>$\omega_{\text{min}}$, rad/sec</th>
<th>Frequency Range</th>
<th>Derived Analogue Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CA2-1</td>
<td>yes</td>
<td>Gal</td>
<td>560</td>
<td>1.42</td>
<td>0.501</td>
<td>64</td>
</tr>
<tr>
<td>CA4-1</td>
<td>yes</td>
<td>Pot</td>
<td>315</td>
<td>1.02</td>
<td>1.855</td>
<td>25.9</td>
</tr>
<tr>
<td>CA5-1</td>
<td>yes</td>
<td>Pot</td>
<td>560</td>
<td>1.19</td>
<td>0.725</td>
<td>65.30</td>
</tr>
<tr>
<td>CA5-4</td>
<td>yes</td>
<td>Gal</td>
<td>560</td>
<td>1.21</td>
<td>0.854</td>
<td>48.9</td>
</tr>
<tr>
<td>CA5-2</td>
<td>yes</td>
<td>Gal</td>
<td>177</td>
<td>1.20</td>
<td>1.916</td>
<td>32.6</td>
</tr>
<tr>
<td>CC1-5</td>
<td>no</td>
<td>Gal</td>
<td>628</td>
<td>0.90</td>
<td>-</td>
<td>3.05</td>
</tr>
<tr>
<td>CC1-6</td>
<td>no</td>
<td>Gal</td>
<td>628</td>
<td>0.89</td>
<td>-</td>
<td>2.88</td>
</tr>
<tr>
<td>CC2-1</td>
<td>no</td>
<td>Gal</td>
<td>560</td>
<td>0.85</td>
<td>-</td>
<td>1.88</td>
</tr>
<tr>
<td>CC2-2</td>
<td>no</td>
<td>Gal</td>
<td>560</td>
<td>0.85</td>
<td>-</td>
<td>1.88</td>
</tr>
</tbody>
</table>

Different electrodes were used in every experiment. Impedance curves were obtained either under Potentiostatic (Pot) control or Galvanostatic (Gal) Control. Changes in the $R_s$ values reflect differences in the distance between the reference electrode and the working electrode. The spectra obtained in the absence of addition agents were curve fitted to the impedance function described by Eq. 1 while the spectra obtained in the presence of addition agents was fitted to the function described by Eq. 2.

---

1 The statistical parameters related to the quality of the curve fitting procedure are presented in Appendix 9.
A. AC behaviour in the absence of addition agents in the bulk electrolyte

The AC impedance spectrum of a typical lead anode (in the absence of slimes) under rest potential conditions and in the absence of addition agents is presented in Fig. 1. The uncompensated ohmic resistance, $R_u$, has been removed in this impedance diagram by subtracting it from the $Z_\text{eq}$ component of the impedance. This impedance spectrum is similar to the obtained using a pure lead electrode (see Fig. 5.16) and can be described by a Warburg semi-infinite diffusion element which follows the response of a CPE element:

$$Z_{\text{CPE}} = B_1(j\omega)^{-\psi_{ZC}}$$  ...1

The impedance curve shown in Fig. 1 was curve-fitted to Eq. 1 to obtain the $B_1$ and $\psi_{ZC}$ values. $B_1$ and $\psi_{ZC}$ were found to be equal to 2.88 $\Omega \text{ cm}^2 \text{ sec}^{-\psi_{ZC}}$ and 0.45 respectively. By comparing these values with those obtained when pure lead was studied ($B_1 \sim 0.14 \Omega \text{ cm}^2 \text{ sec}^{-\psi_{ZC}}$ and $\psi_{ZC} \sim 0.5$) it is seen that $\psi_{ZC}$ remains practically unchanged, while $B_1$ shows a marked increase in its absolute value. The increase

---

1. Due to software limitations in the graphics program the axes of the Argand plots are not marked $Z_\text{Re}$ and $Z_\text{Im}$ as in the main text but as $Z_{\text{real}}$ and $Z_{\text{imag}}$ respectively.
2. An impedance diagram is also known as an Argand plot.
3. $R_u = 0.90 \Omega \text{ cm}^2$. $R_u$ was obtained from the high frequency interception of the impedance curve with the real axis.
4. For a description of the relationship between the CPE element and the semi-infinite Warburg impedance see Chapter 5 (section III.B, Eqs. 6 to 9).
5. Different CPE analogues may have the same slope but quite different $B_1$ values. By using de Moivre's theorem, the impedance of the CPE analogue can be expressed as follows:

$$Z_{\text{CPE}} = B_1(j\omega)^{-\psi_{ZC}} = B_1\omega^{-\psi_{ZC}}\left[\cos\frac{\pi}{2}\psi_{ZC} - j\sin\frac{\pi}{2}\psi_{ZC}\right]$$

thus,

$$Z_\text{Re} = B_1\omega^{-\psi_{ZC}}\cos\frac{\pi}{2}\psi_{ZC}$$

$$Z_\text{Im} = -B_1\omega^{-\psi_{ZC}}\sin\frac{\pi}{2}\psi_{ZC}$$

and the slope, $m$, between $Z_\text{Re}$ and $Z_\text{Im}$ is given by:

$$m = \tan\frac{\pi}{2}\psi_{ZC}$$

from which:

$$\psi_{ZC} = \frac{2}{\pi}\tan^{-1}m$$

Thus, it can be seen that $\psi_{ZC}$ does not depend on $B_1$ which is only a multiplying factor (i.e. the impedance curve shrinks or contracts according to its value).
**AC behaviour in the absence of addition agents in the bulk electrolyte**

**Experimental**

**A.**

- $R_s$ was subtracted from the $Z_r$ component of the impedance ($R_s=0.89 \ \Omega \text{cm}^2$).
- Some frequencies (in rad/sec) are shown for both the experimental (solid line) and the curve fitting data (dotted line).
- The impedance curve was fitted to a CPE element from which the following values were obtained $B_1=2.88 \ \Omega \text{cm}^2 \text{sec}^{-\Psi_{ZC}}$, $\Psi_{ZC}=0.45$.

in the $B_1$ value is attributed to differences in the roughness and electrochemically active surface areas between these electrodes. Also, the distinct electrochemical characteristics of the impure lead bullion electrodes may account for the observed increases in the $B_1$ values. As indicated in Table 3 (see sets CC1 and CC2), the $B_1$ values change significantly from one experiment to the next but remain within $0.2 \ \Omega \text{cm}^2$ during the same experiment. The relatively constant values of the $\Psi_{ZC}$ exponent ($0.40<\Psi_{ZC}<0.60$) is a clear indication that diffusional processes are the only ones being observed in the impedance spectra. While quantitative values of

**Fig. 1** Impedance diagram of a typical lead bullion electrode (Exp. CC1-6) under rest potential conditions and in the absence of addition agents.

1 As a result of surface irregularities at the micrometer level, the thickness of the electrode boundary layer may not be uniform and that results in increases in the $B_1$ value.

[119]
the diffusion coefficients cannot be obtained. The shape of the impedance curves unequivocally indicates that there are no charge transfer limitations for the dissolution/precipitation of Pb\textsuperscript{2+} from/to the lead bullion electrodes.

**B. AC behaviour in the presence of addition agents in the bulk electrolyte**

The AC spectrum obtained in the presence of addition agents is shown in Fig. 2. Three different regions can be identified depending on the frequency range:

a) A high frequency arc (ω>4000 rad/sec) assigned to the charge transfer process taking place across the electrode Helmholtz double layer. The point where the arc intercepts the \( Z_\omega \) axis is equal to the \( R_\omega \) value.

b) A distorted arc observed at medium range frequencies (100<ω<4000 rad/sec) assigned to addition agents effects in the diffuse double layer.

c) A quasi-linear impedance region (at ω<100 rad/sec) assigned to diffusional processes in the hypothetical Nernst boundary layer.

---

1 The lack of knowledge of the electrochemically active surface area poses a serious hindrance for the computation of the diffusion coefficient: the penetration depth of the AC wave and the thickness of the boundary layer have to be uniform across the electrode in the whole range of frequencies for meaningful diffusion coefficient values to be obtained.

[120]
Analysis of the impedance spectra obtained at $\omega$>200 rad/sec was carried out using the electrical analogue shown in Fig. 5.20. The impedance of this analogue can be described by the following equation $^1,^2$:

$$Z(j\omega) = R_s + \frac{R_{ct} + B_1(j\omega)^{-\Psi_{ZC}}}{1 + R_{ct}C_{dl}(j\omega) + B_1(j\omega)^{1-\Psi_{ZC}}} \quad \ldots 2$$

The $R_s$ values were obtained directly from the high frequency intercept of the impedance curves with the $Z_R$ axis. The four remaining parameters in Eq. 2 ($R_{ct}$, $C_{dl}$, $B_1$, and $\Psi_{ZC}$), were obtained by curve fitting the experimental data to Eq. 2.

![Impedance diagram](image.png)

**Fig. 3** Detail of the high frequency region of the impedance diagram shown in Fig. 2

$R_s$ was subtracted from the $Z_R$ component of the impedance ($R_s=1.42 \ \Omega \ \text{cm}^2$).
Some frequencies (in rad/sec) are shown for both the experimental (solid line) and the curve fitting data (dotted line).

The impedance curve was fitted to the analogue circuit shown in Fig. 5.20 from which the following values were obtained $B_1=23.71 \ \Omega \ \text{cm}^2 \ \text{sec}^{-\Psi_{ZC}}$, $\Psi_{ZC}=0.64$, $R_{ct}=0.501 \ \Omega \ \text{cm}^2$, and $C_{dl}=64$ $\mu\text{F cm}^2$.

As can be seen in Figs. 3 and 4, the analogue model describes accurately the experimental data. The values of the analogue parameters varied from one

---

1 For a description of the characteristics of this circuit see Chapter 5 section III.c.
2 Again, it is worth repeating that the presence of a CPE in the circuit shown in Fig. 5.20 does not represent a purely diffusional process and is included only to aid in the curve fitting procedure to obtain the $R_s$ and $C_{dl}$ values.
Fig. 4 Detail of the high frequency regions of the impedance diagrams obtained under rest potential conditions

(A) Exp. CA4-1  (B) Exp. CA5-1

The values of the derived analogue values are shown in Table 3.

experiment to the next. Nevertheless, the impedance curves reproduced within 10% the indicated parameter values in the same experiment (i.e. for the same electrode and electrolyte composition).
In experiments CA4, CA5, and CA6 the electrolyte composition was kept constant, yet, the derived kinetic parameters varied widely. These variations can be attributed to differences in the electrode roughness among the different electrodes. In any case, the exchange current densities were not lower than 70 Amp/m² (70<iₜ<270 Amp/m²) while the double layer capacitances varied between 25 and 66 μF/cm². These large values of iₜ indicate that dissolution of the lead present in the lead rich phases takes place under nearly reversible conditions and that the noble impurities present in the lead bullion are not significantly affecting the kinetics for lead dissolution (or deposition).

![Impedance spectra obtained under potentiostatic (solid line) and galvanostatic control (dashed line).](image)

From Exp. CA5 (Sweeps CA5-1 and CA5-4 in Table 3).

Finally, the impedance spectrum obtained under potentiostatic control was found to be a variation of that obtained under galvanostatic control (Fig. 5). As in the pure lead case, the observed changes are related to different concentration

1 The same electrolyte was used in Exps. CA4, CA5, and CA6 but since the amount of solids filtered prior to the introduction of electrolyte to the cell varied in each case, the final addition agent content may vary.

2 Small changes in the bulk electrolyte recirculation rate, electrode microstructure, and cell temperature may also produce the observed changes in the parameter values.

3 Notice that large capacitance values are associated with high exchange current densities indicating that electrochemically active surface areas are different in every case.
waves created by the different amplitude of the perturbing signal. The parameters obtained from both curves are close to each other indicating that similar information was obtained from both techniques (see Table 3, Exp. CA5 sets 1 and 4).

III. DC and AC Studies in Corroded Electrodes

A. Studies under galvanostatic, potentiostatic, and current interruption conditions.

1. Experimental results

Lead bullion working electrodes were either galvanostatically or potentiostatically dissolved. The movement of the anode/slimes interface was computed assuming that 100% of the current flow was at that interface. During the dissolution process, the AC impedance was measured at preset slimes thicknesses. After dissolving the electrodes up to a certain slimes thickness the overpotential decay was followed as a function of time. During this decay, the AC impedance was also measured. The DC current and anodic overpotential recorded during the AC measurements were analyzed to obtain the components of the concentration overpotential.

(a) Variation of the anodic overpotential as a function of the electrolysis time and the current interruption time

Fig. 6A shows the anodic overpotential response observed during the galvanostatic dissolution of lead at a current density of 194.44 Amp/m² (Exp. CA2 in Table 1). The cell potential follows closely the recorded anodic overpotential values (Fig. 6B). Upon subtraction of the initial \( \eta_0 \) from both measurements, it is seen (Fig. 6C) that even though a net current was being passed through the counter electrode (a pure lead cathode), it can act very well as a reference electrode due to the high reversibility of lead in this system.

1 Theoretically both curves should have been identical if the processes under study behaves linearly. Instrumental artifacts (i.e. Potentiostat bandwidth) may also contribute to the observed discrepancies.

5 mV R.M.S does not exactly produce a sinusoidal current waveform of 35 Amp/m² of amplitude and vice versa.

2 The fraction of electronic current going through the slimes filaments was assumed to be negligible compared to the amount of current crossing the anode/slimes interface. The validity of this assumption was confirmed by measuring the distance between the anode/slimes electrolyte interface and the slimes/bulk electrolyte interface at the end of the experiment which was in agreement with the computed value. Furthermore, the slimes composition does not seem to change much with slimes thickness.
Variation of the anodic overpotential as a function of the electrolysis time and the current interruption time.

Fig. 6 Overpotential response of a typical lead bullion anode as a function of the slimes thickness (Exp. CA2).

The ac impedance was measured at preset slimes thicknesses indicated by the spikes shown in the curves.

(A) Anodic overpotential as a function of the slimes thickness (uncorrected for initial $\eta_0$).

(B) Cell potential as a function of the slimes thickness (uncorrected for initial $\eta_0$).

(C) Anodic overpotential measured by the counter and reference electrodes as a function of the slimes thickness (corrected for initial $\eta_0$).
Variation of the anodic overpotential as a function of the electrolysis time and the current interruption time

Further analysis of Fig. 6 shows that as the anode dissolves, $\eta_A$ increases quasi-linearly up to the point at which impurities dissolution occurs at a significant rate (at ~8 mm slimes and ~350 mV)\(^1\). At this point, increases in $\eta_A$ are also the result of the precipitation of secondary products (such as PbF\(_2\) and SiO\(_2\)) which hinder the movement of ions and increase the concentration gradients across the slimes layer.

In Fig. 6, the small departures of the anodic overpotential (so-called "spikes") result from the application of the AC waveform used to measure the impedance of the system at preset slimes thicknesses. Such overpotential changes were detected only at low AC frequencies ($\omega<6.3$ rad/sec). Potential variations produced by the AC waveform at higher frequencies were either very small or were undetected by the potentiostat digitized readings \(^2\).

Fig. 7 shows the anodic overpotential changes (corrected from initial $\eta_A$) observed during the dissolution of lead at a current density of 800 Amp/m\(^2\) (Exp. CA5 in Table 1). By comparing the $\eta_A$ response at low and high current densities (Figs. 6C and 7 respectively), it can be seen that increasing the current density resulted in decreasing the time required for impurities to dissolve at excessive rates \(^3\). Moreover, increases in current density do not appear to have a significant effect on the critical point at which the anodic overpotential rises exponentially. This indicates that if impurities are to dissolve to a large extent, a minimum overpotential value must be overcome.

The large $\eta_A$ values obtained at high current densities as compared to those values obtained at lower current densities, arise primarily as the result of changes in the concentration of the slimes electrolyte. Also, at high current densities steeper concentration gradients become established. This results in potential differences that increase monotonically with the concentration gradients. Steeper concentration gradients develop larger potential differences

---

\(^1\) Abrupt dissolution of phases containing noble impurities was not observed in the case study presented in Chapter 4 because a low current density was applied, the electrode was larger, only a 14 mm thick slimes layer was formed, and the maximum value of $\eta_A$ was <200 mV.

\(^2\) The potentiostat follows continuously (among other parameters) the difference in potential between the reference electrode and the current. At finite sampling times (i.e. once every 3 min.), these data are digitized and saved as "DC" data. If during the digitization process the AC waveform was being applied, a net DC overpotential and DC current may be observed as "spikes".

\(^3\) A 400% increase in the current density (from 200 to 800 Amp/m\(^2\)) resulted in a corresponding reduction in the amount of lead that could be removed before impurities dissolve at an excessive rate (i.e. at similar $\eta_A$ values, the equivalent amount of lead dissolved is ~4 times smaller).
Variation of the anodic overpotential as a function of the electrolysis time and the current interruption time

Fig. 7 Anodic overpotential (corrected for initial \( \eta_0 \)) measured by the counter and reference electrodes as a function of the slimes thickness (Exp. CA5).

Galvanostatic conditions \( I=800 \text{ Amp} \cdot \text{m}^{-2} \)

between the slimes and the electrolyte promoting their earlier dissolution. In addition, passage of larger currents increases the "ohmic" drop component of the anodic overpotential \(^\text{1}\).

Fig. 8A shows the changes in current density as a function of the electrolysis time during a potentiostatic experiment (Exp. CA4 in Table 1). In this experiment the dissolution of noble impurities present in the slimes layer was restricted by limiting the potential difference between the reference electrode and the lead anode to 220 mV. From the numerical integration of the data presented in Fig. 8A, the amount of lead dissolved as a function of the electrolysis time was found (Fig. 8B). At short electrolysis times, large current densities can flow because ionic transport proceeds relatively unhindered. As the slimes layer thickens, its presence restrains the flow of current up to the point at which only very small currents can flow through the cell. These decreases in current are

\(^\text{1}\) See section III.2.a
Variation of the anodic overpotential as a function of the electrolysis time and the current interruption time

Fig. 8 Current density changes as a function of the electrolysis time and of the amount of lead dissolved (Exp. CA4, potentiostatic conditions $E_{control}=220$ mV)

(A) Changes in the anodic current density as a function of the electrolysis time
(B) Changes in the amount of lead dissolved as a function of the electrolysis time. This curve was obtained from numerical integration of the data presented in (A)
(C) Current density changes as a function of the amount of lead dissolved
also the result of the presence of secondary products which block the movement of ions even further until the lead dissolution process is nearly halted (Fig. 8C). At long electrolysis times, lead ions are still being generated whereas concentration overpotential no longer changes and the precipitation of secondary products must take place for $\eta_c$ to remain constant.

During experiment CA4 the difference in potential between the reference and working electrodes was kept constant and equal to 220 mV ($E_{\text{control}} = 220$ mV). As a result of the presence of $\eta_a$ between such electrodes, the potential difference applied between the working electrode and the slimes/bulk electrolyte interface is not constant. The anodic overpotential changes as a function of $R_s$ and of the current density can be described by the following equation:

$$\eta_a = E_{\text{control}} - IR_s$$  ...3

$\eta_a$ changes as a function of the amount of lead dissolved are shown in Fig. 9. The anodic overpotential increases continuously as the current density decreases, up to the point at which current flow is negligible and $\eta_a = E_{\text{control}}$.

---

1 $R_s$ was obtained from AC impedance measurements at preset electrolysis times.
Variation of the anodic overpotential as a function of the electrolysis time and the current interruption time.

Fig. 10 Anodic overpotential changes upon current interruption (Exps. CA2, CA5, and CA4).

\( \eta_0 \) prior to current interruption was not subtracted from these measurements. The AC impedance was measured at preset times indicated by the spikes shown in the curves.

(A) From Exp. CA2  (B) From Exp. CA5  (C) From Exp. CA4
Variation of the anodic overpotential as a function of the electrolysis time and the current interruption time

Changes in anodic overpotential upon current interruption for the three cases described previously (Exps. CA2, CA5, and CA4) are shown in Fig. 10. A steep decrease in the overpotential is observed at the beginning of the interruption cycle. This steep change is followed by a quasi-exponential decrease in the $\eta_A$ value. On the other hand, the shape of the $\eta_A$ decay at times smaller than 1.6 Hrs is different for the three cases shown in Fig. 10. This indicates that upon current interruption, processes with different time constants can take place. The presence of these processes appears to be a function of the $\eta_A$ value and the electrode's history.

In the three previous cases AC impedance measurements did not seem to affect the pseudo-equilibrium present within the slimes layer. On the other hand, when the impedance measurements were made more frequently, transient excursions in the anodic overpotential were observed (in Exps. CA6 and CC1, see Fig. 11). As in the case study presented in Chapter 4, these potential excursions cannot be unambiguously explained. These excursions in potential were reproducible and indicate that the changes created by the AC waveform induce a shift of part of the Faradaic current towards the slimes filaments \(^1\). The fraction of the current going to the slimes filaments may be insignificant; yet it increases the corrosion potential of the electrode. The transient character of these excursions and the fact that after a certain time the overpotential decreases to a value that can be obtained by extrapolation of the $\eta_A$ curve (see Fig. 11A), indicates that the reaction at the anode/slimes interface was taking place at its normal rate even during the excursions in potential. Finally, upon current interruption, the anodic overpotential decay did not indicate any abrupt changes related to the potential excursions observed during the passage of current (Fig. 12).

\(^1\) The AC wave may have changed the conditions at the anode/slimes electrolyte interface by promoting precipitation and/or hydrolysis reactions at that interface. Under these conditions, Faradaic currents can divert to the slimes filaments and cause the excursions in potential shown in Fig. 11.
Variation of the anodic overpotential as a function of the electrolysis time and the current interruption time

Fig. 11 Anodic overpotential (corrected for initial $\eta_0$) as a function of the slimes thickness (Exps. CA6 and CC1).

(A) From Exp. CA6  (B) From Exp. CC1
(b) Changes in the impedance as a function of the slimes layer thickness and of the current interruption time

The AC spectra obtained at different slimes thickness are presented in Fig. 13 (Exp. CA2). Each spectrum was taken in the presence of a net Faradaic current and at different stages of the electrolysis cycle (see Fig. 6). Both the reactive ($Z_r$) and the capacitative ($-Z_c$) parts of the impedance increase as the slimes layer grows.

The impedance spectra in Fig. 13 show the presence of a low frequency arc which at high frequencies bends quasi-linearly towards the $Z_r$ axis.

AC impedance spectra obtained in the overpotential region above 350 mV are shown in Figs. 14 and 15. These spectra are significantly different from those presented in Fig. 13. The presence of high frequency arcs (i.e. arcs whose time constant is at least of the order of msec) shown in the respective Bode plots (Figs. 14B and 15B) indicates that reaction of noble compounds present in the slimes layer takes place in this region.
Changes in the impedance as a function of the slimes layer thickness and of the current interruption time

Fig. 13 Impedance spectra obtained during Exp. CA2 at slimes layer thicknesses between 0.8 and 7.8 mm.

Each impedance curve was obtained at a different slimes thickness as indicated in this Argand plot.
Changes in the impedance as a function of the slimes layer thickness and of the current interruption time

Fig. 14 Impedance spectra obtained during Exp. CA2 at a slimes layer thickness of 8.4 mm

(A) Argand plot  (B) Bode plot

1 In a Bode plot, the high frequency arcs are better resolved by analyzing the variations in the phase angle (dotted line, right vertical axis) as a function of the logarithm of the frequency.
Changes in the impedance as a function of the slimes layer thickness and of the current interruption time

Fig. 15 Impedance spectrum obtained during Exp. CA2 at a slimes layer thickness of 8.65 mm

(A) Argand plot  (B) Bode plot

1 In a Bode plot, the high frequency arcs are better resolved by analyzing the variations in the phase angle (dotted line, right vertical axis) as a function of the logarithm of the frequency. Thus, for example, in Fig. 15B a hump can be observed at log \( \omega = 4.20 \). Thus, \( \tau = 6.3 \times 10^3 \) sec (\( \tau \) is the time constant, \( \tau = \omega^{-1} \)).
The high frequency intercept of the impedance curves with the $Z_\infty$ axis was used to find the changes in $R_s$ as a function of the slimes thickness. As Fig. 16 indicates, the $R_s$ values measured by AC impedance were in agreement with those obtained by current interruption. Discrepancies between the $R_s$ values were only observed at slimes thicknesses larger than 8 mm.

**Fig. 16** Changes in the value of $R_s$ as a function of the slimes thickness (Exp. CA2).

From the AC and DC data obtained in Exp. CA2.

AC impedance measurements done while the anode was being galvanostatically dissolved at 800 Amp/m² (Exp. CA5) are shown in Figs. 17 and 18. Changes in $R_s$ as a function of the slimes thickness are plotted in Fig. 19. $R_s$ changes the most at slimes thickness larger than 2 mm where dissolution of noble impurities takes place. The small changes in the $R_s$ values at small slimes thickness are partially due to changes in the concentration of the electrolyte between the reference electrode and the slimes/bulk electrolyte interface as a result of the large current density applied.

1 Current interruption was done prior to obtaining the AC impedance spectrum. Appendix 6 describes how the current interruption measurement was implemented.

2 The invariability of the $R_s$ values at slimes thicknesses smaller than 8 mm confirms the results obtained in Chapter 4 in which upon current interruption $\eta_\alpha$ remained constant (Fig. 3.8).
Changes in the impedance as a function of the slimes layer thickness and of the current interruption time

Fig. 17 Impedance spectra obtained during Exp. CA5 at slimes layer thicknesses between 0.64 and 1.89 mm.

Each impedance curve was obtained at a different slimes thicknesses as indicated in this Argand plot. $R_s$ was subtracted from the $Z_{in}$ component of the impedance.
Changes in the impedance as a function of the slimes layer thickness and of the current interruption time

Fig. 18 Impedance spectra obtained during Exp. CA5 at a slimes layer thickness of 2.2 mm ($R_0$ was subtracted from the $Z_\pi$ component of the impedance).

(A) Argand plot  (B) Bode plot

Fig. 19 Changes in the value of $R_0$ as a function of the slimes thickness (Exp. CA5).

From the AC data obtained in Exp. CA5.
Fig. 20 Impedance spectra obtained during Exp. CA4 at slimes layer thickness between 0.87 and 2.87 mm.

Each impedance curve was obtained at a different slimes thickness as indicated in this Argand plot. $R_s$ was subtracted from the $Z_r$ component of the impedance.
While the impedance curves obtained during Exps. CA2 and CA5 increased uniformly with the slimes thickness, those obtained during Exp. CA4 showed marked increases and variations in their magnitude and shape (Fig. 20). This different behaviour is believed to be the result of the precipitation of secondary products across the slimes layer. Thus, impedance arcs whose time constant is large are present throughout the whole electrolysis cycle. The absence of high frequency arcs is a clear indication that Faradaic dissolution of noble impurities did not occur in this experiment.

Changes in $R_\infty$ as a function of the amount of lead dissolved are shown in Fig. 21. Again, minor variations in the $R_\infty$ values result from changes in the concentration of the electrolyte between the reference electrode and the slimes/bulk electrolyte interface. As lower currents go through the cell $R_\infty$ returns to its original value because such variations in concentration disappear.

---

1 As indicated by the frequency values at which the capacitative part (i.e. the imaginary part) of the impedance reaches a maximum value, the relaxation processes have very large time constants (of the order of sec).

2 These changes in $R_\infty$ were used to compute the anodic overpotential as a function of the amount of lead dissolved (Fig. 9).
Changes in the impedance as a function of the slimes layer thickness and of the current interruption time

Fig. 22 Argand plot showing the changes in the impedance spectra obtained in the presence of a layer of slimes and in the absence of a net Faradaic current (Exp. CA2).

The anode was corroded up to the formation of ~8.7 mm of slimes (Fig. 6). Subsequently, current was halted for ~115 hrs (Fig. 10A). During this period, impedance spectra were obtained at preset times as indicated in this Argand plot.

Curve A was obtained ~0.17 Hrs after current interruption
Curve B was obtained ~86.9 Hrs after current interruption

The AC impedance spectra obtained in the absence of a net Faradaic current (i.e. under current interruption conditions) are significantly different from those obtained during the passage of a net DC current. The impedance curves indicate the presence of a linear region which bends towards a small arc as high frequencies are approached (Fig. 22, Exp. CA2). The impedance decreases as a function of the current interruption time and the anodic overpotential. Also, $R_g$ decreases up to a limiting value often higher than observed at the beginning of the experiment (compare Figs. 16 and 23). Such a difference arises partially as a result of the prior reaction of the slimes compounds which changed the microstructure of the slimes layer.

The impedance spectra obtained at the end of Exp. CA5 (Fig. 24) are similar to those obtained in Exp. CA2 (Fig. 22). The decrease in $R_g$ in this experiment follows the pattern previously explained because dissolution of the slimes layer also took place in this experiment (Fig. 25).
Changes in the impedance as a function of the slimes layer thickness and of the current interruption time

Fig. 23 Changes in the value of $R_e$ as a function of the current interruption time (Exp. CA2)

From AC data obtained in Exp. CA2.

Fig. 24 Argand plot showing the changes in the impedance spectra obtained in the presence of a layer of slimes and in the absence of a net Faradaic current (Exp. CA5).

The anode was corroded up to the formation of $\sim$2.2 mm of slimes (Fig. 7). Subsequently, current was halted for $\sim$46 hrs (Fig. 10B). During this interval, impedance spectra were obtained at preset times as indicated in this Argand plot.

- Curve A was obtained $\sim$0.63 Hrs after current interruption
- Curve B was obtained $\sim$7.88 Hrs after current interruption
- Curve C was obtained $\sim$38.4 Hrs after current interruption
In experiment CA4 slimes dissolution was restricted by holding the anodic overpotential at values lower than 220 mV (Fig. 9). This resulted in nearly constant $R_n$ values during both the potentiostatic dissolution (Fig. 21) and the current interruption cycle. During current interruption, ionic concentration gradients within the slimes layer relax. This results in re-dissolution of precipitates and in ensuing impedance decreases (Fig. 26 Exp. CA4). The shape and magnitude of the impedance arcs are different from those observed in Exps. CA2 and CA5 as the precipitated products can generate an electrical double layer which affects the dielectric properties of the slimes filaments and of the lead electrode through changes in their relative permittivity. This results in impedance arcs with a large capacitative component.

![Graph showing changes in the value of $R_n$ as a function of the current interruption time (Exp. CA5).](image)

1 During current interruption conditions, $R_n$ remained nearly constant ($1.09 < R_n < 1.13 \ \Omega \text{cm}^2$).

2 The (static) relative permittivity is defined as $\varepsilon_r = \frac{C}{C_0}$. $C$ is the capacitance of a parallel plate condenser with plates of large area separated by a small gap, the whole being in a vacuum whereas $C_0$ is the capacitance of a parallel plate condenser when an isotropic material is present between the plates [5].
Changes in the impedance as a function of the slime layer thickness and of the current interruption time

Fig. 26 Argand plot showing the changes in the impedance spectra obtained in the presence of a layer of slime and in the absence of a net Faradaic current (Exp. CA4)

The anode was corroded up to the formation of ~2.8 mm of slime (Fig. 9). Subsequently, current was halted for ~23 hrs (Fig. 10C). During this interval, impedance spectra were obtained at preset times as indicated in this Argand plot.

Curve A was obtained ~0.27 Hrs after current interruption
Curve B was obtained ~2.08 Hrs after current interruption
Changes in the impedance as a function of the slime layer thickness and of the current interruption time

Each impedance curve was obtained at a different slime thickness as indicated in this Argand plot. $R_s$ was subtracted from the $Z_m$ component of the impedance.

(A) Impedance spectra acquired in the region where potential excursions were not observed (Fig. 11A).

(B) Impedance spectrum obtained at ~3.7 mm of slime

(C) Impedance spectrum obtained at ~7.7 mm of slime

Fig. 27 Impedance spectra obtained during Exp. CA6 at slime layer thicknesses between 0.43 and 7.7 mm.
Changes in the impedance as a function of the slimes layer thickness and of the current interruption time

As previously described, in Exps. CA6 and CC1 excursions in potential appeared to be triggered by the AC measurements (Fig. 11) 1. The impedance spectra obtained in Exp. CC1 are shown in Fig. 27 while those obtained in Exp. CA6 are shown in Fig. 28. The spectra measured in the region in which no potential excursions were observed increase uniformly as the slimes layer thickens (Figs. 27A and 28A). On the other hand, the impedance spectra measured in the region where the potential excursions were observed indicate the presence of arcs whose time constant is of the order of $10^{-5}$ sec 2. These spectra were reproducible and did not show any large changes in magnitude at different electrolysis times. Such high frequency phenomena can only be related to very fast processes such as found across the Helmholtz electrical double layer.

In Exps. CA6 and CC1, changes in $R_s$ were observed only in the region where the anodic overpotential excursions occur (Fig. 29). Upon current interruption, the impedance spectra show the presence of high frequency arcs whose size decreases as the current interruption time increases (Fig. 30). Also, $R_s$ decreases as a function of the current interruption time up to a limiting value which in the case of Exp. CA6 is nearly equal to that observed at the beginning of the experiment (compare Figs. 29A and 31).

1 Exps. CA6 and CC1 were performed using working electrodes from different sides of the lead anode and in the presence and absence of addition agents (see Table 1). In both experiments the potential excursions appeared at about the same slimes thickness (~3.2 mm). Consequently, the outset of the excursions in potential must be related to changes in the slimes electrolyte rather than in the slimes layer or in the anode.

2 In Figs. 27B, 27C, 28B and 28C, the maximum of the imaginary part occurs at $2\times10^4<\omega<3\times10^5$ rad/sec, thus $5\times10^{-3}<\tau<3.3\times10^{-4}$ sec.
Changes in the impedance as a function of the slimes layer thickness and of the current interruption time

Fig. 28 Impedance spectra obtained during Exp. CC1 at slimes layer thicknesses between 0.14 and 5.3 mm.

Each impedance curve was obtained at a different slimes thickness as indicated in this Argand plot. R, was subtracted from the Zr component of the impedance.

(A) Impedance spectra acquired in the region where potential excursions were not observed (Fig. 11B) (B) Impedance spectrum obtained at -4.5 mm of slimes (C) Impedance spectrum obtained at -5.3 mm of slimes
Changes in the impedance as a function of the slimes layer thickness and of the current interruption time

Fig. 29 Changes in the value of the $R_0$ as a function of the slimes thickness (Exps. CA6 and CC1).

(A) From the AC and DC data obtained in Exp. CA6
(B) From the AC data obtained in Exp. CC1
Changes in the impedance as a function of the slimes layer thickness and of the current interruption time

Fig. 30 Argand plot showing the changes in the impedance spectra obtained in the presence of a layer of slimes and in the absence of a net Faradaic current (Exp. CA6).

The anode was corroded up to the formation of ~8 mm of slimes (Fig. 11A). Subsequently, current was halted for ~113 hrs (Fig. 12). During this interval, impedance spectra were obtained at preset times as indicated in this Argand plot.

Curve A was obtained ~0.63 Hrs after current interruption
Curve B was obtained ~2.44 Hrs after current interruption
Curve C was obtained ~112.8 Hrs after current interruption

Fig. 31 Changes in the value of $R_\parallel$ as a function of the current interruption time (Exp. CA6).

From AC data obtained in Exp. CA6.
2. Analysis of the experimental data

In the study of the establishment of concentration gradients across the slime layer an electrical analogue could be used to describe how these gradients affect the dissolution of noble impurities present in the slime layer. This analogue has to evolve from fundamental DC and AC studies and must include parameters that provide a physico-chemical insight of the system. In the following section the main characteristics of such a model are introduced. The DC data are analyzed prior to the AC data to provide a framework for the elaboration of the analogue model. Subsequently, this model is used to relate the experimental DC and AC behavior of lead bullion electrodes covered with a layer of slime.

(a) Relationship between the DC anodic overpotential and the DC current density

As shown in Chapter 4, concentration gradients produce concentration overpotentials which can be linked to the resistivity of the electrolyte present within the slime layer. Concentration overpotential is also the major component of the $\eta_a$ curves presented in this chapter.

According to Newman $[23,24]$ concentration overpotential can be defined as follows $^1,2$:

$$\eta_c = I_x = \int_0^\infty \left( \frac{1}{\kappa} - \frac{1}{\kappa_w} \right) dx + \sum \frac{s_iRT}{nF} \ln \frac{C_{i_m}}{C_{i_0}} + F \int_0^\infty \left[ \sum \frac{Z_i D_i \partial c_i}{\kappa} \right] dx$$

Eq. 4 can be expressed as a linear equation:

$$\eta_c = IR_m + b$$

With

$$R_m = \int_0^\infty \left( \frac{1}{\kappa} - \frac{1}{\kappa_w} \right) dx$$

$$b = \sum \frac{s_i RT}{nF} \ln \frac{C_{i_m}}{C_{i_0}} + F \int_0^\infty \left[ \sum \frac{Z_i D_i \partial c_i}{\kappa} \right] dx$$

$^1$ Despite the different definitions of concentration overpotential available in the literature there is no conclusive evidence that any of them describes accurately the physical phenomena involved, yet, there is an agreement that because of the presence of concentration gradients, an ohmic drop is included in the concentration overpotential measurement (Compare refs. [23-24] and [8-9]).

$^2$ The ohmic part in Eq. 5 of $\eta_c$ has more physical meaning when it is equal to $I_x = \int_0^\infty \left( \frac{1}{\kappa} - \frac{1}{\kappa_w} \right) dx$ than when it is equal to $I_x = \int_0^\infty \left( \frac{1}{\kappa} - \frac{1}{\kappa_w} \right) dx$.
Eq. 4 indicates that \( \eta_c \) is composed of at least 2 contributions: (A) an ohmic drop due to variations of conductivity in the diffusion layer and (B) the potential difference of a concentration cell.

In Chapter 4 the determination of the electrical conductivity of the slimes electrolyte was attempted by using current interruption techniques. Such measurement was not really applicable because as Eq. 4 indicates, even though the ohmic term ought to disappear upon current interruption (I→0), the relaxation of concentration gradients creates a counter E.M.F. that avoids the direct measurement of the conductivity of the slimes electrolyte.

Under steady state conditions, Eq. 4 indicates that small changes in the applied current density ought to result in changes in \( \eta_c \) due exclusively to the ohmic component of the slimes electrolyte. If linearity between applied current density and the observed concentration overpotential is observed, the average resistivity of the slimes electrolyte, \( R_m \), could be obtained from Eq. 5. In addition, the parameter \( b \) should provide complementary information about the extent to which concentration gradients vary across the slimes layer.

The validity of Eq. 5 in the determination of the resistivity of the slimes electrolyte is studied in this section by analyzing the current and anodic overpotential changes observed during the application of a small amplitude sinusoidal waveform. Thus, these changes are analyzed according to Eq. 5 using the following assumptions:

1) Upon subtracting \( \eta_\alpha \) from the anodic overpotential observed upon the dissolution of lead, the main component of the remaining overpotential is due to the presence of concentration overpotential.

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1 As explained in Chapter 4, even though the external current may had been halted, processes that support the passage of internal currents may still be present after current interruption.

2 Steady state conditions are such that the concentration gradients across the slimes layer remain constant during the measurement of the \( \eta_c^{-1} \) relationship.

3 As Eq. 4 indicates, Ohm's law is not useful in a region where concentration gradients are present. Nevertheless, in such a region, an integral value of the changes in conductivity can be obtained.

4 Notice that \( R_m \) and \( b \) are a function of the local electrolyte conductivity and concentration gradients across the slimes layer.

5 AC and DC currents and overpotentials are terms that can easily be confused: An AC wave varies sinusoidally as a function of time and can be described by the following equation:

\[
f(t, \omega) = M_0 \sin(\omega t + \phi)\]

where: \( M_0 \) is the amplitude of the waveform, \( \omega \) is its frequency, \( \Phi \) is the phase angle, and \( t \) is the time. By knowing \( M_0 \), \( \omega \), and \( \Phi \), the DC "instantaneous" component of the AC waveform can be obtained.
2) Upon application of a small amplitude sinusoidal current waveform (less than 35 Amp/m²) at low frequencies (ω<6.3 rad/sec) and for a short period of time, ionic concentrations and concentration gradients throughout the slimes electrolyte remain unchanged 1.

3) The only overpotential increase that results in a linear dependance between potential and current is that due to the ohmic drop of the slimes electrolyte (R_m term in Eq. 5).

4) The restriction to ionic flow caused by the slimes can be obtained from the R_m value and its dependance with the electrolysis conditions.

5) The part of the overpotential that does not depend on the current density is due to the presence of concentration gradients across the slimes electrolyte (b term in Eq. 5) and to related increases on the corrosion potential of the lead anode.

6) The lead dissolution process proceeds unhindered (R_{ct}=0) whereas the slimes layer remains unreacted (R_{ct}→∞) 2

7) Ionic concentration gradients are present throughout the slimes layer (i.e. δ is equal to the thickness of the slimes layer). Furthermore, these gradients are only observed in the direction normal to the anode.

(I) Data analysis

The steps that were followed to analyze the \( \eta_A \) spikes produced by the AC current waveform are as follows:

A) From the \( \eta_A \) readings obtained during the application of the AC current waveform, \( \eta_A \) 3, was subtracted 4.

B) The resulting anodic overpotential and the current density were curve-fitted to a straight line according to Eq. 5.

---

1 The exact values for the amplitude and frequency of the waveform may change depending on whether a DC current is applied or not.

2 This is equivalent to implying that all the current flow is at the anode/slimes interface without any significant Faradaic current crossing the slimes/electrolyte interface.

3 \( R_n \) is known prior to and after the application of the current steps. An average \( R_n \) value can be used to correct the \( \eta_A \) readings.

4 Notice that the anodic overpotentials shown in Figs. 6C, 7, and 11 are all corrected only for the initial \( \eta_A \) (\( \eta_A=1R_n \)). The approach in this section is to analyze the anodic overpotential corrected for \( \eta_A \) present at the local time the current sweeps were applied.
Fig. 32 Detail of the "spikes" observed at -0.8 mm slimes (Exp. CA2, Table 4).

From Exp. CA2 (see Fig. 6)

The data points shown in (A) and (B) were linked using cubic splines interpolation. Had more points been available these curves would have looked like distorted sinusoidal waveforms with equal amplitudes.

(A) Variation of the anodic current density as a function of time
(B) \( \eta_a \) variation as a function of time (corrected for \( \eta_W \))
(C) Current density vs anodic overpotential curve [obtained from the data shown in (A) and (B)]
The current density changes observed during the application of one of the AC sweeps (Exp. CA2) are shown in Fig. 32A. The anodic overpotential spikes (corrected for $\eta_0$) that result from variations in the cell current are shown in Fig. 32B. The linear relationship between these two quantities can be seen in Fig. 32C. This relationship was found to be frequency independent, indicating nearly steady state conditions. Further analysis of the $\eta_a$ spikes produced during the application of the AC waveform at different slimes thickness showed that linearity was observed only up to anodic overpotentials smaller than 250 mV (Fig. 33).

**Fig. 33** Variations in the anodic overpotential as a function of the anodic current density at various slimes thickness (Exp. CA2, Table 4).

X axis: Anodic current density, Amp/m²
Y axis: Anodic overpotential (corrected for $\eta_0$)

Each curve corresponds to the analysis of the spikes observed at the following slimes thickness: (A) 1.6 mm (B) 4.7 mm (C) 6.6 mm (D) 8.6 mm
Table 4 Analysis of the spikes produced during the application of the AC waveform, in the presence of a net DC current (Exp. CA2, Figs. 32 to 35)

| Slimes Thickness (mm) | Slope $R_m$ (Ω cm$^2$) | Intercept, $b$ (mV) | $r^2$ | $|y_i|^2$, mV$^2$ | $\frac{b}{IR_m}$ | $\rho_m$, Ω cm | $IR_m$, mV | $IR_m + b$, mV | $\eta_\lambda$, mV |
|----------------------|------------------------|---------------------|-------|-----------------|-----------------|----------------|------------|----------------|----------------|
| 0.80                 | 0.62                   | 30.8                | 0.850 | 6.8             | 2.54            | 7.78           | 12.1       | 42.9           | 41.9           |
| 2.23                 | 1.45                   | 45.8                | 0.986 | 6.4             | 1.63            | 6.48           | 28.1       | 73.9           | 73.3           |
| 3.10                 | 2.15                   | 54.4                | 0.988 | 12.6            | 1.30            | 6.93           | 41.8       | 96.1           | 95.5           |
| 5.33                 | 3.93                   | 75.3                | 0.981 | 59.8            | 0.98            | 7.38           | 76.5       | 151.8          | 150.4          |
| 5.95                 | 4.57                   | 82.4                | 0.961 | 163.7           | 0.93            | 7.68           | 88.8       | 171.2          | 170.0          |
| 6.56                 | 5.23                   | 93.1                | 0.920 | 375.1           | 0.92            | 7.98           | 101.7      | 194.8          | 193.3          |
| 7.18                 | 5.71                   | 113.9               | 0.905 | 633.5           | 1.03            | 7.95           | 110.9      | 224.8          | 221.8          |
| 7.79                 | 7.22                   | 124.9               | 0.888 | 1192.5          | 0.89            | 9.27           | 140.3      | 265.2          | 262.4          |
| 8.41                 | 4.96                   | 361.0               | 0.051 | 4386.0          | 3.74            | 5.90           | 96.5       | 457.5          | 436.0          |
| 8.65                 | 9.40                   | 360.6               | 0.558 | 5688.7          | 1.97            | 10.86          | 182.7      | 543.3          | 520.0          |

Between 18 and 20 experimental points were used to obtain the regression coefficient. These points were collected during ~55 min and correspond to digitized samples taken when the frequency of the applied AC waves was between 0.063 and 6.3 rad/sec. 

Abstracted from Table 4, Appendix 9

As seen in Table 4, both $R_m$ and $b$ increase as a function of the slimes thickness (see Eq. 5 and Fig. 34A) indicating that larger concentration gradients across the slimes layer generate larger ohmic drops. Thus, the ohmic drop generated by these concentration gradients can promote the dissolution of the slimes layer only if large concentration gradients are also present. Furthermore, the ohmic drop generated by the slimes electrolyte ($IR_m$) is smaller than the "current independent" term $b$ only up to ~5.3 mm slimes (i.e. $\frac{b}{IR_m}$ reaches a value of ~1 at 5.3 mm slimes). After this slimes thickness, the $IR_m$ term not only becomes larger than the $b$ term, but it increases at a faster rate. The large variations in the values of these terms above ~5.3 mm slimes are related to the precipitation of secondary products. Precipitation of secondary products changes both local ionic concentrations and local electrolyte conductivities. Moreover, the changes in the $\rho_m$ value, (Fig. 34B) also indicate increases in its value towards the end of the electrolysis cycle. Dissolution of slimes compounds at slimes thicknesses larger than 8 mm results in non-linear

$\rho_m$ is the resistance of the slimes electrolyte per cm of slimes:

$$\rho_m[\text{Ω cm}] = \frac{R_m[\text{Ω cm}^2]}{\text{SlimesThickness [cm]}}$$
Fig. 34 Changes in the value of the resistance of the slimes electrolyte as a function of the slimes thickness (Exp. CA2, Table 4)

(A) \( R_m (\Omega \text{cm}^2) \) changes (B) \( \rho_m (\Omega \text{cm}) \) variations

Fig. 35 Changes in the parameters \( b \) and \( IR_m \) with relationship to the experimental variations of the anodic overpotential (Exp. CA2, Table 4).
relationships between overpotential and current\(^1\). Under these conditions, DC current enters the slimes electrolyte from both the anode/slimes electrolyte interface and the slimes/slimes electrolyte interface and this produces non-uniformities in the distribution of current across the slimes layer.

The relationship between \(\eta_a\), \(b\), and \(IR_m\) is graphically presented in Fig. 35. The jump in the value of \(b\) at slimes thicknesses larger than 8 mm indicates that noble compounds have reached the potential at which they can react Faradaically. By adding the value of \(IR_m\) to the \(b\) value, the experimental \(\eta_a\) is obtained\(^2\). This is a very important relationship: It links the slimes solution properties to the changes taking place in the lead anode and in the slimes layer. Thus, for different electrolysis conditions and anode compositions, optimum parameters for lead electrorefining can be obtained by studying the variations in the \(b\) and \(IR_m\) values at different slimes thickness. Moreover, it appears as if by merely applying a sinusoidal galvanodynamic scan (i.e. one scan whose amplitude is \(-20\ \text{Amp/m}^2\) at \(\omega \sim 0.1\ \text{rad/sec}\) at preset slimes thickness, the same information obtained using the FRA can be derived\(^3\).

| Slimes Thickness (mm) | Slope \(R_m\), \(\Omega\text{cm}^2\) | Intercept, \(b\), (mV) | \(r^2\) | \(|y|, \text{mV}\) | \(\frac{b}{IR_m}\) | \(\rho_m\), \(\Omega\text{cm}\) | \(IR_m\), mV | \(IR_m+b\), mV | \(\eta_a\), mV |
|-----------------------|-------------------------------|----------------------|--------|-----------------|----------------|-----------------|--------|--------------|---------|
| 0.70                  | 0.36                          | 24.9                 | 0.95   | 0.17            | 3.56           | 5.14            | 7.0    | 32.0         | 32.6    |
| 2.11                  | 1.00                          | 38.3                 | 0.99   | 0.14            | 1.96           | 4.75            | 19.5   | 57.8         | 59.5    |
| 3.06                  | 1.52                          | 47.0                 | 0.99   | 0.40            | 1.59           | 4.98            | 29.6   | 76.6         | 78.3    |
| 5.37                  | 1.89                          | 93.8                 | 0.85   | 15.64           | 2.55           | 3.52            | 36.8   | 130.3        | 134.1   |
| 6.64                  | 2.70                          | 113.6                | 0.88   | 10.16           | 2.16           | 4.06            | 52.5   | 166.1        | 168.2   |
| 7.49                  | 3.13                          | 140.9                | 0.97   | 4.09            | 2.31           | 4.18            | 60.9   | 201.9        | 205.2   |

4 experimental points were used to obtain the regression coefficient. These points were collected during \(-12\ min) and correspond to digitized samples taken when the frequency of the applied AC waves was between 0.63 and 6.3 rad/sec.

Abstracted from Table 5.a, Appendix 9

\(^1\) Non-linearities are identified when \(|y|\) increases and \(r^2\) decreases.

\(^2\) e.g. compare columns \((IR_m+b)\) and \(\eta_a\) in Table 4.

\(^3\) Use of linear polarization techniques such as SACV (small amplitude cyclic voltammetry) should provide the same results [10-13].
Table 5.B Analysis of the spikes produced during the application of the AC waveform, under current interruption conditions (Exp. CA6)

<table>
<thead>
<tr>
<th>Parameters Derived from Regression Analysis Computations</th>
<th>From Eq. 4</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time, hrs</td>
<td>Slope ( R_m ), ( \Omega )cm(^2)</td>
<td>Intercept, ( b ), (mV)</td>
</tr>
<tr>
<td>0.63</td>
<td>2.23</td>
<td>60.8</td>
</tr>
<tr>
<td>2.44</td>
<td>3.62</td>
<td>48.4</td>
</tr>
<tr>
<td>3.83</td>
<td>3.83</td>
<td>44.5</td>
</tr>
<tr>
<td>43.07</td>
<td>1.64</td>
<td>5.3</td>
</tr>
<tr>
<td>112.8</td>
<td>0.99</td>
<td>0.2</td>
</tr>
</tbody>
</table>

9 experimental points were used to obtain the regression coefficient. These points were collected during \(-27\) min and correspond to digitized samples taken when the frequency of the applied AC waves was between 0.63 and 6.3 rad/sec.

Abstracted from Table 5.b, Appendix 9

The \( \eta_A \) spikes observed in Exps. CA6 and CC1 were also analyzed according to Eq. 5. The results obtained from such an analysis are shown in Tables 5A and 6. A linear relationship between overpotential and current was only found in the region where the potential excursions were absent. Furthermore, a quasi-linear relationship between overpotential and current was also found under current interruption conditions (Table 5B, Exp. CA6)\(^1\).

Table 6 Analysis of the spikes produced during the application of the AC waveform, in the presence of a net DC current (Exp. CC1)

<table>
<thead>
<tr>
<th>Parameters Derived from Regression Analysis Computations</th>
<th>From Eq. 4</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slimes Thickness mm</td>
<td>Slope ( R_m ), ( \Omega )cm(^{-1})</td>
<td>Intercept, ( b ), (mV)</td>
</tr>
<tr>
<td>1.37</td>
<td>0.52</td>
<td>32.4</td>
</tr>
<tr>
<td>1.79</td>
<td>0.63</td>
<td>38.0</td>
</tr>
<tr>
<td>2.22</td>
<td>0.74</td>
<td>42.8</td>
</tr>
<tr>
<td>2.65</td>
<td>0.81</td>
<td>48.0</td>
</tr>
<tr>
<td>3.07</td>
<td>0.92</td>
<td>52.4</td>
</tr>
<tr>
<td>3.50</td>
<td>0.96</td>
<td>58.4</td>
</tr>
</tbody>
</table>

5 experimental points were used to obtain the regression coefficient. These points were collected during \(-12\) min and correspond to digitized samples taken when the frequency of the applied AC waves was between 0.63 and 6.3 rad/sec.

By comparing the data presented in Tables 4, 5A, and 6 it can be seen that:

---

\(^{1}\) In Table 5B, \( r^2 \) and \( |y| \) vary widely yet the predicted (\( \text{IR}_m + b \)) and experimental (\( \eta_A \)) overpotentials are nearly equal.

[159]
i) The anodic overpotential values observed at slimes thicknesses lower than 3.5 mm (before potential excursions appeared in Exps. CA6 and CC1) are different in the three analyzed experiments: $\eta_A$ (Exp CA2) $> \eta_A$ (Exp CA6) $> \eta_A$ (Exp CC1). This results in differences among the computed $R_m$ and $b$ values.

ii) The smallest $R_m$ and $b$ values obtained at a fixed slimes thickness are observed in Exp. CC1. The fact that in this experiment $\rho_m$ decreases as the slimes layer thickens is significant.

iii) A relationship that relates the slope $b$ to the average slimes electrolyte resistance, $R_m$, and to the local electrolyte concentrations cannot be inferred yet. The observed differences in the values of the $\eta_A$ components ($IR_m$ and $b$) at a fixed slimes thickness are related to the bulk electrolyte composition, to the presence of addition agents, and to the changes in the slimes physico-chemical properties (i.e. porosity, tortuosity).

Addition agents appear to play an important role in the anodic overpotential increases. This was also observed in the sulphamic acid system [25]. Thus, in Exp. CC1 the distinct $R_m$ and $b$ values indicate that the addition agents increase $\eta_A$ mainly by restricting the flow of ions. In the presence of a Faradaic current, $I$, this restriction can be related to the $\frac{b}{IR_m}$ ratio: The larger this ratio, the smaller the restriction for the movement of electrolyte across the slimes layer and the lower the observed overpotential. In Exp. CC1 the $\frac{b}{IR_m}$ ratio is ~3 and remains nearly constant. On the other hand, at similar slimes thickness, for the other experiments this ratio shows marked decreases (from 2.5 to 1.3 for Exp. CA2 and from 3.4 to 1.6 for Exp. CA6).

\[\text{i.e. } b \text{ values cannot be derived from } R_m \text{ values and vice versa: Average electrical conductivities may be equal yet local concentrations may be different.}\]

\[\text{The amount and nature of addition agents incorporated during the refining of Pb using a sulphamic acid electrolyte has also been shown to have a strong impact on the permeability of the anode slimes [25].}\]

\[\text{Notice that whereas Exps. CA2 and CA6 were carried out using the lead anode "mould" cooled face, Exp. CC1 was performed using the "air" cooled face. The microstructures of these electrodes were found to be similar. Thus, the anodic overpotential variations can hardly be related to microstructural differences between the different electrodes.}\]
Analysis of the $\eta_A$ spikes obtained upon current interruption also indicated a linear relationship between $\eta_A$ and current (Table 5B). Under current interruption conditions $I=0$ and $\eta_A$ does not have an ohmic component, yet, by slowly displacing the dynamic pseudo-equilibrium observed during the relaxation of the concentration gradients, it was possible to obtain the integral value of the resistivity of the slimes electrolyte, $R_m^1$. As seen in Table 5B this value decreases as the concentration gradients relax. Furthermore, at the end of the current interruption cycle, $\eta_A\sim0$, yet, as indicated by the finite $R_m$ value, the electrolyte present within the slimes was found to have a different conductivity than the bulk electrolyte.

(b) Proposed analogue representation of a lead bullion electrode covered with a layer of slimes.

So far in this thesis it has been shown that the response of electrochemical systems to AC waveforms can be used to obtain kinetic and diffusional parameters. Resistors, capacitors, and CPE's have been used to link changes in the AC spectra to associated physico-chemical parameters. A general model is to be proposed to analyze the observed AC impedance spectra. This model is based on a set of assumptions. From this model and from the experimental data, several electrical analogues are developed to examine the AC impedance data and to find the link between these analogues and the physical phenomena they may represent.

Fig. 36 shows a general analogue model of a lead bullion electrode covered with a layer of slimes. Six interfaces can be identified in this figure. Each one of these interfaces has an associated impedance $^2$:

---

1 i.e. the pseudo-steady state observed during the relaxation of the concentration gradients in the entrained electrolyte was slowly displaced by applying a sinusoidal current waveform.

2 The impedance of the reference electrode is neglected in this analogue.
Proposed analogue representation of a lead bullion electrode covered with a layer of slimes.

- $Z_{a/s_e}$ = Faradaic impedance at the lead anode/slimes electrolyte interface.
- $Z_{ni/se}$ = Faradaic impedance at the slimes/slimes electrolyte interface.
- $Z_{ni/be}$ = Faradaic impedance at the slimes/bulk electrolyte interface.
- $Z_{a/si}$ = Electronic impedance at the lead anode/slimes interface.
- $Z_w$ = Warburg ionic diffusional impedance throughout the slimes electrolyte.
- $Z_w,se$ = Warburg ionic diffusional impedance in the slimes electrolyte/bulk electrolyte interface.

The value and mathematical expressions that each of these impedances can adopt is a function of the current density, the slimes electrolyte composition, the slimes layer microstructure and composition, and the electrode's thermal history and composition. Thus, a single mathematical representation of the overall impedance may be too difficult to determine unambiguously. Moreover, some of these impedances are distributed (i.e. their value changes as a function of the position) and coupled (i.e. they change only if other impedances change). Despite the complex interrelationships existing among the different impedances, their individual contribution to the total impedance can be assessed by analyzing each of them separately. From this analysis and from experimental data, the relative magnitude of each of these impedances with respect to the total impedance can be inferred.

The individual analysis of the components of the impedance has to start from the simplest scenario. This will be the case when only a DC current is applied to the electrode. In this case the total impedance of the system has only a real component [$Z_{DC} = Z(j\omega)_{\omega=0}$]. Thus, while the impedance is not an explicit function of time, if measured in a system where changes are taking place, its value at a fixed frequency will be a time dependent quantity. Thus at $\omega=0$ the changes in impedance as a function of time, $Z_{DC}(t)$, can be defined as follows:

$$Z_{DC}(t) = \frac{\eta(t)}{I(t)}$$

where:

$\eta(t)$ = overpotential (compensated for $\eta_0$) observed upon passage of current as a function of the electrolysis time. By using a reference electrode reversible to Pb$^{2+}$ no corrections for liquid junction at the reference electrode/electrolyte interface have to be incorporated in the $\eta(t)$ values.
During the galvanostatic dissolution of a lead bullion electrode, $\eta$ increases as the slimes layer forms. Thus, all the information on the impedance comes from knowledge of the changes in $\eta$ as a function of time. By subtracting $\eta_0$ \(^1\) from the $\eta(t)$ values one of the most obvious contributions to the impedance has been identified and subtracted from the overall impedance. However, other contributions to the overall impedance cannot be as easily identified and/or quantified.

By analyzing the path of the DC current on its way from the anode to the bulk electrolyte a deeper insight in the $Z_{\infty}$ components can be obtained. Thus, as shown in Fig. 36 there are two main paths for the DC current: One through the anode/slimes electrolyte interface and the second through the anode/slimes interface. If current enters the slimes filaments it can either leave them through the bulk electrolyte (path A) or through the slimes electrolyte (path C). On the other hand if any current crosses the anode/slimes interface it can either go across the slimes electrolyte (path B) or return to the anode via a ground loop (path D).

For current to go through the slimes filaments it will first have to overcome a resistance associated with $Z_{a/sl}$. As the slimes filaments were found to be grounded to the anode \(^2\) such resistance must be negligible. Any current entering the slimes filaments can only produce Faradaic work at the slimes/slimes electrolyte interface if and only if the activation energy barrier of such process is overcome. This requires large overpotentials and ionic gradients across the slimes layer. If any current diverts towards the slimes filaments it can either go across the slimes/slimes electrolyte interface (path A) or across the slimes/bulk electrolyte interface (path C). The experimental evidence is that Faradaic reactions of the slimes compounds are insignificant at overpotentials less than 200 mV. For example, the amount of bismuth corroded is less than 30 ppm, too small to account for significant Bi corrosion currents crossing the slimes filaments. Thus, during most of the electrorefining cycle, any current going through the anode/slimes interface can only result in charging of the

---

1 $\eta_0$ is equal to the current density, $I$, times the uncompensated ohmic resistance, $R_\infty$ ($\eta_0=IR_\infty$).
2 See Chapter 4 section II.A.1
Fig. 36 Proposed analogue model representation of a lead bullion electrode covered with a layer of slimes.
Proposed analogue representation of a lead bullion electrode covered with a layer of slimes.

electrical double layer of the slimes filaments and are insignificant. Thus, from this analysis it can be assumed that for the DC case, up to $\eta(t)$ values equal to 200 mV: $Z_{a/ai} \rightarrow 0$, $Z_{al/aec} \rightarrow \infty$, and $Z_{al/bc} \rightarrow \infty$.

From the previous description it can be assumed that almost all of the applied DC current flows across the anode/slimes electrolyte interface and continues in its way towards the bulk electrolyte by overcoming the diffusional impedance $Z_w$ (path B). All this current is transferred to the electrolyte mainly as a result of the Faradaic transfer of Pb$^{2+}$ to the slimes electrolyte. For such a transfer to take place, an energy barrier associated with $Z_{a/se}$ has to be overcome. Such impedance is small (lead dissolves almost reversibly), yet it can increase if conditions at the interface change (i.e. as a result of the presence of secondary products blocking the interface). Once Pb$^{2+}$ ions are transferred to the slimes electrolyte, an ionic current is established. The resistance that the ions find in their movement across the slimes is a function of $Z_w$ which is an intensive and position dependent quantity. The larger the effective distance the ions have to travel before reaching the bulk electrolyte the larger this impedance. The complex migrational/diffusional processes taking place across the slimes electrolyte can be described by $Z_w$. Furthermore, if as a result of the movement of ions across the slimes electrolyte/bulk electrolyte interface a diffusion layer is established, a semi-infinite Warburg impedance has to be included as well, although for well mixed bulk electrolytes its presence can be neglected. Once the Pb$^{2+}$ ions reach the bulk electrolyte they are transferred to the cathode by convection, migration and diffusion.

Thus, the analysis of the DC experimental data presented in Section III.2 of this chapter can now be related to the analogue model shown in Fig. 36. In the DC analysis of the anodic overpotential changes, the lead dissolution processes were assumed to proceed unhindered whereas the slimes layer was assumed to remain unreacted. This is equivalent to assuming that $Z_{a/se} \rightarrow 0$ and that $Z_{al/aec} \rightarrow \infty$, and $Z_{al/bc} \rightarrow \infty$, which is in agreement with the statements on the characteristics of the electrical analogue here presented. Thus, the $R_m$ value obtained from the analysis of the changes in overpotential as a function of

---

1 Notice that under DC conditions a capacitor will act as an open circuit and will have an infinite impedance. The impedance of a capacitor, $Z_c$, is given by: $Z_c = \frac{1}{j\omega C}$, thus at $\omega=0$, $Z_c \rightarrow \infty$. 

[165]
current can only be related to changes in the value of $Z_w$. A relationship between the observed $b$ values and $Z_w$ may also exist, yet, impedance values obtained at frequencies other than zero have to be provided (see Eq. 9).

The previously introduced DC model also must be consistent with the experimental evidence observed under current interruption conditions. Depending on the extent to which concentration gradients had been established prior to the current interruption, an overpotential decay will always be observed. Eventually, the electrolyte compositions inside and outside the slimes electrolyte equilibrate, ionic movement virtually stops, and the impedance disappears as the overpotential vanishes (i.e. as $\eta_{\text{int}} \to 0$). On the other hand, as a result of the ionic concentration differences between the slimes electrolyte/bulk electrolyte and the anode/slimes electrolyte interfaces, a series of concentration cells may be established because electronic current can flow across the slimes filaments (path D). This process may consist of (as an example) continued corrosion of the lead anode, accompanied by deposition of noble elements in the electrolyte, as $\text{Bi}^{3+}$, $\text{SbO}^+$, or $\text{Ag}^+$ on slimes filaments. These internal currents may be too small or difficult to measure, however, they can affect the characteristics of the overpotential decay and consequently of the impedance. As concentration gradients disappear, the rate of these internal processes declines, up to the point at which they become negligible.

The phenomena associated to the current interruption case can also be represented by the analogue circuit shown in Fig. 36. Diffusional processes can be represented by $Z_w$ and $Z_{w,\infty}$. However, as concentration gradients within the slimes layer relax, $Z_w$ describes diffusional processes that resemble more semi-infinite diffusion than diffusion in a bounded region. As described previously, $Z_w$ is linked to the components of the concentration overpotential, and for a purely diffusional process, $R_m$ should be equivalent to the diffusion resistance $R_d$ (i.e. to the value of $Z_w$ at $\omega=0$).

In the analysis of the components of the AC impedance, the same line of thought followed during the DC analysis will be used: First, the different paths that the AC wave can follow will be traced. Then the relative contribution of each of the associated impedances to the overall impedance will be estimated. On the basis of this and from experimental evidence, simplifications of the general
analogue model will be proposed. The validity of the proposed model will be tested by analyzing the changes in impedance in the presence and in the absence of a net Faradaic DC current.

In the previous analysis it was found that all the applied DC current can be assumed to flow across the anode/slimes electrolyte interface. On the other hand, a superimposed AC wave can either cross the same interface and/or divert through the slimes filaments. If it diverts to the slimes filaments, it can cross the slimes/slimes electrolyte interface without actually performing any Faradaic work. This will happen if the slimes layer can be considered to have only a capacitative component. For these processes to take place, the AC waveform will have to produce alternating potential fields at the slimes/slimes electrolyte double layer interface. This will result in large capacitative effects being observed in the impedance spectrum. Thus, if any AC current crosses the slimes/slimes electrolyte interface, equivalent impedances related to the capacitative part of the slimes impedance should be observed even in the absence of a net Faradaic current. As the experimental impedance spectra obtained under current interruption conditions did not indicate the presence of large interfacial areas, AC current transfer across the slimes layer in the presence of a net Faradaic current can be neglected.

The experimental data indicate that while a net DC current is being applied, formation of Pb$^{2+}$ is the preferred reaction. Such a reaction takes place without a significant energy expenditure and is the path of least resistance for the flow of current. If this is the path for least resistance for DC current, it can also be assumed to be the path of least resistance for the AC current. Thus, assuming that all the AC current crosses this interface, the overall impedance will have only three components: $Z_{an/e}$, $Z_{w}$, $Z_{w,e}$ (notice the similarity between the DC and the AC cases). Accordingly, in the absence of a net Faradaic current, the polarity of the double layer can be switched and/or its potential difference changed simultaneously in the slimes/electrolyte and the anode/slimes interface. Only then, the capacitative and resistive process associated with these impedances can be observed as changes in the impedance of the system. Consequently,

---

1 Notice that in the worst scenario in which in the presence of a DC current the AC current actually crosses the slimes/slimes electrolyte interface and causes Faradaic reactions, a wide non-uniform current distribution can result. If this had taken place the system would had been changed to the extent that steady state concentration gradients during the AC measurements would not have been observed, the system would have oscillated to the extent that the impedance measurement could not have been taken.
other processes overlooked by the anodic overpotential measurements under current interruption conditions may be better analyzed by AC impedance techniques.

Basically, the main difference between the DC and the AC experiments is that while DC currents cannot cross the slimes/slimes electrolyte interface at $\eta$ lower than 200 mV, AC waveforms can cross such an interface and by doing so induce changes in the measured AC impedance. However, in the presence of a net Faradaic current such process may be hindered to the extent that such transfer does not take place at all. If this is the case, then all the DC and AC current flow is at the anode/slimes electrolyte interface. Nonetheless, if any AC current flows across the slimes layer it may result in impedance changes only in the high frequency region of the impedance spectrum at which point charge transfer phenomena are isolated from diffusional processes in the slimes electrolyte. The situation changes at overpotentials at which Faradaic reaction of the slimes filaments can take place. Under these conditions, both DC and AC currents will cross the slimes/electrolyte interface and in doing so, at that point, abrupt changes in impedance will take place. On the other hand, in the absence of a net Faradaic current (i.e. under current interruption conditions) the hindrance for the current flow across the slimes layer disappears (as the whole electrode can change polarity and/or act as a corrosion or concentration cell) and impedances associated with the slimes filaments will be observed in the total impedance.

---

**Summary of assumptions used in the development of the analogue model:**

1) A one dimensional representation of the lead bullion electrode covered with a layer of slimes.

2) Electrolysis takes place under isothermal conditions.

3) The Warburg diffusional impedance can be used to describe the ionic mass transfer processes that take place across the slimes electrolyte.

4) The AC impedance measurement is obtained without significantly affecting the quasi-equilibrium conditions within the slimes layer.

---

1 These abrupt impedance changes upon Faradaic reaction of the slimes filaments can be seen by comparing Figs. 13 and 14.

2 Isothermal temperature of the slimes electrolyte can be assumed on the basis of sufficient thermal conductivity of $\text{H}_2\text{SiF}_6-\text{PbSiF}_6$ solutions and of the large porosity of the slimes layer, contributing to convection.
5) In the presence of a net Faradaic current the lead anode and the slimes layer are equipotential.

6) Changes in the microstructure of the slimes layer as a result of blockage of ionic flow (i.e. by the precipitation of secondary products) can be incorporated within the Warburg diffusional impedance or by additional impedances connected in series with it.

7) Blockage of the anode/slimes electrolyte interface (i.e. by the precipitation of secondary products) inhibits charge transfer processes and increases the Faradaic impedance, $Z_{a/se}$.

8) Dissolution of noble impurities present within the slimes layer takes place only at overpotentials larger than 200 mV.

9) In the presence of a net Faradaic current and at overpotentials values smaller than 200 mV, 100% of the current transfer occurs across the anode/slimes electrolyte interface and: $Z_{a/se} \to 0$, $Z_{al/se} \to \infty$, and $Z_{al/be} \to \infty$.

10) In the presence of a net Faradaic current capacitance effects associated with the slimes layer are prone to be observed only in the high frequency region of the impedance spectrum.

11) The impedance changes attributed to the presence of addition agents can be incorporated within the proposed Faradaic and diffusional impedances.

12) Impedances associated with the reference electrode can be neglected.

(1) Data analysis

In this section, several electrical circuits derived from the proposed analogue model are introduced. These electrical circuits were formulated so as to follow the assumptions used in the development of the general analogue model. Among all the analyzed circuits, only those that actually matched the experimental data are presented and discussed. The characteristics of these circuits are established by comparing their parameter values with physico-chemical processes taking place across the slimes layer.

1 Non-uniform porosity across the slimes layer can be expected when secondary products precipitate or re-dissolve.

2 Capacitance effects associated with the noble compounds present in the slimes layer are more significant as the $\eta_a$ approaches values larger than 200 mV (i.e. in the region where their Faradaic reaction can occur).
(i) **Case I: impedance spectra obtained in the presence of a net Faradaic current**

The impedance spectra obtained in Exps. CA2, CA5, CA6, and CC1 were found to be described accurately \(^1\) by two different yet related electrical circuits (see Fig. 37). The values of the parameters associated with the proposed electrical circuits were obtained by curve fitting \(^2\) the experimental data to the theoretical impedance functions.

The first of these circuits is a \(Z_{ZARC1}-Z_{ZARC2}-\text{CPE}_0\) analogue (circuit A.1, Fig. 37) \(^3\). The impedance of each of the components of this circuit is given by the following equations:

\[
\begin{align*}
Z_{\text{CPE}_1} &= b_1(j\omega)^{w_{z1}} \\
Z_{\text{CPE}_2} &= b_2(j\omega)^{w_{z2}} \\
Z_{\text{CPE}_0} &= b_0(j\omega)^{w_{z0}} \\
Z_{R_1} &= R_1 \\
Z_{R_2} &= R_2
\end{align*}
\]

From which the total impedance, \(Z_A\), can be obtained as follows:

\[
Z_A = \frac{R_1}{1 + D_1(j\omega)^{w_{z1}}} + \frac{R_2}{1 + D_2(j\omega)^{w_{z2}}} + b_0(j\omega)^{w_{z0}}
\]

with

\[
D_1 = \frac{R_1}{b_1} \quad \text{and} \quad D_2 = \frac{R_2}{b_2}
\]

The overall impedance of the circuit A.1 was re-arranged as described in Eq. 10, so that the relaxation times can be obtained from the \(D_1\) and \(D_2\) parameters. The relaxation time associated with each one of the \(ZARC\) circuits can be obtained as follows:

\[
\tau_1 = D_1^{\frac{1}{w_{z1}}} \quad \text{and} \quad \tau_2 = D_2^{\frac{1}{w_{z2}}}
\]

---

1 As presented in the various Tables shown in Appendix 9. "described accurately" means that from a statistical regression analysis perspective, good correlation existed between the experimental and the curve-fitted data. The number of parameters involved in the curve fitting routine was never in excess to that required to obtain significant fits according to statistical rules (i.e. as derived from ANOVA statistical tables).

2 This process required the use of complex non-linear square fitting routines. The \(Z_0\) component of the total impedance was used to obtain the values of individual parameters in the different electrical circuits. Once an initial set of values was obtained, they were used to compute the \(Z_A\) component of the impedance and improve the accuracy of the fitting process.

3 For an in-depth review of the characteristics of the \(ZARC\) circuits see ref. [15].
The electrical parameters associated with circuit A.1 were correlated with the individual impedances shown in Fig. 36. Thus, the first ZARC circuit was used to represent high frequency phenomena associated with the Faradaic impedances \( Z_{a/sc} \) and \( Z_{al/sc} \). The second ZARC circuit was used

---

1 \( R_1 \) was chosen to represent charge transfer resistances associated with the lead dissolution processes, while \( R_2 \) was related to the DC conductivity of the slimes electrolyte. CPE\( _1 \) represents the distributed nature of the anode/slimes and the slimes/slimes electrolyte interface while CPE\( _2 \) represents the presence of a distributed capacitance generated by the concentration gradients present in the slimes electrolyte.

2 The high frequency term refers to the part of the impedance that was observed at \( \omega > 100 \) rad/sec.
to represent the low frequency response associated with ionic diffusion across the slimes layer (i.e. with $Z_{w}$). The third component of this circuit, a CPE element was introduced to represent diffusional processes (i.e. $Z_{w,\alpha}$).

The second analogue circuit was indirectly assembled by finding an electrical circuit whose impedance matched the impedance of circuit A. Such a circuit is shown in Fig. 37B (Circuit B.1). The impedance of each of the components of this circuit can be described as follows:

$$Z_{CPE_a} = b_a(j\omega)^{-\psi_{CPE}}$$

$$Z_{CPE_b} = b_b(j\omega)^{-\psi_{CPE}}$$

$$Z_{r_a} = r_a$$

$$Z_{r_b} = r_b$$

$$Z_{c_b} = C_b(j\omega)$$

From these components the total impedance, $Z_b$, can be obtained as follows:

$$Z_B = \left[ \frac{r_b}{1 + r_b C_b(j\omega)} + B_b(j\omega)^{-\psi_{CPE}} \right]^{-1} + \frac{1}{B_a(j\omega)^{-\psi_{CPE}}}$$

A direct correspondence between the parameters in this circuit and those in the analogue model shown in Fig. 36 is not immediately evident. Yet, this circuit was found to reproduce the experimental data and it was considered worthwhile to try to find some analogies among both circuits. Thus, it was found that the $Z_{w,\alpha}$ component could be associated with the CPEB component and that the RC circuit could be associated with the Faradaic impedances $Z_{a/\alpha e}$ and $Z_{m/\alpha e}$. Diffusional processes can be included in both $R_1$ and $CPE_A$ components.

When diffusional processes in the bulk electrolyte are neglected (i.e. when $Z_{w,\alpha} \rightarrow 0$) \(^1\), the two proposed electrical analogue circuits can be related through their impedances at $\omega = 0$ (by their DC resistances). Thus, the total DC resistance of these circuits can be obtained as follows \(^2\):

$$Z_{A(\omega = 0)} = R_{A,\text{total}} = R_1 + R_2$$

$$Z_{B(\omega = 0)} = R_{B,\text{total}} = r_a + r_b$$

\(^1\) Notice that by neglecting $Z_{w,\alpha}$ in circuits A and B the only elements that disappear are CPE$_a$ and CPE$_b$ respectively.

\(^2\) Once the parameter values were obtained the impedance at $\omega = 0$ was found to be nearly equal for the two electrical circuits shown in Fig. 37.
In the analysis of the experimental impedance spectra, the impedance values at $\omega=0$, were related to the total DC resistance, $R_m$, obtained from analysis of the spikes obtained during the application of the AC waveform.

The values of the parameters obtained by curve fitting the impedance spectra obtained in Exp. CA2 to the $Z_{ARC1}-Z_{ARC2}$ analogue (circuit A.2 in Fig. 37) are shown in Table 7. The characteristics of this circuit stressed the fact that the impedance spectra are composed of at least two distributed components with different time constants. The presence of two humps in the impedance spectra was clearly observed at slimes thicknesses lower than 3 mm. At larger slimes thicknesses the separation of these humps was not immediately evident, yet, from the curve fitting process, it was found that the spectra could be deconvoluted to produce two arcs whose center lay below the $Z_R$ axis (see Fig. 38).
Fig. 38 Correlation between the experimental and theoretical impedance spectra (Exp. CA2, circuit A.2, Table 7).

From the AC data presented in Fig. 13.

Circuit A.2 was used to fit the experimental data. The derived analogue parameters are shown in Table 7.
### Analysis of the parameter values shown in Table 7 indicate the following relationships (see also Fig. 39):

**a)** The impedance obtained at \( \omega=0 \), \( R_{A,totol} \), was found to be similar to \( R_m \) (see Table 4). This correspondence provides an important link between the DC and the AC experiments.\(^1\)

**b)** \( \tau_{R_1} \) values are small (of the order of msec) while \( \tau_{R_2} \) values are large (of the order of sec). The separation in the magnitudes of these time constants decreases as the slimes layer thickens.

**c)** The largest changes in the values of the derived analogue parameters appears at slimes thicknesses larger than 6.5 mm. These changes can be

---

1. \( R_{A,totol} \) is expected to be larger than \( R_m \) because in addition to include ionic processes it also includes resistances associated with charge transfer processes.
associated with the precipitation and hydrolysis of secondary products. Moreover, changes in these parameters correspond to changes in the \( \frac{b}{I R_m} \) ratio ².

Among the previously drawn relationships, one of the most significant appears to be that related to the precipitation/hydrolysis of secondary products. If the hydrolysis point actually took place at ~6.6 mm of slimes, that would have resulted in blockage of the reacting interface (the anode/slimes electrolyte interface) and in ensuing increases in \( Z_{a/se} \). This appears to be in agreement with the observed increases in \( R_1 \) at slimes thicknesses larger than 6.6 mm. On the other hand, upon precipitation of secondary products, an increase in \( Z_w \) (i.e. in the impedance associated with \( Z_{ARC2} \)) should have been observed had the movement of ions been blocked by these products. As observed in Table 7, even though \( R_2 \) and \( b_2 \) decrease between 6 and 6.6 mm of slimes, \( \tau_{R_2} \) increases almost a 100% in the same interval. Thus, increases in \( \tau_{R_2} \) seem to be inversely proportional to \( R_2 \) and \( b_2 \) because the fractional exponent \( \Psi_{z_2} \) is also changing. The large values of \( \tau_{R_2} \) observed after 6.6 mm are an indication that movement of ions across the slimes layer proceeds more slowly because such movement is being hindered by precipitated products.

---

¹ See Table 4 and focus on the changes in \( \frac{b}{I R_m} \), \( R_m \), and \( \rho_m \) between 6.6 and 7.8 mm of slimes.
Fig. 39 Variation of the derived electrical analogue parameters as a function of the slimes thickness (Exp. CA2, Circuit A.2, Table 7)

From the parameters value presented in Table 7

(A) Changes in the relaxation times $\tau_{R1}$ and $\tau_{R2}$.
(B) Changes in the resistance values $R_{A,\text{total}}$, $R_i$, and $R_j$. [\(\Omega \text{cm}^2\)]
(C) Changes in the specific resistance $\rho_{A,\text{total}}$, $\rho_i$, and $\rho_j$. [\(\Omega \text{cm}\)] as obtained from:

$$\rho_i \ [\Omega \text{cm}] = \frac{R_i \ [\Omega \text{cm}^2]}{\text{Slimes Thickness} \ [\text{cm}]}$$

Compare $R_{A,\text{total}}$ with $R_m$ (Fig. 34A)
Analysis of the experimental impedance spectra obtained in Exp. CA2 using the electrical circuit B.2 resulted in the parameter values shown in Table 8. Only the impedance spectrum obtained at 0.80 mm slimes thickness was fitted to circuit B.1 (see Fig. 40). This was possible because at very low frequencies (less than 1 rad/sec) a tail related to diffusion in the bulk electrolyte (i.e. to $Z_{w,\infty}$) was observed in this impedance spectrum.

1 This tail was found to be described by the CPE$_a$ element shown in the analogue circuit B.1.
2 Notice that $B_a$ is nearly equal to the $B_1$ value obtained under rest potential conditions and in the absence of addition agents [$B_a\sim1.9 \ \Omega \ cm^2 \ sec^{\gamma_{zc}}$ while $B_1\sim2-3 \ \Omega \ cm^2 \ sec^{\gamma_{zc}}$ (see Table 3, Exps. CC1-5 to CC2-2)].
**Table 8** Parameters derived from the fitting of the impedance spectra obtained in Exp. CA2 (Circuit B.2, Figs. 40, 41)

<table>
<thead>
<tr>
<th>Slimes Thickness (mm)</th>
<th>( r_a ) (( \Omega ) cm(^2))</th>
<th>( r_b ) (( \Omega ) cm(^2))</th>
<th>( C_b ) (F cm(^{-2}))</th>
<th>( B_a ) (( \Omega ) cm(^2) sec(^{-\frac{1}{2}}))</th>
<th>( \Psi_{ZCa} )</th>
<th>( R_{B,total} ) (( \Omega ) cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.43</td>
<td>0.23</td>
<td>0.026</td>
<td>11.48</td>
<td>0.58</td>
<td>0.66</td>
</tr>
<tr>
<td>2.23</td>
<td>1.15</td>
<td>0.49</td>
<td>0.102</td>
<td>7.46</td>
<td>0.53</td>
<td>1.64</td>
</tr>
<tr>
<td>3.10</td>
<td>1.64</td>
<td>0.66</td>
<td>0.146</td>
<td>8.59</td>
<td>0.56</td>
<td>2.30</td>
</tr>
<tr>
<td>5.33</td>
<td>3.35</td>
<td>0.90</td>
<td>0.398</td>
<td>9.51</td>
<td>0.60</td>
<td>4.25</td>
</tr>
<tr>
<td>5.95</td>
<td>3.87</td>
<td>1.13</td>
<td>0.570</td>
<td>9.88</td>
<td>0.61</td>
<td>5.00</td>
</tr>
<tr>
<td>6.56</td>
<td>4.36</td>
<td>1.60</td>
<td>0.749</td>
<td>10.48</td>
<td>0.61</td>
<td>5.96</td>
</tr>
<tr>
<td>7.18</td>
<td>4.80</td>
<td>2.40</td>
<td>0.975</td>
<td>11.25</td>
<td>0.62</td>
<td>7.20</td>
</tr>
<tr>
<td>7.79</td>
<td>5.29</td>
<td>3.82</td>
<td>1.35</td>
<td>12.61</td>
<td>0.64</td>
<td>9.12</td>
</tr>
</tbody>
</table>

For the AC sweep done at 0.8 mm slimes: \( B_b = 1.92 \Omega \) cm\(^2\) sec\(^{-\frac{1}{2}}\), and \( \Psi_{ZCa} = 0.78 \) (this was the only sweep fitted to circuit B.1, all the other sweeps were fitted to circuit B.2)

*Abstracted from Table 8, Appendix 9*

![Fig. 41](image-url) Variation of the derived electrical analogue parameters as a function of
the slimes thickness (Exp. CA2, Circuit B.2, Table 8)

**(A)** Changes in the resistance values, \( [\Omega \) cm\(^2\)] \( R_{B,total} \) (marked with \( \diamond \)), \( r_a \) (marked with \( O \)) and \( r_b \) (marked with \( X \)).

**(B)** Changes in the specific resistance, \( [\Omega \) cm\(^{-1}\)] \( \rho_{B,total} \) (marked with \( \diamond \)), \( \rho_a \) (marked with \( O \)), and \( \rho_b \) (marked with \( X \)).
As seen in Fig. 41, $r_a$ and $r_b$ increase continuously during the lead dissolution process. Moreover, it was found that at slimes thicknesses smaller than 6 mm, $r_a=R_2$ and $r_b=R_1$ (see Tables 7 and 8). This correspondence agrees with the assigned physical meaning of the parameters present in the electrical circuit. Thus, $r_a$ is related to the DC resistance of the slimes electrolyte while $r_b$ is related to the charge transfer resistance associated with the lead dissolution process. The only parameter that indicates significant changes in its value as the slimes layer thickens is $r_b$. These changes are observed at slimes thicknesses larger than 5.4 mm and indicate a restriction in the charge transfer process for lead dissolution. Such a restriction agrees with the proposed mechanism of precipitation of secondary products and ensuing increases in $Z_{a/se}$.

The two electrical circuits shown in Fig. 37 were also used to analyze the impedance spectra from exp. CA5. The parameters obtained from the curve fitting process are shown in Tables 9 and 10. From the analysis of the data presented in these tables, precipitation of secondary products appeared to take place between 1.2 and 1.76 mm of slimes. Furthermore, the large $R_1$ value at 1.89 mm of slimes and the small time constant associated with it, appear to indicate that charge transfer processes were strongly hindered as a result of the continuous precipitation of secondary products (see Table 10).

By comparing the results obtained in Exp. CA2 with those obtained in Exp. CA5, it can be seen that increases in current density resulted in corresponding increases in $r_a$ and decreases in $r_b$ (compare Tables 8 and 10). This indicates that higher current densities produce larger diffusional impedances which can induce precipitation of secondary products and earlier dissolution of impurities present in the slimes layer.
Table 9  Parameters derived from the fitting of the impedance data obtained in Exp CA5 to the $Z_{\text{MARC}}$-$Z_{\text{MARC}}$ analogue (Circuit A.2)

<table>
<thead>
<tr>
<th>Slimes Thickness (mm)</th>
<th>$R_1$, $\Omega \text{cm}^2$</th>
<th>$b_1$, $\Omega \text{cm}^2 \text{sec}^{-1}$</th>
<th>$\tau_{R_1}$, sec</th>
<th>$R_2$, $\Omega \text{cm}^2$</th>
<th>$b_2$, $\Omega \text{cm}^2 \text{sec}^{-1}$</th>
<th>$\tau_{R_2}$, sec</th>
<th>$R_{A,\text{total}} = \frac{1}{R_1 + R_2}$ $\Omega \text{cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.64</td>
<td>0.101</td>
<td>0.91</td>
<td>75.04</td>
<td>0.0007</td>
<td>0.68</td>
<td>8.19</td>
<td>0.00088</td>
</tr>
<tr>
<td>1.20</td>
<td>0.017</td>
<td>0.68</td>
<td>1.47</td>
<td>0.0015</td>
<td>0.83</td>
<td>0.59</td>
<td>11.10</td>
</tr>
<tr>
<td>1.76</td>
<td>0.069</td>
<td>0.83</td>
<td>0.35</td>
<td>0.1423</td>
<td>1.61</td>
<td>0.53</td>
<td>9.26</td>
</tr>
<tr>
<td>1.89</td>
<td>0.817</td>
<td>0.58</td>
<td>13.64</td>
<td>0.0079</td>
<td>0.99</td>
<td>0.81</td>
<td>6.77</td>
</tr>
</tbody>
</table>

* All measurements refer to the geometrical area of the electrode.
** Low and high frequency terms refer to the ranges of frequencies used during the deconvolution process.
*** Low and high frequency arcs were fitted to the whole frequency range ($6.3 < \omega < 23000$ rad/sec)

Abstracted from Table 9, Appendix 9

Table 10  Electrical analogue parameters derived from the fitting of the impedance data obtained in Exp. CA5 (Circuit B.2)

<table>
<thead>
<tr>
<th>Slimes Thickness (mm)</th>
<th>$r_a$, $\Omega \text{cm}^2$</th>
<th>$r_b$, $\Omega \text{cm}^2$</th>
<th>$C_b$, $\Omega \text{cm}^2 \text{sec}^{-1}$</th>
<th>$B_a$, $\Omega \text{cm}^2 \text{sec}^{-1}$</th>
<th>$\Psi_{ZCA}$</th>
<th>$R_{B,\text{total}}$, $\Omega \text{cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.64</td>
<td>0.38</td>
<td>0.04</td>
<td>0.017</td>
<td>16.10</td>
<td>0.65</td>
<td>0.42</td>
</tr>
<tr>
<td>1.20</td>
<td>0.72</td>
<td>0.08</td>
<td>0.036</td>
<td>16.10</td>
<td>0.64</td>
<td>0.80</td>
</tr>
<tr>
<td>1.76</td>
<td>1.44</td>
<td>0.16</td>
<td>0.063</td>
<td>11.39</td>
<td>0.57</td>
<td>1.60</td>
</tr>
<tr>
<td>1.89</td>
<td>1.50</td>
<td>0.32</td>
<td>0.062</td>
<td>14.71</td>
<td>0.62</td>
<td>1.82</td>
</tr>
</tbody>
</table>

The impedance spectra obtained in Exp. CA4 was not analyzed directly by any of the two proposed electrical analogues because of the complex characteristics of the observed spectra. On the other hand, enough information on the precipitation of secondary products was obtained by solely plotting the maximum $Z_{\Re}$ and $-Z_{\Im}$ values as a function of the slimes thickness, as obtained from the following relationships:

$$Z_{\Re,\text{max}} = [Z_{\Re}]_{\omega \rightarrow \infty} - [Z_{\Re}]_{\omega \rightarrow 0}$$

$$-Z_{\Im,\text{max}} = [Z_{\Im}]_{\omega = \omega_o}$$
As can be seen in Fig. 42, both components increase at the same rate up to 2.1 mm, after which sudden increases in their values are observed. This point appears to mark the onset of precipitation of secondary products. This precipitation is continuous and produces exponential increases in the impedance towards the end of the electrolysis cycle. These impedance increases result from both charge transfer and diffusional restrictions created by the presence of these products. Secondary products act as a barrier for ionic movement across the whole layer of slimes and create a nearly motionless region in which only very small currents can flow. Thus, this represents the limiting case in which $Z_w \rightarrow \infty$. As there is no other path for current flow (see Fig. 37) other than through Path A\(^1\), the dissolution process has to stop (so called "anode passivation").

\(^1\) Exp. CA4 was performed under potentiostatic conditions and, as found by analyzing the cathodic deposit, impurity dissolution did not take place.
Data analysis

(ii) Case II: impedance spectra obtained in the absence of a net Faradaic current

Upon current interruption the impedance spectra were found to be capable of being described by the modified Randles analogue circuit 1 shown in Fig. 43. Such a circuit has the following impedance:

\[
Z(j\omega) = \frac{R_{ct} + B_1(j\omega)^{-\eta_c}}{1 + R_{ct}C_d(j\omega) + C_dB_1(j\omega)^{1-\eta_c}} \quad \ldots 14
\]

The CPE circuit shown in Fig. 46 represents semi-infinite diffusional processes. \(R_{ct}\) is the charge transfer resistance and \(C_{dl}\) is the double layer capacitance.

From the analysis of the data obtained in Exp. CA2 (see Table 11 and Fig. 44) it can be seen that:

---

1 Notice that the fact that the impedance could be fitted to Randles circuits implies that: \(Z_{\text{ Viso}} \to \infty\), and \(Z_{\text{ Viso}} \to \infty\) while \(Z_{\text{ Viso}}\) and \(Z_{\text{ Viso}}\) have finite values.

[183]
From the AC data presented in Fig. 22
The Randles circuit shown in Fig. 43 was used to fit the experimental data. The derived analogue parameters are shown in Table 11

(A) From the impedance spectrum obtained ~0.17 Hrs after current interruption
(B) From the impedance spectrum obtained ~86.9 Hrs after current interruption

**Table 11** Parameters derived from the fitting of the impedance data obtained in Exp. CA2 to the Randles analogue circuit (Figs. 43, 44)

<table>
<thead>
<tr>
<th>Time, Hrs</th>
<th>$R_{ct}$, $\Omega$ cm$^2$</th>
<th>$C_{dl}$, $\mu F$ cm$^2$</th>
<th>$B_1$, $\Omega$ cm$^2$ sec$^{-\Psi_{zc}}$</th>
<th>$\Psi_{zc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17</td>
<td>0.044</td>
<td>23.75</td>
<td>3.83</td>
<td>0.19</td>
</tr>
<tr>
<td>0.64</td>
<td>0.112</td>
<td>167.42</td>
<td>3.63</td>
<td>0.33</td>
</tr>
<tr>
<td>12.03</td>
<td>0.070</td>
<td>206.32</td>
<td>3.13</td>
<td>0.31</td>
</tr>
<tr>
<td>86.90</td>
<td>0.048</td>
<td>274.37</td>
<td>2.23</td>
<td>0.30</td>
</tr>
</tbody>
</table>

*Abstracted from Table 11, Appendix 9*

a) Charge transfer resistances, $R_{ct}$, are very small and do not seem to change significantly during the current interruption cycle. This indicates that only highly reversible processes are present and that charge transfer phenomena associated with the noble elements present in the slimes layer do not contribute to the measured impedance spectra.
b) Double layer capacitances, $C_{dl}$, increase only during the first hour after the current interruption. The small $C_{dl}$ values do not indicate the presence of large electrochemically active surface areas. Consequently, $C_{dl}$ values in excess of those observed in the absence of slimes, are mostly due to changes in the relative permittivity of the anode/slimes electrolyte interface as a result of the presence of secondary products at that interface.

c) $B_1$ decreases the most at the beginning of the current interruption, to reach a limiting value after ~70 Hrs. These decreases are the result of the relaxation of concentration gradients across the slimes layer.

d) $\Psi_{zc}$ is nearly constant.

From these relationships it can be concluded that both $R_a$ and $C_{dl}$ represent only phenomena associated with $Z_{a/sec}$ (i.e. with the Pb/Pb$^{2+}$ equilibrium). This is a very important relationship because it proves that charge transfer and capacitative phenomena related to the slimes filaments are not affecting significantly the impedance of the system. In addition, processes that support the passage of internal currents do not appear to result in characteristic contributions to the impedance, except at very short current interruption times, at which large $C_{dl}$ changes were found. Finally, diffusional processes across the slimes electrolyte can be successfully described by a single CPE element because upon current interruption no more Pb$^{2+}$ ions are being generated at the anode/slimes electrolyte interface (i.e. ionic concentrations are fixed only at the slimes/bulk electrolyte interface).

The electrical analogue parameters obtained by analyzing the spectra obtained in Exp. CA5 are shown in Table 12 (see also Fig. 45). From these parameters the following relationships can be observed:

---

1 Remember that both the $R_a$ and $C_{dl}$ measurements are given with respect to the geometrical area of the electrodes.

2 $R_a$ and $C_{dl}$ are also a function of ionic concentrations at the anode/slimes electrolyte interface and the roughness of the anode.

3 $B_1$ decreases also as a result of the re-dissolution of secondary products and ensuing tortuosity and porosity changes.

4 For ionic diffusion across a porous electrode $0.5<\Psi_{zc}<0.25$ [13,16,19-21]
Fig. 45 Correlation between the experimental and theoretical impedance spectra (Exp. CA5, current interruption conditions, Table 12).

From the AC data presented in Fig. 24, the Randles circuit shown in Fig. 43 was used to fit the experimental data. The derived analogue parameters are shown in Table 12.

(A) From the impedance spectrum obtained 0.63 Hrs after current interruption.

(B) From the impedance spectrum obtained 34.6 Hrs after current interruption.

Table 12 Electrical analogue parameters derived from the fitting of the impedance data obtained in Exp. CA5 to the Randles analogue circuit (Fig. 45)

<table>
<thead>
<tr>
<th>Time, Hrs</th>
<th>$R_{ct}$, $\Omega \text{ cm}^2$</th>
<th>$C_{dl}$, $\mu \text{F cm}^2$</th>
<th>$B_1$, $\Omega \text{ cm}^2 \text{ sec}^{-}\Psi_{zc}$</th>
<th>$\Psi_{zc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.63</td>
<td>0.010</td>
<td>804.67</td>
<td>1.11</td>
<td>0.21</td>
</tr>
<tr>
<td>11.67</td>
<td>0.021</td>
<td>1588.19</td>
<td>0.71</td>
<td>0.25</td>
</tr>
<tr>
<td>34.59</td>
<td>0.023</td>
<td>1308.61</td>
<td>0.70</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Abstracted from Table 12, Appendix 9

a) $R_{ct}$ values are small and of the same order of magnitude as those obtained in Exp. CA2.

b) Even though the slimes layers are not as thick as those formed in Exp. CA2, double layer capacitances are larger. This indicates that in Exp. CA5 secondary products precipitated to a larger extent than in Exp. CA2.
c) $B_1$ values are smaller than in Exp. CA2 because the region over which concentration gradients span is ~3 times smaller.

d) $\Psi_{zc}$ values are smaller than in Exp. CA2. Thus, due the larger presence of secondary products there is a larger blockage for ionic flow and a reduction in the available space for ionic diffusion.

---

**Fig. 46** Argand plot of a typical lead bullion electrode (Exp. CC2) in the presence of a 2.2 mm layer of slimes

AC impedance spectra obtained under rest potential conditions 20 Hrs after current interruption $R_i$ was subtracted from the $Z_i$ component of the impedance

The impedance curve was fitted to a CPE element from which the following values were obtained $B_1 = 0.14 \ \Omega \ cm^2 \ sec^{-1/2}$, $\Psi_{zc} = 0.42$

*Compare with Figs. 5.16 and Fig. 6.1*
Similar experiments in which neither noble impurities dissolution nor secondary products precipitation took place, provided analogous spectra that could be fitted to a modified Randles circuit, from which very small $R_c$ and $C_d$ values were obtained. Thus, for example, the impedance spectrum obtained with an electrode that had been previously dissolved (up to $-2.2$ mm at $200$ Amp/$m^2$, $\eta_{la_{max}} \approx 55$ mV) shows only a straight line which indicates the presence of a purely diffusional controlled process that proceeds without kinetic limitations (Fig. 46). Moreover, the derived $B_1$ value is nearly equal to that obtained when pure lead was studied. The absence of a charge transfer arc confirms that the slimes layer is not contributing to the measured impedance. Furthermore, as no secondary products were precipitated, the equilibrium Pb/Pb$^{2+}$ was not hindered to the extent that significant capacitances could be observed.

In Exp. CA4 large amounts of secondary products precipitated and this resulted in impedance spectra that could be fitted to circuits A.1 and A.2 (see Table 13). The physical meaning assigned previously to each of the impedance components was found to be valid also under these conditions. This correspondence is due to the enhanced restriction in ionic flow produced by the large amount of precipitated products. Furthermore, these products create a nearly stagnant environment in which bounded diffusional processes can take place. Additionally, these products block the anode/slimes electrolyte interface and increase the charge transfer resistance for the Pb/Pb$^{2+}$ equilibrium. Thus, as ionic concentrations across the slimes layer diminish, secondary products re-dissolve and the impedance in the whole frequency range decreases as a function of time.

1 In the absence of slimes, the AC impedance spectra were also fitted to a Randles circuit from which a $B_1$ value of $1.88 \Omega \cdot cm^2 \cdot sec^{-1/2}$ was obtained (see Table 3). Thus, as a result of the uniform corrosion of the electrode, surface irregularities observed at the slimes/bulk electrolyte interface diminish at the anode/slimes electrolyte interface and this results in equivalent $B_1$ values for lead bullion and pure lead working electrodes (see section II.A).

2 Upon current interruption concentration gradients relax and local ionic concentrations decrease. This results in re-dissolution of the precipitated products. Upon re-dissolution ionic species are released creating an environment in which bounded diffusional processes take place (i.e. the precipitated products during their re-dissolution maintain a fixed Pb$^{2+}$ concentration at the slimes/slimes electrolyte interface).
Data analysis

(see Fig. 47). These phenomena can be followed by analyzing the variations in the analogue parameters as a function of the current interruption time (see Table 13).

**Fig. 47** Correlation between the experimental and theoretical impedance spectra (Exp. CA4, current interruption conditions, Table 13).

From the ac data presented in Fig. 26. Circuits A.1 and A.2 (Fig. 37) were used to fit the experimental data. The derived analogue parameters are shown in Table 17. Each spectrum was obtained at the following current interruption times: (A) 2.1 Hrs (B) 9.3 Hrs (C) 11.2 Hrs (D) 19.6 Hrs.
### Table 13

**Electrical Analogue Parameters derived from the fitting AC impedance data obtained in Exp. CA4 to the $Z_{ZARC} - Z_{ZARC}$ analogue (Circuit A.2, Fig. 47)**

<table>
<thead>
<tr>
<th>Time, Hrs</th>
<th>$R_1$, $\Omega \text{cm}^2$</th>
<th>$\Psi_{ZC1}$, $\Omega \text{cm}^2 \text{sec}^{-\omega}$</th>
<th>$b_1$, $\Omega \text{cm}^2 \text{sec}^{-\omega}$</th>
<th>$\tau_{R_1}$, sec</th>
<th>$R_2$, $\Omega \text{cm}^2$</th>
<th>$\Psi_{ZC2}$, $\Omega \text{cm}^2 \text{sec}^{-\omega}$</th>
<th>$b_2$, $\Omega \text{cm}^2 \text{sec}^{-\omega}$</th>
<th>$\tau_{R_2}$, sec</th>
<th>$R_{A\text{total}}$, $\Omega \text{cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.08</td>
<td>0.87</td>
<td>0.73</td>
<td>94.77</td>
<td>0.00167</td>
<td>1.77</td>
<td>0.43</td>
<td>1.98</td>
<td>0.77</td>
<td>2.64</td>
</tr>
<tr>
<td>9.33</td>
<td>0.32</td>
<td>0.79</td>
<td>108.92</td>
<td>0.00062</td>
<td>1.26</td>
<td>0.47</td>
<td>1.65</td>
<td>0.56</td>
<td>1.58</td>
</tr>
<tr>
<td>11.18</td>
<td>0.34</td>
<td>0.73</td>
<td>79.97</td>
<td>0.00057</td>
<td>0.99</td>
<td>0.55</td>
<td>1.79</td>
<td>0.34</td>
<td>1.33</td>
</tr>
<tr>
<td>19.55</td>
<td>0.32</td>
<td>0.72</td>
<td>75.11</td>
<td>0.00052</td>
<td>0.99</td>
<td>0.59</td>
<td>1.70</td>
<td>0.40</td>
<td>1.31</td>
</tr>
</tbody>
</table>

The AC sweeps obtained at current interruption times longer than 11 hrs were fitted to the $Z_{ZARC1} - Z_{ZARC2} - \text{CPE}_0$ analogue (circuit A.1). Thus, 2 additional parameters were obtained:

<table>
<thead>
<tr>
<th>Time, Hrs</th>
<th>$b_o$, $\Omega \text{cm}^2 \text{sec}^{-\omega}$</th>
<th>$\Psi_{ZCo}$, $\Omega \text{cm}^2 \text{sec}^{-\omega}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.18</td>
<td>0.050</td>
<td>0.74</td>
</tr>
<tr>
<td>19.55</td>
<td>0.046</td>
<td>0.79</td>
</tr>
</tbody>
</table>

* All measurements refer to the geometrical area of the electrode.

** The regression coefficients $r_1^2$ and $r_2^2$ were larger than 0.99

*Abstracted from Table 13, Appendix 9*
Chapter 7 Physico-Chemical Properties of H₂SiF₆-PbSiF₆ Electrolytes and their Relationship to the Transport Processes Across the Slimes Layer

I. Introduction

In the previous chapters, the electrochemistry of lead bullion electrodes and of the phases and compounds present in the slimes was shown to be linked to the ionic concentration gradients across the slimes layer. The extent to which these gradients change was found to be a function of the current density and the bulk electrolyte composition. From an analysis of the ohmic and diffusional components of the anodic overpotential, increases in $\eta_A$ were linked to changes in ionic composition across the slimes layer. $\eta_A$ changes were also related to precipitation of secondary products and to hydrolysis of the acid. Precipitated products hinder the ionic movement across the slimes layer, increase $\eta_A$, and thereby enhance the dissolution rate of noble impurities.

In this chapter lead and acid concentration gradients within the slimes layer are related to hydrolysis of the acid and precipitation of secondary products. The mean ionic compositions present within the slimes layer during the industrial operation of the BEP are used to indicate the magnitude of such gradients. Additionally, Eh-pH diagrams are used to describe the conditions under which secondary reactions across the slimes layer can take place. The shape of the concentration gradients and their effect on the anodic processes are assessed by solving numerically the Nernst-Planck flux equations in their fundamental form. Some of the experimental data required to solve these equations were derived from an analysis of the physico-chemical properties of H₂SiF₆-PbSiF₆ electrolytes (pH, viscosity, density, and electrical conductivity) and from data available in the literature.

II. Average Slimes Electrolyte Composition

Table 1 shows the range of electrolyte compositions found within the slimes layer at the end of the electrorefining cycle during normal industrial operation of the BEP. Pb⁺² concentrations within this electrolyte are between 5 and 10 times

---

1 In-situ electrolyte concentrations of the slimes electrolyte are likely to be smaller than the reported compositions shown in Table 1. During the extraction of electrolyte samples from the separated slimes, some re-dissolution of precipitates (mainly of PbF₂) may have taken place.
larger than their corresponding bulk electrolyte values while \( \text{H}_2\text{SiF}_6 \) concentrations are between 2 and 6 times smaller. Thiet et al. [1,2] and Wenzel et al. [3-5] found similar mean ionic concentrations. Furthermore, Thiet [1] also found that increases in current density result in corresponding increases in ionic concentrations.

Table 1 Composition of the electrolyte samples extracted from anode slimes obtained under industrial operation of the BEP (Cominco Ltd.)

<table>
<thead>
<tr>
<th>Test Number</th>
<th>Anode Composition</th>
<th>Anode Face</th>
<th>Slime Cake Assay, wt%</th>
<th>Anode Slimes Filrate M (mol l^{-1})</th>
<th>mM</th>
<th>Current Efficiency %</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 Compo</td>
<td>1.51 0.42 0.07 0.01 0.31 0.14</td>
<td>air mold</td>
<td>49.8 11.8 8.2</td>
<td>1.86 0.24 0.046</td>
<td>0.043 0.17</td>
<td>84</td>
</tr>
<tr>
<td>#1 Anode 9</td>
<td>1.49 0.47 0.10 0.01 0.28 0.11</td>
<td>air mold</td>
<td>49.1 12.2 7.8</td>
<td>2.03 0.17 0.038</td>
<td>0.048 0.15</td>
<td>79</td>
</tr>
<tr>
<td>#2 Anode 22</td>
<td>1.65 0.54 0.11 0.01 0.31 0.12</td>
<td>air mold</td>
<td>50.0 14.9 6.9</td>
<td>1.28 0.28 0.038</td>
<td>0.057 0.21</td>
<td>73</td>
</tr>
<tr>
<td>#2 Anode 6</td>
<td>1.51 0.42 0.07 0.01 0.31 0.14</td>
<td>air mold</td>
<td>47.5 12.5 12.3</td>
<td>2.15 0.21 0.018</td>
<td>0.048 0.16</td>
<td>74</td>
</tr>
<tr>
<td>#3 Compo</td>
<td>1.57 0.57 0.12 0.01 0.36 0.15</td>
<td>air mold</td>
<td>49.2 14.3 7.5</td>
<td>2.24 0.21 0.040</td>
<td>0.043 0.43</td>
<td>79</td>
</tr>
<tr>
<td>#3 Anode 3</td>
<td>1.65 0.6 0.15 0.01 0.36 0.16</td>
<td>air mold</td>
<td>48.4 14.7 7.6</td>
<td>1.98 0.21 0.038</td>
<td>0.014 0.27</td>
<td>77</td>
</tr>
<tr>
<td>#4 Compo</td>
<td>1.49 0.47 0.10 0.01 0.28 0.11</td>
<td>air mold</td>
<td>51.7 14.7 7.8</td>
<td>1.52 0.28 0.052</td>
<td>0.043 0.17</td>
<td>77</td>
</tr>
<tr>
<td>103-1</td>
<td>1.5 0.44 0.09 0.02 0.31 0.10</td>
<td>air mold</td>
<td>45.1 10.3 21.0</td>
<td>2.97 0.14 0.016</td>
<td>0.038 0.03</td>
<td>96</td>
</tr>
<tr>
<td>103-2</td>
<td>1.44 0.37 0.08 0.01 0.29 0.10</td>
<td>air mold</td>
<td>46.9 10.3 22.6</td>
<td>2.24 0.21 0.031</td>
<td>0.033 0.13</td>
<td>76</td>
</tr>
<tr>
<td>104-1</td>
<td>1.5 0.30 0.09 0.01 0.35 0.11</td>
<td>air mold</td>
<td>47.1 12.6 9.5</td>
<td>2.05 0.24 0.018</td>
<td>0.029 0.08</td>
<td>78</td>
</tr>
<tr>
<td>104-2</td>
<td>1.44 0.38 0.08 0.01 0.36 0.11</td>
<td>air mold</td>
<td>45.2 9.7 21.3</td>
<td>2.53 0.17 0.027</td>
<td>0.033 0.12</td>
<td>94</td>
</tr>
</tbody>
</table>

In the BEP the only cause for lost current efficiency is cathode-to-anode short circuits and current lost to ground. Without shorts, a lead bullion electrorefining cell gives 100% current efficiency [52].

---

1 Thiet [1] found the following mean ionic concentrations within the slimes layer:

- at 200 A/m²: 1.75 M Pb²⁺ and 0.20 M \( \text{H}_2\text{SiF}_6 \)
- at 250 A/m²: 1.85 M Pb²⁺ and 0.12 M \( \text{H}_2\text{SiF}_6 \)
- at 300 A/m²: 2.23 M Pb²⁺ and 0.02 M \( \text{H}_2\text{SiF}_6 \)
As shown in Table 1, the concentration of noble impurities (As, Sb, and Bi) in the entrapped electrolyte is very small. The indicated Bi and As concentrations are of the same order of magnitude as found from in-situ measurements (see Section 4.2.B Chapter 4) while Sb concentrations are larger. Within the slimes layer the concentration of noble impurities is small because the noble phases do not react to a significant extent and cementation reactions maintain their concentration at small levels (see Eq. 1.1). Furthermore, the presence of equilibrium quantities of these impurities in the recirculating electrolyte (see Table 1.1, Electrolyte composition row) indicates that these impurities can be tolerated up to a certain level without serious impairment of the cathode quality. This was also indicated by Thiet [1] and others [6-9], who showed the relationship between the concentration of noble species in the bulk electrolyte and the cathode composition.

The mean Pb\(^{+2}\) concentration across the slimes layer for all the data presented in Table 1 is ~2.15 M while the mean acid concentration is ~0.20 M. Assuming linear concentration gradients across the slimes layer, the maximum amount of Pb\(^{+2}\) at the anode/slimes electrolyte interface can be considered to be close to 4 M while the H\(_2\)SiF\(_6\) concentrations at such an interface can be considered to be smaller than 0.10 M. Even at this large Pb\(^{+2}\) concentration, PbSiF\(_6\).4H\(_2\)O is not expected to crystallize because of the low acid concentrations. Furthermore, the presence of small amounts of acid at such an interface aids in the stabilization of PbSiF\(_6\) by suppressing its hydrolysis.

In an acid depleted environment PbSiF\(_6\) can undergo hydrolysis and decomposition according to the following equations:

\[
PbSiF_6 + 2H_2O \rightleftharpoons PbF_2 + SiO_2 + 4HF \quad ...1
\]
\[
PbSiF_6 \rightleftharpoons PbF_2 + SiF_4 \quad ...2
\]

As indicated by Eq. 1 the hydrolysis of PbSiF\(_6\) will be buffered by the formation of the weakly dissociated HF. On the other hand, as soon as PbF\(_2\) is

---

1 Larger Sb concentrations shown in Table 1 as compared to those shown in section 4.2.B can be attributed to partial re-solution during the filtering process of antimony oxides present in the slimes layer.
2 Because of migrational-diffusional effects, H\(^+\) concentrations are expected to decrease exponentially rather than linearly.
3 The maximum solubility of pure PbSiF\(_6\).4H\(_2\)O at 40 °C is ~5 M (see Appendix 7).
formed, Pb$^{+2}$ local concentrations will decrease to a steady-state value determined by the combination of Pb$^{+2}$ precipitation and its continuous generation at the anode/slimes interface.

In the context of lead refining by the Betts process, hydrolysis of the SiF$_6^{-2}$ ion in moderately strong acid solutions (pH between 1 and 2) can be better described by the following equation $^{1,2}$:

$$3\text{Pb}^{+2} + \text{SiF}_6^{-2} + 3H_2O \rightleftharpoons 3\text{PbF}_2 + \text{H}_2\text{SiO}_3 + 4H^+ \quad \ldots3$$

Both PbF$_2$ and SiO$_2$ have been identified and quantified in the slimes layer (e.g. see Table 1.2) $^3$ $^{[5,11,12]}$. As early as 1908 Betts $^{[11]}$ already indicated the presence of SiO$_2$ in the slimes layer and related it to H$_2$SiF$_6$ decomposition. He found that ~2% of SiO$_2$ in the slimes could correspond to ~1 kg of H$_2$SiF$_6$ loss per ton of lead produced. In 1966 Cominco Ltd. reported SiO$_2$ assays in well washed slimes $^4$ that were of the order of 1.6% $^{[13]}$. Thus, according to Eq. 3 and assuming a production of slimes of ~25 kg per ton of lead, an estimated loss of H$_2$SiF$_6$ of ~0.96 kg/ton of Pb can be obtained. This can account for as much as 50% of the acid losses. Furthermore, PbF$_2$ in the slimes can be as high as 19.6% and can account for most of the lead found in the slimes layer. In Table 1.1 only one refinery (Cerro del Pasco) reports SiO$_2$ assays in the slimes layer. From their reported value (0.4% SiO$_2$) an estimated loss of H$_2$SiF$_6$ of ~0.13 kg/ton of Pb was obtained $^5$.

### III. Eh-pH Diagrams

The Eh-pH diagrams shown in this section were generated using the C.S.I.R.O. THERMODATA $^6$ computer program $^{[14,15]}$. A list of the INPUT (*.inp) files used in the generation of these diagrams is provided in Appendix 11. Also, a list of the

---

1 Hydrolysis of the SiF$_6^{-2}$ ion takes place in 3 steps which involve intermediate splitting of F$^-$ and formation of SiF$_3$[H$_2$O]$^-$ (see section III.a).

2 At 25 °C the maximum solubility of monosilicic acid H$_2$SiO$_3$ is $10^{-3}$ M while the solubility product for PbF$_2$ is $7.8 \times 10^{-8}$ $^{[10]}$.

3 Notice that in Table 1.2 ($\frac{n_F}{F}$)$_{\text{wke}}$ is between 4.1 and 5 while in PbF$_2$ ($\frac{n_F}{F}$)$_{\text{wke}}$ is 5.45. Some fluorine may be present in compounds other than PbF$_2$ but most of it can be accounted as PbF$_2$.

4 As shown in section III.b washing of the slimes can lead to further hydrolysis of the acid and removal or formation of precipitates.

5 This number was obtained assuming that 1.4 kg of slimes are produced per ton of lead.

6 C.S.I.R.O. means Commonwealth Scientific and Industrial Research Organization (Mineral Engineering Division, Port Melbourne, Australia).
species considered and their free energy values is provided.

A. (F⁻)-Si-H₂O system

As can be seen in Fig. 1 the stability region of SiF₆²⁻ extends over a considerable pH range. At pH values larger than 6.75, SiF₆²⁻ hydrolysis takes place according to the following reaction:

\[ SiF_6^{2-} + 3H_2O \rightleftharpoons H_2SiO_3 + 6F^- + 4H^+ \]  

The equilibrium constant of reaction 4 is a function of the ionic strength [19]. Moreover, it has been shown [19] that in the presence of F⁻ ([F⁻] > 6[SiF₆²⁻]) the maximum thermodynamic stability of SiF₆²⁻ occurs at a pH between 2.6 and 2.7.

In dilute solutions, hydrolysis of the hexafluosilicate ion takes place in elementary steps which involve splitting of one F⁻ and formation of SiF₅[H₂O]⁻ (reaction 5). This species losses a F⁻ ion in a second step forming SiF₄ which subsequently undergoes hydrolysis towards H₂SiO₃ (reactions 6 and 7) [18,20-23]:

\[ SiF_6^{2-} + 2H_2O \rightleftharpoons SiF_5[H_2O]^- + F^- \]  
\[ SiF_5[H_2O]^- + H_2O \rightleftharpoons SiF_4 + F^- + 2H_2O \]  
\[ SiF_4 + 3H_2O \rightleftharpoons H_2SiO_3 + 4HF \]

In the acidic range (pH<1) formation of SiF₅[H₂O]⁻ and SiF₄[H₂O]₂ takes place [24]:

\[ SiF_6^{2-} + H_2O + H^+ \rightleftharpoons SiF_5[H_2O]^- + HF \]  
\[ SiF_5[H_2O]^- + H_2O + H^+ \rightleftharpoons SiF_4[H_2O]_2 + HF \]

Conductometric and cryoscopic measurements have shown that the solubility of SiO₂ in H₂SiF₆ is due to the formation of SiF₄[H₂O]₂ [25]. This compound behaves as a strong acid [26]:

---

1 The diagrams were drawn assuming unit activities for all the solid species and T=25 °C.
2 Either H₂SiO₃ or Si(OH)₄ can be formed during the hydrolysis of the acid [16,17]. The polymerization of orthosilicic acid, Si(OH)₄, has been shown to be very slow [18].
3 The dashed vertical lines in Fig. 1 extend the region in which HF, HF₂⁻, and F⁻ may be present.

[195]
Thus, depending on the equilibrium position of reaction 10, F to Si ratios, \( \frac{F}{Si} \), other than 6 can be obtained [25-29].

\[
\frac{F}{Si} = \frac{6 \cdot [H_2SiF_6] + [HF]}{[H_2SiF_6] + [SiO_2]}
\]

**B. (Pb-F)-Si-H_2O system**

The stability region of SiF_6^{2-} decreases significantly in the presence of Pb^{2+} according to Eq. 3 (see Fig. 2):

\[
3Pb^{2+} + SiF_6^{2-} + 3H_2O \leftrightarrow 3PbF_2 + H_2SiO_3 + 4H^+
\]

The minimum pH at which PbF_2 precipitation can take place is a function of the activities of the species indicated in Eq. 3. The thermodynamic equilibrium constant for this reaction can be described as follows:

\[
K_3 = \frac{a_{PbF_2}^3 \cdot a_{H_2SiO_3} \cdot a_{H^+}^4}{a_{H_2O} \cdot a_{SiF_6^{2-}} \cdot a_{Pb^{2+}}^3}
\]
Assuming that $a_{H_2O} = a_{PbF_2} = a_{H_2SiO_3} = 1$, the pH values above which PbF$_2$ precipitation can take place are given by the following equation (see also Fig. 3):

$$pH = 1.78 - 0.25 \log [a_{SiF_6^{2-}} \cdot a_{Pb^{2+}}]$$

...13

Thus, the larger $a_{SiF_6^{2-}}$ and $a_{Pb^{2+}}$ the smaller the pH at which PbF$_2$ precipitation can occur.

Once the activities of the individual species are known, Eq. 13 can be used to obtain an upper limit for the ionic concentrations across the slimes layer to avoid obstruction of the ionic flow due to SiO$_2$ and PbF$_2$ precipitation 1.

1 The extra weight of these precipitates can also lead to falling slimes.
Further analysis of Eq. 3 indicates the difficulties encountered during the washing of the slimes to obtain accurate PbF₂ and SiO₂ assays. Depending on the pH and ionic strength of the washing solution, PbF₂ and SiO₂ may either precipitate and/or re-dissolve indicating erroneous assays. Only by slowly displacing the concentrated electrolyte with solutions of varying PbSiF₆⁻⁻·H₂SiF₆ composition and matching pH but different strength, can the extent to which these secondary reactions take place be diminished. This process involves a trial and error procedure using "slices" of slimes taken at different slimes thickness. In a first try the composition of the slimes electrolyte is measured and solutions with similar pH but diminishing ionic strength are prepared. The slimes are put in contact with these solutions until all the SiF₆⁻² and Pb⁺² are extracted. Once these ions are removed, the slimes can be washed with dilute HNO₃ solutions at the same pH as before.

1 Notice that for the washing process to be successful, activities of Pb⁺², H⁺, and SiF₆⁻² are required to remain in a fixed ratio given by the following equation (see Eq. 12):

$$\frac{a_{SiF_6^{2-}} \cdot a_{Pb}^{3+}}{a_{H^+}^4} = K$$
C. (Sb-F)-Si-H_{2}O, (As-F)-Si-H_{2}O, and (Bi-F)-Si-H_{2}O systems

As shown in Fig. 4, Sb, As, and Bi are noble with respect to lead and their dissolution will not take place unless the potential and/or the pH rises permit the formation of oxides and/or soluble species. Sb is the least noble of these three elements and is expected to react earlier than the others. Upon dissolution, Sb forms soluble oxides some of which have been detected in lead slimes (e.g. see Tables 1.2 and 4.2). Arsenic also forms highly soluble oxides such as the amphoretic arsenious anhydride, As_{4}O_{6}. When As is exposed to moist air it becomes covered with oxidation products. This poses a problem in its identification in the slimes layer. Bi does not form oxides to the same extent as Sb and As, but rather, forms polynuclear complexes such as Bi_{36}(OH)_{12}{^{+6}}. These ions have been found to be the predominant species at pH=1.5 and total Bi concentrations of 0.01 M.

Fig. 4A System (Sb-F)-Si-H_{2}O at 25 °C

Activity of Sb soluble species = 10^{-4}

1 The fat dashed lines in Figs. 4A, 4B, and 4C mark the stability region of Pb^{2+} according to Fig. 2.
2 In the pH range between 0 and 1, Sb in solution is present mainly as SbO^{+} [30].
3 The solubility of As (as As_{4}O_{6}) at 25°C is ~0.17 M [31].
(Sb-F)-Si-H$_2$O, (As-F)-Si-H$_2$O, and (Bi-F)-Si-H$_2$O systems

**Fig. 4B System (Bi-F)-Si-H$_2$O at 25 °C**

A  Bi + SiF$_6^{-2}$
B  Bi + SiF$_6$(H$_2$O)$^+$ + HF
C  Bi$^{3+}$ + SiF$_6$(H$_2$O)$^+$ + HF
D  BiO$^+$ + SiF$_6^{-2}$ + HF
E  BiO$^+$ + SiF$_6$(H$_2$O)$^+$ + HF
F  Bi + HF

Activity of Bi soluble species = 10$^4$

**Fig. 4C System (As-F)-Si-H$_2$O at 25 °C**

A  As + SiF$_6^{-2}$
B  As + SiF$_6$(H$_2$O)$^+$ + HF
C  AsO$_4^{3-}$ + SiF$_6^{-2}$
D  AsO$^+$ + SiF$_6^{-2}$ + HF
E  AsO$^+$ + SiF$_6$(H$_2$O)$^+$ + HF
F  H$_2$AsO$_4^-$ + SiF$_6^{-2}$
G  H$_2$AsO$_4^-$ + SiF$_6$(H$_2$O)$^+$ + HF
H  H$_2$AsO$_3^-$ + SiF$_6^{-2}$
I  AsH$_3$(g) + SiF$_6^{-2}$
J  AsH$_3$(g) + SiF$_6$(H$_2$O)$^+$ + HF
K  AsH$_3$(g) + HF

Activity of As soluble species = 10$^4$
IV. Physico-Chemical Properties of $\text{H}_2\text{SiF}_6$-$\text{PbSiF}_6$ Electrolytes

To model the concentration changes across the slimes layer, data on the physico-chemical properties of $\text{H}_2\text{SiF}_6$-$\text{PbSiF}_6$ electrolytes are required. In the next section, the experimental data generated in this work are analyzed alongside data available in the literature.

A. $\text{pH}$, density, viscosity, and activity of $\text{H}_2\text{SiF}_6$ solutions

The pH of $\text{H}_2\text{SiF}_6$ solutions is shown in Fig. 5. These pH values agree with those reported in the literature [20,32].

$\text{H}_2\text{SiF}_6$ and $\text{H}_2\text{SO}_4$ are very similar in their electrolytic properties [20,33]. $\text{H}_2\text{SiF}_6$ is an acid of moderate strength similar to that displayed by $\text{H}_2\text{SO}_4$ solutions. The first and second dissociation constants of $\text{H}_2\text{SiF}_6$ at 25 °C are as follows [34]:

\[
\begin{align*}
\text{H}_2\text{SiF}_6 & \Leftrightarrow \text{HSiF}^- + \text{H}^+ & pK_1 &= -0.13 & \ldots 14 \\
\text{HSiF}^- & \Leftrightarrow \text{SiF}_6^{2-} + \text{H}^+ & pK_2 &= 1.79 & \ldots 15 
\end{align*}
\]
Arkhipova et al. [27,28] have indicated that the pH of H$_2$SiF$_6$ solutions (among other properties) is a function of $\frac{F}{Si}$ and varies according to the way the acid was produced.

Leonte et al. [35] measured the density, viscosity, specific heat, and electrical conductivity of solutions containing between 0.3 and 2 M H$_2$SiF$_6$. They showed that due to the technique under which their acid was produced, minor impurities such as P$_2$O$_5$ and SO$_4$$^{2-}$ were present in concentrations that increased with the acid composition. On the other hand, no $\frac{F}{Si}$ values were reported in their samples. Leonte et al. derived empirical equations for the density and viscosity changes as a function of the acid composition $^1$:

$$\rho = 0.9982 + (8.53 \cdot 10^{-3} - 1.96 \cdot 10^{-5} t)w - (2.99 \cdot 10^{-4} + 8.06 \cdot 10^{-6} w)(t - 20)$$

$$\eta = A \cdot e^{\frac{Q}{T}}$$

$\rho$ and $\eta$ = empirical coefficients which depend on the solution composition (see Table 2).
$T$ = temperature K
$t$ = temperature °C

<table>
<thead>
<tr>
<th>[H$_2$SiF$_6$], M</th>
<th>A</th>
<th>Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.219x10$^{-4}$</td>
<td>1965.93</td>
</tr>
<tr>
<td>0.334</td>
<td>1.908x10$^{-3}$</td>
<td>1857.05</td>
</tr>
<tr>
<td>0.663</td>
<td>2.027x10$^{-3}$</td>
<td>1860.40</td>
</tr>
<tr>
<td>0.972</td>
<td>2.434x10$^{-4}$</td>
<td>1834.36</td>
</tr>
<tr>
<td>1.298</td>
<td>2.937x10$^{-3}$</td>
<td>1803.40</td>
</tr>
<tr>
<td>1.708</td>
<td>2.485x10$^{-3}$</td>
<td>1884.70</td>
</tr>
</tbody>
</table>

Folov et al. [36] measured the osmotic and activity coefficients of H$_2$SiF$_6$ solutions at 25°C using isopiestic measurements and H$_2$SO$_4$ as standard. As can be seen in Table 3, $\gamma_2$ do not change significantly with ionic strength.

$^1$ Söhnel et al. [37] also present a $\rho$-[H$_2$SiF$_6$] correlation from which the apparent partial molar volume of H$_2$SiF$_6$ at infinite dilution, $\phi_v$, was obtained: $\phi_v = 23.5$ cm$^3$ mol$^{-1}$ at 17.5°C.
Table 3 Changes in the osmotic and activity coefficients as a function of the molal ionic strength, [34]

<table>
<thead>
<tr>
<th>molality, m</th>
<th>molal ionic strength</th>
<th>Osmotic Coefficient, ( \varphi )</th>
<th>Mean Activity Coefficient, ( \gamma_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.30</td>
<td>0.931</td>
<td>0.611</td>
</tr>
<tr>
<td>0.20</td>
<td>0.60</td>
<td>0.925</td>
<td>0.577</td>
</tr>
<tr>
<td>0.30</td>
<td>0.90</td>
<td>0.927</td>
<td>0.562</td>
</tr>
<tr>
<td>0.40</td>
<td>1.20</td>
<td>0.934</td>
<td>0.555</td>
</tr>
<tr>
<td>0.50</td>
<td>1.50</td>
<td>0.944</td>
<td>0.553</td>
</tr>
<tr>
<td>0.60</td>
<td>1.80</td>
<td>0.954</td>
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<tr>
<td>0.70</td>
<td>2.10</td>
<td>0.964</td>
<td>0.559</td>
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<tr>
<td>0.80</td>
<td>2.40</td>
<td>0.975</td>
<td>0.559</td>
</tr>
<tr>
<td>0.90</td>
<td>2.70</td>
<td>0.987</td>
<td>0.564</td>
</tr>
<tr>
<td>1.00</td>
<td>3.00</td>
<td>0.999</td>
<td>0.571</td>
</tr>
<tr>
<td>1.20</td>
<td>3.60</td>
<td>1.026</td>
<td>0.588</td>
</tr>
<tr>
<td>1.40</td>
<td>4.20</td>
<td>1.060</td>
<td>0.612</td>
</tr>
</tbody>
</table>

**B. Density, viscosity, and electrical conductivity of \( \text{H}_2\text{SiF}_6\text{-PbSiF}_6 \)**

Some of the experimental data obtained from measurements of the physico-chemical properties of \( \text{H}_2\text{SiF}_6\text{-PbSiF}_6 \) electrolytes are shown in Table 4. Each sample was analyzed for \( \text{H}_2\text{SiF}_6 \), \( \text{PbSiF}_6 \), \( \text{SiO}_2 \), and \( \text{HF} \) \(^{2,3,4}\).

Two different values of \( \frac{F}{S_i} \) are indicated in Table 4, and each one of them can be related to the presence or absence of \( \text{SiO}_2 \) or \( \text{HF} \) in \( \text{H}_2\text{SiF}_6\text{-PbSiF}_6 \) electrolytes:

---

1 \( \text{H}_2\text{SiF}_6\text{-PbSiF}_6 \) electrolytes were prepared by neutralizing \( \text{H}_2\text{SiF}_6 \) solutions with \( \text{PbO} \).

2 The dynamic viscosity, \( \eta \), is the ratio between the applied shear stress and rate of shear. The cgs unit of dynamic viscosity is one gram per centimeter per second and its called one poise (symbol P). One centipoise, \( 1 \text{ cP} = 10^{-2} \text{ P} \).

3 The kinematic viscosity, \( \nu \), is a measure of the resistive flow of a fluid under gravity, the pressure head being proportional to the density of the fluid \(^{[44]}\). The cgs unit of kinematic viscosity is one centimeter squared per second and it is called one Stoke (symbol St). \( 1 \text{ centistoke, cSt} = 10^{-2} \text{ St} \).
Table 4 Physico-chemical properties of H$_2$SiF$_6$-PbSiF$_6$ electrolytes

<table>
<thead>
<tr>
<th>Solution [PbSiF$_6$]</th>
<th>[H$_2$SiF$_6$]</th>
<th>[SiO$_2$]</th>
<th>[HF]</th>
<th>$\left(\frac{F}{Si}\right)_a$</th>
<th>$\left(\frac{F}{Si}\right)_b$</th>
<th>$\kappa_{max}$ (mmhos cm$^{-1}$)</th>
<th>$\eta_1$ (cP)</th>
<th>$\nu_1$ (cSt)</th>
<th>$\rho$ (g cm$^{-3}$)</th>
<th>Density, $\rho$, g cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>s1</td>
<td>0</td>
<td>2.040</td>
<td>0.4</td>
<td>0</td>
<td>5.0</td>
<td>5.0</td>
<td>525.1</td>
<td>443.7</td>
<td>1.229</td>
<td></td>
</tr>
</tbody>
</table>

From mother solutions prepared using acid sample S1 (Technical H$_2$SiF$_6$ supplied by Cominco Ltd.):

- v17: 0.215, 0.04
- v18: 0.332, 0.05
- v19: 0.400, 0.06
- v20: 0.847, 0.13
- v21: 1.017, 0.20
- k6: 0.27, 0.09
- v13: 0.32, 0.09
- v11: 0.32, 0.13
- v12: 0.34, 0.11
- v14: 0.36, 0.04
- K2: 0.35, 0.09
- k1: 0.37, 0.06
- v4: 0.50, 0.15
- v9: 0.64, 0.14
- v16: 0.8, 0.06
- v15: 0.96, 0.12
- v8: 0.96, 0.12
- v7: 1.19, 0.06
- v2: 1.21, 0.07
- v6: 1.21, 0.00
- AL10: 1.45, 0.09
- AL1: 1.46, 0.10
- k4: 1.53, 0.31
- v5: 1.58, 0.30
- v1: 1.61, 0.02
- sol 42: 1.62, 0.06
- pba01: 1.75, 0.11
- v0: 1.75, 0.12
- sol 6: 1.8, 0.15

From mother solutions prepared using acid sample VV71 (Technical Reactive BDH Chemicals):

- v65: 0.97, 0.00
- v62: 1.46, 0.07
- v61: 2.02, 0.09
- v60: 2.58, 0.12
- v64: 2.74, 0.06
- v50: 2.86, 0.86
- v63: 2.98, 0.66
- v61: 3.25, 0.15

Dynamic viscosity values were obtained by assuming that $\rho_{23^\circ C} \equiv \rho_{40^\circ C}$, $\eta = \nu \cdot \rho$
Density, viscosity, and electrical conductivity of $H_2SiF_6-PbSiF_6$ electrolytes

$$\left( \frac{F}{Si} \right)_a = \frac{6 \cdot ([H_2SiF_6] + [PbSiF_6]) + [HF]}{[H_2SiF_6] + [PbSiF_6] + [SiO_2]}$$

... 18

$$\left( \frac{F}{Si} \right)_b = \frac{6 \cdot [H_2SiF_6] + [HF]}{[H_2SiF_6] + [SiO_2]}$$

As can be seen in Table 4, for pure $H_2SiF_6$ solutions, the amount of dissolved SiO$_2$ increases with acid strength without significant changes in $\left( \frac{F}{Si} \right)_b$ (samples V17 to V21). This relationship holds even in the presence of PbSiF$_6$. The amount of dissolved SiO$_2$ appears to decrease with the PbSiF$_6$ concentration but by comparing the $\frac{F}{Si}$ values it can be seen that $\left( \frac{F}{Si} \right)_b$ remains close to 5 even in the presence of large amounts of PbSiF$_6$ (e.g. compare $\left( \frac{F}{Si} \right)_a$ and $\left( \frac{F}{Si} \right)_b$ in samples V13, V7, and AL1). This indicates that soluble silica is present as $H_2SiF_6$ reaction products such as those shown in Eq. 10. Similar SiO$_2$ solubilities for $H_2SiF_6-PbSiF_6$ electrolytes are reported in the literature [10]. In the absence of $H_2SiF_6$, minor amounts of HF are required to avoid PbSiF$_6$ hydrolysis (Samples WW50 to WW65). As seen in Table 4 only when HF is present can $\frac{F}{Si}$ reach values larger than 6.

By neglecting the presence of SiO$_2$ and HF $^1$, empirical equations were used to correlate $\kappa$, $\rho$, and $\nu$, as a function of the $H_2SiF_6$ and PbSiF$_6$ concentrations. These correlations are as follows $^2, 3$:

---

1 The presence of SiO$_2$ appears to increase $\rho$ and $\nu$. On the other hand, HF appears to have a larger effect on $\kappa$ than on $\rho$ or $\nu$.

2 From these correlations $\kappa$, $\rho$, and $\nu$, values that are within 6% of the experimental measurements can be obtained.

3 A simple relationship between $\kappa$, $[PbSiF_6]$ and $[H_2SiF_6]$, for the range of compositions shown in Fig. 6A could not be found because of the changes in $\kappa$ at $[H_2SiF_6]>0.4$ M. Eq. 19 although cumbersome describes accurately the electrical conductivity changes as a function of $[PbSiF_6]$ and $[H_2SiF_6]$. 

[205]
Density, viscosity, and electrical conductivity of H$_2$SiF$_6$-PbSiF$_6$ electrolytes

$k_s = A_1 x_1 + A_2 x_1^{1.5} + A_3 x_1^2 + A_4 x_1 x_2 + A_5 x_1 x_3 + A_6 x_2 + A_7 x_2^{1.5} + A_8 x_2^2 + A_9 x_3 x_2 + A_{10} x_2 x_3 + A_{11} x_3 + A_{12} x_3^{1.5} + A_{13} x_3^2 + A_{14} x_1 x_3 + A_{15} x_2 x_3 \quad \ldots 19$

$\rho_s = A_1 + A_2 y_1 + A_3 y_2 \quad \ldots 20$

$v_s = A_1 + A_2 y_1 + A_3 y_1^2 + A_4 y_2 \quad \ldots 21$

Where:

$k_s$ = electrical conductivity at 40 °C, [mmhos cm$^{-1}$]

$v_s$ = Kinematic viscosity [coefficient of] at 40 °C, [cSt]

$\rho_s$ = density at 23 °C, [g cm$^{-3}$]

$x_1, x_2, x_3, y_1, y_2, y_3$ : variables related to the H$_2$SiF$_6$ and PbSiF$_6$ concentrations as follows:

$x_1 = [\text{PbSiF}_6]$  $x_2 = [\text{PbSiF}_6] + [\text{H}_2\text{SiF}_6]$  $x_3 = 2 \times [\text{H}_2\text{SiF}_6]$

$y_1 = [\text{PbSiF}_6]$  $y_2 = [\text{H}_2\text{SiF}_6]$  $y_3 = [\text{PbSiF}_6] \times [\text{H}_2\text{SiF}_6]$

$A_1$ to $A_{15}$ are constants whose value is given in Table 5.

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Electrical conductivity, $k_s$ (Eq. 19)</th>
<th>Density, $\rho_s$ (Eq. 20)</th>
<th>Kinematic Viscosity, $v_s$, (Eq. 21)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>-1.212E+08</td>
<td>9.951E-01</td>
<td>6.423E-01</td>
</tr>
<tr>
<td>$A_2$</td>
<td>5.666E+01</td>
<td>3.223E-01</td>
<td>4.340E-02</td>
</tr>
<tr>
<td>$A_3$</td>
<td>2.244E+07</td>
<td>1.668E-01</td>
<td>4.320E-02</td>
</tr>
<tr>
<td>$A_4$</td>
<td>1.473E+07</td>
<td></td>
<td>1.606E-01</td>
</tr>
<tr>
<td>$A_5$</td>
<td>2.981E+07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_6$</td>
<td>1.212E+08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_7$</td>
<td>3.090E+02</td>
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<td>$A_8$</td>
<td>-3.717E+07</td>
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<td>$A_9$</td>
<td>-2.713E+01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{10}$</td>
<td>1.273E+01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{11}$</td>
<td>-6.062E+07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{12}$</td>
<td>1.677E+02</td>
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<td></td>
</tr>
<tr>
<td>$A_{13}$</td>
<td>9.293E+06</td>
<td></td>
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</tr>
<tr>
<td>$A_{14}$</td>
<td>3.563E+00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_{15}$</td>
<td>1.129E+01</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Eqs. 19 to 21 can be used to compute $k$, $\rho$, and $v$ of solutions whose composition range within $0<[\text{PbSiF}_6]<2$ M and $0<[\text{H}_2\text{SiF}_6]<1$ M.

Fig. 6 shows changes in $k$, $\rho$, and $v$ as a function of the electrolyte composition. Both $\rho$ and $v$ increase uniformly with $[\text{PbSiF}_6]$ and $[\text{H}_2\text{SiF}_6]$ while $k$ shows a decrease in value with PbSiF$_6$ additions at $[\text{H}_2\text{SiF}_6]$ larger than 0.4 M.
Density, viscosity, and electrical conductivity of $\text{H}_2\text{SiF}_6$-$\text{PbSiF}_6$ electrolytes

T = 40°C

Data points were obtained from the empirical correlations shown in Eqs. 19, 20, and 21.

Fig. 6 Electrical conductivity, density, and viscosity of $\text{H}_2\text{SiF}_6$-$\text{PbSiF}_6$ electrolytes
Further analysis of the conductivity changes as a function of the composition of the individual salts, indicated that the equivalent conductivity of H$_2$SiF$_6$-PbSiF$_6$ mixtures can be represented by the following relationship:

$$\Lambda_{\text{mix}} = x \Lambda_{\text{PbSiF}_6} + (1 - x) \Lambda_{\text{H}_2\text{SiF}_6}$$  \[22\]

where:

$$\Lambda_{\text{mix}} = \frac{\kappa_{\text{mix}}}{2 \cdot ([\text{PbSiF}_6] + [\text{H}_2\text{SiF}_6])}$$

$$\Lambda_{\text{PbSiF}_6} = \frac{\kappa_{[\text{PbSiF}_6]_l}}{2 \cdot [\text{PbSiF}_6]_l}$$

$$\Lambda_{\text{H}_2\text{SiF}_6} = \frac{\kappa_{[\text{H}_2\text{SiF}_6]_l}}{2 \cdot [\text{H}_2\text{SiF}_6]_l}$$

Thus, for example, for an electrolyte mixture containing 0.36 M PbSiF$_6$ and 0.252 M H$_2$SiF$_6$ at 40 °C:

- $I_t = 2.196$
- $I_{(\text{PbSiF}_6)} = 1.44$
- $x = 0.66$
- $[\text{PbSiF}_6]_l = 0.549$
- $\kappa_{[\text{PbSiF}_6]_l} = 87.8$
- $\Lambda_{\text{PbSiF}_6} = 80.0$
- $[\text{H}_2\text{SiF}_6]_l = 0.732$
- $\kappa_{[\text{H}_2\text{SiF}_6]_l} = 334.9$
- $\Lambda_{\text{H}_2\text{SiF}_6} = 228.8$

$$\Lambda_{\text{mix}} = 0.66 \times 80 + (1 - 0.66) \times 228.8 = 131.2$$

$$\kappa_{\text{mix}} = 2 \times 0.612 \times 131.2 = 160.6$$

$\kappa_{\text{mix}}$ obtained from Eq. 22 is within ~4% of the experimentally measured value$^1$. In general, Eq. 22 could be used to obtain $\Lambda_{\text{mix}}$ values that are within 6% of those experimentally measured. This indicates that both PbSiF$_6$ and H$_2$SiF$_6$ are highly dissociated.

The validity of Eq. 22 to describe $\Lambda_{\text{mix}}$ changes in strong electrolytes has been related to a lack of simple dependence of the ionic mobilities on electrolyte concentration$^{[45]}$ and is a reflection of Walden's rule$^{[2]}$:

$$\eta \lambda_i = \text{constant}$$  \[23\]

$\lambda_i$ and $\mu_i$ are related through the following relationship:

---

$^1$ This $\kappa_{\text{mix}}$ value compares well with the experimental $\kappa$ value shown in Table 4 ($\kappa_{\text{mix}} = 160.6$ vs $\kappa = 167.1$ mmho cm$^{-1}$ for solution V14).

$^2$ Walden's rule is based on a model for ionic mobility that obeys Stokes law in the laminar flow region$^{[51]}$. 

[208]
The validity of Walden's rule has been confirmed in a variety of systems [46]. Recently, Peters et al. [47] have shown that in strong chloride mixtures, Walden's rule is not followed by H⁺ because its movement in electrolytic solutions is not a function of the viscosity of the medium but of the activity of water. Similarly, in H₂SiF₆-PbSiF₆ electrolytes Walden's rule is expected to be followed by Pb⁺² and SiF₆⁻² while ηλₜ values should decrease with increasing ionic strength as the water activity decreases.

To obtain λᵢ values from electrical conductivity measurements in H₂SiF₆-PbSiF₆ electrolytes the following assumptions were made:

1) H₂SiF₆ and PbSiF₆ are completely dissociated and the formation of ion-pairs can be neglected.

2) Only three ions contribute to the total electrical conductivity: Pb⁺², SiF₆⁻², and H⁺.

3) The electrical conductivity in concentrated H₂SiF₆-PbSiF₆ electrolytes can be represented by the following relationship:

$$\kappa = \sum |C_i Z_i \lambda_i |$$  \[25\]

4) The individual equivalent conductivity of SiF₆⁻² is equal to the individual equivalent conductivity of Pb⁺² (i.e. $\lambda_{SiF_6} = \lambda_{Pb}^+ )^1$.

5) λᵢ values in pure H₂SiF₆ and PbSiF₆ solutions are the same as those of H₂SiF₆-PbSiF₆ mixtures of equivalent ionic strength:

$$\kappa_{[PbSiF_6]_{lt}} = 2 \cdot C_{Pb}^+ \cdot \lambda_{Pb}^+ + 2 \cdot C_{SiF_6}^- \cdot \lambda_{SiF_6}^- = 4 \cdot [PbSiF_6]_{lt} \cdot \lambda_{Pb}^+$$ \[26\]

$$\kappa_{[H_2SiF_6]_{lt}} = C_{H^+} \cdot \lambda_{H^+} + 2 \cdot C_{SiF_6}^- \cdot \lambda_{SiF_6}^- = 2 \cdot [H_2SiF_6]_{lt} \cdot \lambda_{H^+} + 2 \cdot [H_2SiF_6]_{lt} \cdot \lambda_{Pb}^+$$ \[27\]

thus, $\kappa_{mix}$ should be equal to:

---

1 Individual equivalent conductivities at infinite dilution and at 25 °C reported in the literature are: $\lambda_{SiF_6} = 59$ [53] and $\lambda_{Pb}^+ = 65$ [46]
Density, viscosity, and electrical conductivity of H$_2$SiF$_6$-PbSiF$_6$ electrolytes

\[ \kappa_{\text{mixt}} = 2 \cdot C_{\text{Pb}^{2+}} \cdot \lambda_{\text{Pb}^{2+}} + 2 \cdot C_{\text{Si}^{2+}} \cdot \lambda_{\text{Si}^{2+}} + C_{\text{H}^+} \cdot \lambda_{\text{H}^+} \]  

\[ = 2 \cdot [\text{PbSiF}_6] \cdot \lambda_{\text{Pb}^{2+}} + 2 \cdot [\text{H}_2\text{SiF}_6] \cdot \lambda_{\text{H}^+} + 2 \cdot ([\text{H}_2\text{SiF}_6] + [\text{PbSiF}_6]) \cdot \lambda_{\text{Si}^{2+}} \]  

\[ = 2 \cdot [\text{H}_2\text{SiF}_6] \cdot \lambda_{\text{H}^+} + 2 \cdot [\text{H}_2\text{SiF}_6] + 4 \cdot [\text{PbSiF}_6] \cdot \lambda_{\text{Pb}^{2+}} \]

...28.a

...28.b

...28.c

Assumptions 1 and 2 can be considered to be fair approximations of the real behavior of H$_2$SiF$_6$-PbSiF$_6$ electrolytes as indicated by the validity of Eq. 22. Assumptions 3, 4, and 5 are linked through Eqs. 26 to 28. They are valid only to the extent to which \( \lambda_i \) values from binary solutions (i.e. from Eqs. 26 and 27) can be used to obtain the conductivity of ternary mixtures (i.e. from Eq. 28). Such correspondence has been found to occur in chloride electrolytes [48] for which \( \lambda_{K^+} = \lambda_{CI^-} \).

Thus, to obtain \( \lambda_i \) values and their dependance with concentration, the following steps have to be followed:

1) Given [PbSiF$_6$] and [H$_2$SiF$_6$] in the mixture obtain the total ionic strength, 
\[ I_t = 4 \cdot [\text{PbSiF}_6] + 3 \cdot [\text{H}_2\text{SiF}_6] \]

2) Obtain the composition of pure H$_2$SiF$_6$ and PbSiF$_6$ solutions at the total ionic strength and the specific conductivities of these solutions (From Eq. 19):

\[ [\text{PbSiF}_6]_{lt} = \frac{l}{4} \quad \text{with} \quad \kappa = \kappa_{[\text{PbSiF}_6]_{lt}} \]

\[ [\text{H}_2\text{SiF}_6]_{lt} = \frac{l}{3} \quad \text{with} \quad \kappa = \kappa_{[\text{H}_2\text{SiF}_6]_{lt}} \]

3) Obtain \( \lambda_{\text{Pb}^{2+}} \) and \( \lambda_{\text{H}^+} \) from Eqs. 26 and 27 respectively:

\[ \lambda_{\text{Pb}^{2+}} = \frac{\kappa_{[\text{PbSiF}_6]_{lt}}}{4 \cdot [\text{PbSiF}_6]_{lt}} \]

\[ \lambda_{\text{H}^+} = \frac{\kappa_{[\text{H}_2\text{SiF}_6]_{lt}} - 2 \cdot [\text{H}_2\text{SiF}_6]_{lt} \cdot \lambda_{\text{Pb}^{2+}}}{2 \cdot [\text{H}_2\text{SiF}_6]_{lt}} \]

4) Introduce \( \lambda_{\text{Pb}^{2+}} \) and \( \lambda_{\text{H}^+} \) in Eq. 28.c and compare the \( \kappa_{\text{mixt}} \) with the obtained from Eq. 19.

For example, for an electrolyte mixture containing 0.36 M PbSiF$_6$ and 0.252 M H$_2$SiF$_6$ at 40 °C (\( \eta_{\text{mixt}} = 0.769 \)):
Density, viscosity, and electrical conductivity of \( \text{H}_2\text{SiF}_6 \)-\( \text{PbSiF}_6 \) electrolytes

\[
I_t = 2.196 \quad I_{(\text{PbSiF})} = 1.44
\]

\[ [\text{PbSiF}_6]_{\text{H}+} = 0.549 \quad k_{(\text{PbSiF})\text{H}+} = 87.8 \quad \lambda_{\text{Pb}}^n = \frac{87.8}{4 \times 0.549} = 40.0 \]

\[ [\text{H}_2\text{SiF}_6]_{\text{H}+} = 0.732 \quad k_{(\text{H}_2\text{SiF})\text{H}+} = 334.9 \quad \lambda_{\text{H}}^n = \frac{334.9 - 2 \times 0.732 \times 40}{2 \times 0.732} = 188.8 \]

\[
\eta_{\text{mix}} \lambda_{\text{H}+} = 0.769 \times 188.8 = 145.2 \quad \eta_{\text{mix}} \lambda_{\text{Pb}}^n = 0.769 \times 40.0 = 30.8
\]

Thus, it can be seen that \( \kappa_{\text{mix}} \) obtained from Eqs. 26 to 28 is only \( \sim 4\% \) different from the experimentally measured value \(^1\). For other electrolyte compositions, the maximum deviation between the experimental and predicted values is \( \sim 8\% \) (see Table 6). Finally, transference numbers, \( t_i \), were also obtained as follows:

\[
t_i = \frac{|Z_i \cdot C_i \cdot \lambda_i|}{\sum_i |Z_i \cdot C_i \cdot \lambda_i|} \quad \ldots 29
\]

Changes in Walden's product as a function of \( I_t \)\(^2\) are shown in Fig. 7. Large decreases in \( \lambda_{\text{H}+} \) as the ionic strength increases are due to decreases in water activity. At high \( I_t \) less water is available for \( \text{H}^+ \) to move via a proton jump mechanism and this reflects in lower \( \lambda_{\text{H}+} \). On the other hand, \( \text{Pb}^{2+} \) transport depends mostly on the viscosity of the medium rather than on the water activity \(^2\). Furthermore, by comparing Figs. 7A and 7B it can also be seen that in binary solutions \( \eta \lambda_i \) values are nearly equal to those obtained in ternary solutions of equivalent ionic strength (see also Table 6).

---

\(^1\) This \( \kappa_{\text{mix}} \) value compares well with the experimental \( \kappa \) value shown in Table 4 (\( \kappa_{\text{mix}} = 172.9 \) vs \( \kappa = 167.1 \) mmho cm\(^{-1}\) for solution V14). The difference between these values is partially due to inaccuracies in the computation of \( \kappa \) values using Eq. 19.

\(^2\) Water activities for this system are not available. Yet, by analysis of similar phenomena taking place in other systems \(^{47}\) this analogy can be drawn.
Table 6 Changes in the individual ionic mobilities as a function of the electrolyte composition

<table>
<thead>
<tr>
<th>Solution</th>
<th>Solution Properties</th>
<th>Total Ionic Strength</th>
<th>Binary Properties</th>
<th>Binary Properties</th>
<th>Individual Equivalent Conductivities</th>
<th>( \gamma_{m,2} )</th>
<th>( \gamma_{m,1} )</th>
<th>( \lambda_{m,2} )</th>
<th>( \lambda_{m,1} )</th>
<th>( \eta_{\text{mix}} )</th>
<th>( \eta_{\text{H}+} )</th>
<th>( t_{\text{mix}} )</th>
<th>( t_{\text{H}+} )</th>
<th>Transport numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{PbSiF}_6])</td>
<td>([\text{H}_2\text{SiF}_6])</td>
<td>( \gamma_{\text{mix}} )</td>
<td>( \gamma_{\text{mix}} )</td>
<td>( \rho_{\text{mix}} )</td>
<td>( I_t )</td>
<td>( [\text{PbSiF}_6] )</td>
<td>( \gamma )</td>
<td>( [\text{H}_2\text{SiF}_6] )</td>
<td>( \kappa )</td>
<td>( \lambda_{\text{surf}} )</td>
<td>( \lambda_{\text{H}+} )</td>
<td>( t_{\text{surf}} )</td>
<td>( t_{\text{H}+} )</td>
<td></td>
</tr>
<tr>
<td>2.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
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In Table 6 it can be observed that as the electrolyte gets concentrated in PbSiF₆ and depleted in H₂SiF₆, \( t_{\text{H}+} \to 0 \) while \( t_{\text{surf}} \to 0.5 \). Thus, at the anode/silms interface most of the current should be carried by Pb⁺² and SiF₆⁻² while at the silms/bulk electrolyte interface most of the current should be carried by H⁺. This should create significant concentration gradients as Pb⁺² and SiF₆⁻² are ~5 times less mobile than H⁺.
The Nernst-Einstein relationship \[49\] can be used to obtain diffusion coefficients from ionic mobilities \(^1\):

\[
D_i = \frac{\mu_i RT}{Z_i F^2} = \frac{\lambda_i RT}{Z_i F^2} \quad \ldots 30
\]

Thus, for a solution containing 0.35 M PbSiF\(_6\) and 0.84 M H\(_2\)SiF\(_6\), at 40 \(^\circ\)C, \(\lambda_{\text{Pb}^{2+}} = 35.8\) and \(\lambda_{\text{H}^+} = 137.1\), from which: \(D_{\text{H}^+} = 3.8 \times 10^{-5}\) and \(D_{\text{Pb}^{2+}} = 5.0 \times 10^{-6}\). This diffusion coefficient for Pb\(^{2+}\) is nearly equal to that obtained from chronopotentiometric measurements (see Table 1 Chapter 5). The correspondence between these values and the validity of Walden's rule for species other than H\(^+\) support the assumptions and the model used to derive individual equivalent conductivities from electrical conductivity measurements.

\(^1\) As shown in Appendices 1 and 2 this equation can be modified to include the effects of the effective charge of species \(i\) exposed to the electric field, \(Z_i^*\). When such modification is included: \(D_i = D_i^*\).
V. Mathematical Model: Numerical Solution of the Nernst-Planck Flux Equations.

To obtain local ionic concentrations and potential gradients across the slimes layer as a function of the electrolysis conditions the Nernst-Planck flux equations were solved using a finite interval numerical technique (see Appendix 1). The differential equations that were solved simultaneously are as follows [50]:

\[
\begin{align*}
\frac{1}{N_a} \frac{d}{dx} \left( D_a \frac{d \ln a_a}{dx} + \mu_a C_a \frac{d \Phi}{dx} \right) &= \frac{I(t)}{Z_a F} \quad \ldots[i] \\
\frac{1}{N_b} \frac{d}{dx} \left( D_b \frac{d \ln a_b}{dx} + \mu_b C_b \frac{d \Phi}{dx} \right) &= 0 \quad \ldots[ii] \\
\frac{1}{N_c} \frac{d}{dx} \left( D_c \frac{d \ln a_c}{dx} + \mu_c C_c \frac{d \Phi}{dx} \right) &= 0 \quad \ldots[iii] \\
Z_a C_a + Z_b C_b + Z_c C_c &= 0 \quad \ldots[iv]
\end{align*}
\]

Eq. i states that the only species being generated at the anode is Pb\(^{+2}\) whereas Eqs. ii and iii indicate that H\(^+\) and SiF\(_6\)\(^{2-}\) do not react and their equilibrium concentrations are only a function of the migration and diffusion gradients \(^{1,2,3}\). Eq. iv is the electroneutrality condition.

As presented in Appendix 1, to solve Eqs. [i] to [iv], relationships between the involved variables (\(y_i, D_i, \mu_i\)) and the electrolyte composition (\(C_a, C_b,\) and \(C_c\)) have to be known in advance. Thus, subroutines to compute the values of those variables as a function of the electrolyte composition were incorporated in the computer program. In these subroutines, individual ionic mobilities, \(\mu_i\), were

---

1 \(D_i = D_i^m + D_i^E\): \(D_i^E\) is the eddy diffusion constant which can be considered to be equal for all the ions. Furthermore, it can be modified so as to incorporate changes in porosity and tortuosity of the ionic flow across the slimes layer for different anode compositions and/or electrolysis conditions.

2 Notice that when the molecular diffusion coefficient is smaller than the eddy diffusion constant, the overall diffusion coefficient is nearly the same for all the components. In this case, eddy diffusion practically equalizes the effective diffusivities for all the components [50, p. 238]

3 \(D_i^m\) and \(\mu_i\) can be linked using the Nernst-Einstein relation:

\[
D_i^m = \frac{\mu_i RT}{Z_i^* F}
\]

where \(Z_i^*\) is the effective charge of species i exposed to the electric field, \(Z_i^* \leq Z_i\).
obtained from $\lambda_i$ values (see Eqs. 25 to 27) \( ^1 \). From the computed $\mu_i$ values $D_i^m$ values were obtained using the Nernst-Einstein relationship (Eq. 30). To these values, $D^E$ were added to obtain corresponding $D_i$ values \( ^2 \). Individual ionic coefficients were assumed to remain constant \( ^3 \) in the whole range of concentrations. Changes in $\gamma_i$ as a function of the ionic strength require knowledge of activity changes (and water activities) in $\text{H}_2\text{SiF}_6-\text{PbSiF}_6$ mixtures unavailable in the literature.

The solution of the Nernst-Planck flux equations was obtained by increasing the number of variables analyzed. This was done by first neglecting eddy diffusion, then incorporating it in a re-run. Potential and ionic concentration terms are represented by the following symbols:

$\text{[M}^+\text{n}] = \text{Ionic concentration of ions M, \text{[M]}.}$

$\text{[M}^+\text{n}]_b = \text{Ionic concentration of ions M, at the slimes/bulk electrolyte interface, \text{[M]}.}$

$\text{[M}^+\text{n}]_a = \text{Ionic concentration of ions M, at the anode/slimes electrolyte interface, \text{[M]}.}$

$\{M^*\}_r = \text{Concentration of ions M at the anode/slimes interface with respect to their concentration at the slimes/bulk electrolyte interface.}$

$\Phi_e = \text{Maximum value of the migration potential, mV}$

**A. Case A: constant $\gamma_i$ values**

If activity coefficients are assumed to remain constant \( ^4 \), the Nernst-Planck flux equations can easily be solved numerically or analytically. This also allows the numerical procedure to be compared with the analytical solution \( ^5 \). This comparison indicated that the numerical method provides the same concentration and potential profiles if the step size is chosen to be between 25 and 100 $\mu$m. Therefore, step sizes of this order of magnitude were used in the numerical solution.

---

1 By using the $\lambda_i$ values obtained at 40 °C, concentration and potential profiles are also obtained at that temperature.

2 $D^E$ changes also must be known in advance. $D^E$ is not only a function of the electrolyte composition but of the slimes thickness as well. In the initial computation of the concentration profiles this number can be assumed to be zero. This value can be changed once local concentrations are known (i.e. as a result of changes in $\gamma$ and $\rho$ as a function of the slimes thickness).

3 As shown in Table 3 $\gamma_i$ does not change significantly with ionic strength and therefore this assumption is not unreasonable.

4 This is equivalent to assuming that $\bar{\gamma}_a = \bar{\gamma}_b = \bar{\gamma}_c = 0$ in Eqs. A1.1 to A1.8 (Appendix 1).

5 The analytical solution for the case when activity coefficients are constant, and mobilities and diffusion coefficients are independent of concentration is presented in Appendix 2.
Case A: constant values

**Fig. 8** Variation in the slimes electrolyte composition as a function of the distance from the slimes/bulk electrolyte interface, assuming no changes in activity coefficients (Case A).

\[ [\text{PbSiF}_6^{2-}] = 0.2 \, \text{M} \quad [\text{H}_2\text{SiF}_6] = 0.8 \, \text{M} \]

*Right scale:* Changes in $\Phi$  
*Left scale:* Changes in $[\text{Pb}^{2+}]$, $[\text{SiF}_6^{2-}]$, and $[\text{H}^+]$

(A) $cd = 50 \, \text{A m}^{-2}$. Derived ratios: $\Phi = 22.0 \, \text{mV}$, $[\text{Pb}^{2+}]_r = 22.1$, $[\text{SiF}_6^{2-}]_r = 4.71$, and $[\text{H}^+]_r = 0.38$

(B) $cd = 200 \, \text{A m}^{-2}$. Derived ratios: $\Phi = 40.8 \, \text{mV}$, $[\text{Pb}^{2+}]_r = 76.3$, $[\text{SiF}_6^{2-}]_r = 15.4$, and $[\text{H}^+]_r = 0.19$
Fig. 8 shows the concentration and migration potential \(^1\) changes across the slimes layer for two different current densities. Both \([\text{Pb}^{2+}]\) and \([\text{SiF}_6^{-2}]\) increase linearly as the slimes layer thickens. These increases are accompanied by a quasi-exponential decay in \([\text{H}^+]\). As a direct consequence of the presence of concentration differences across the slimes layer, a migration potential becomes established. Variations in \(\Phi\) are given with respect to the bulk electrolyte \((\Phi = 0\) at the slimes/bulk electrolyte interface). The larger the slope of \(\Phi\) with respect to the distance from the bulk electrolyte, the larger the electric field.

By comparing Figs. 8A and 8B, it can be seen that: (a) increases in current density result in corresponding changes in \([\text{Pb}^{2+}]_r\), \([\text{SiF}_6^{-2}]_r\), \([\text{H}^+]_r\), and \(\Phi_e\); (b) the concentration values found at normal slimes thickness are impossibly high.

**B. Case B: constant \(\gamma_i\) values in the presence of eddy diffusion**

In the current interruption experiments discussed in Chapter 4, ionic concentration gradients were found to be present throughout the slimes layer. The largest decays in overpotential obtained upon current interruption were observed in the vicinity of the slimes/bulk electrolyte interface (see Figs. 4.7 to 4.11). Correspondingly, the closer the potential probes were to the anode/slimes interface the smaller the potential decay. The smaller decays were associated with larger amounts of \(\text{Pb}^{2+}\) and \(\text{SiF}_6^{-2}\) near the anode/slimes interface as compared to those found near the slimes/bulk electrolyte interface. The difference in magnitude of the overpotential decays can also be attributed to the presence of natural convection.

During lead dissolution from lead bullion electrodes, different convection patterns may be present. These convection patterns change local concentrations and potentials across the slimes layer. An estimation of these variations can be obtained by re-plotting the data presented in Fig. 4.12 with respect to the distance from the anode/slimes interface and as a function of the electrolysis time (Fig. 9). The anodic overpotential for a fixed position within the slimes layer decreases as the slimes layer thickens. This indicates that small yet significant changes in

---

\(^1\) The electric field, \(X\), at any point within the slimes layer is equal to the negative gradient of the electrostatic potential at that point:

\[ X = -\frac{d\Phi}{dx} \]

Thus, the electrical field increases in the opposite direction to the electrostatic potential. Likewise, positive charges move in the direction of the electric field [51, P.348].
Case B: constant values in the presence of eddy diffusion

Fig. 9 Changes in the potential of the slimes electrolyte as a function of the distance from the anode/slimes interface.
From the experimental data presented in Chapter 4, Fig. 4.12.
As the slimes layer thickens the potential for a fixed point away from the anode/slimes interface decreases.

Concentrations are continuously taking place. These changes are not only associated with natural convection but also with precipitation of secondary products. This changes the physico-chemical properties of the slimes layer and significantly hinders the ionic movement. Thus, from the data presented in Fig. 10, it can be inferred that precipitation of secondary products takes place after ~10 mm of slimes have been formed: While the difference in potential in the middle of the slimes remains nearly constant, a steep increase in the potential difference between the inner B and inner C reference electrodes can be observed after a slimes thickness of ~10 mm. As a result of the precipitation of secondary products, the inner potential rises because ions can no longer move at the same rate.

The predicted ionic concentration ratios presented in Fig. 8 are several fold larger than those experimentally measured (e.g. see Fig. 4.21, and [3,4]). Furthermore, their magnitude indicates that large differences in viscosity and density across the slimes electrolyte can be present. These differences lead to the development of natural convection. The extent to which natural convection can
be established is a function of the current density, electrolyte concentration gradients, geometry and size of the electrode, porosity and tortuosity of the slimes layer, thickness of the slimes layer, and viscosity gradients.

Mixing of electrolytes as a result of the presence of natural convection is incorporated in the solution of the flux equations through the eddy diffusivity term, $D^E$. For a fixed amount of lead dissolved (i.e. for a fixed slimes thickness), changes in $D^E$ were assumed to comply with the following relationship

$$D^E = |\beta \cdot \ln \frac{x_i + \alpha}{x_{\text{total}}}|$$  \hspace{1cm} \ldots 31

1 Eddy diffusion as expressed by Eq. 31, incorporates mixing of slimes electrolytes as a result of both natural and forced convection. It becomes extremely small at the anode/slimes interface and reaches a maximum value (in this model) at the slimes/bulk electrolyte interface. At a fixed distance from the latter, the contribution of eddy diffusion increases with time, because this point becomes more remote from the anode/slimes interface. Therefore, eddy diffusion leads to an unsteady-state electrolyte composition and thus to a time-dependent polarization at points within the slimes layer that are at a fixed distance from the slimes/electrolyte interface.
where:
\[ x_{\text{total}} = \text{Total slimes thickness, [mm]} \]
\[ x_i = \text{distance from the slimes/bulk electrolyte interface at which point } D^E \text{ is to be computed, [mm]} \]
\[ \alpha \text{ and } \beta = \text{arbitrary positive constants whose value depends on the electrolysis conditions: } \]
\[ \alpha \text{ [mm] and } \beta \text{ [cm}^2\text{ sec}^{-1}] \]

Eq. 31 can be used to obtain \( D^E \) values across the slimes layer for a fixed slimes thickness. As shown in Fig. 11, \( D^E \) decreases logarithmically from the slimes/bulk electrolyte interface towards the anode/slimes interface. For a fixed point away from the anode/slimes interface, the thicker the slimes layer, the smaller \( D^E \). This is equivalent to implying that because of the increasing thickness of the slimes, natural convection will not penetrate deep within the slimes layer, even though large density differences can be found there (i.e. even in the presence of large \([\text{Pb}^{2+}]_e\) and \([\text{SiF}_6^{-2}]_e\)). Wenzel’s [3,4] experiments indicate that such patterns in convection are operative during the dissolution of lead by the BEP.
Fig. 12 Variation in the slimes electrolyte composition as a function of the distance from the slimes/bulk electrolyte interface, when changes in eddy diffusion are accounted for (Case B).

\[
\begin{align*}
&PbSiF_6 - 2 = 0.2\, M \\
&H_2SiF_6 = 0.8\, M
\end{align*}
\]

Right scale: Changes in $\Phi$
Left scale: Changes in $[Pb^{2+}]$, $[SiF_6^{2-}]$, and $[H^+]$

(A) $cd = 50\, A\,m^2$, $\alpha = 1 \times 10^{-2}\, mm$ $\beta = 1 \times 10^{-4}\, cm^2\,sec^{-1}$
Derived ratios: $\Phi_0 = 21.6\, mV$, $[Pb^{2+}] = 3.80$, $[SiF_6^{2-}] = 1.30$, and $[H^+] = 0.68$

(B) $cd = 200\, A\,m^2$, $\alpha = 1 \times 10^{-2}\, mm$ $\beta = 5 \times 10^{-4}\, cm^2\,sec^{-1}$
Derived ratios: $\Phi_0 = 71.6\, mV$, $[Pb^{2+}] = 4.51$, $[SiF_6^{2-}] = 1.35$, and $[H^+] = 0.56$
Fig. 12 shows the concentration and potential gradients obtained by incorporating eddy diffusion in the overall diffusion term, $D_i$. The local concentrations and potential differences shown in this figure are those predicted to be present at the point at which the slimes layer has reached a thickness of 10 mm. By incorporating eddy diffusion, large decreases in the magnitude of the potential gradients are obtained (compare Fig. 12 with Fig. 8). Furthermore, the calculated mean slimes electrolyte concentrations are closer to those experimentally found than those predicted without incorporating an eddy diffusion term.

**C. Anodic overpotential values derived from the mathematical model**

The experimental data used in Exp. LC2 (see Chapter 4) will be used to show how the mathematical model can be used to predict anodic overpotentials.

Fig. 13 - Variation in the slimes electrolyte composition as a function of the distance from the slimes/bulk electrolyte interface, when changes in eddy diffusion are accounted for (Case C).

<table>
<thead>
<tr>
<th>Concentration, mol/l</th>
<th>Migration Potential, $\Phi$, mV</th>
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<tr>
<td>1.60</td>
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Distance from the Slimes/Bulk Electrolyte Interface, mm

$[\text{SiF}_6^{2-}]$ $[\text{Pb}^{2+}]$ $[\text{H}^+]$

Right scale: Changes in $\Phi$  
Left scale: Changes in $[\text{Pb}^{2+}]$, $[\text{SiF}_6^{2-}]$, and $[\text{H}^+]$

$[\text{PbSiF}_6]=0.28 \text{ M}$  
$[\text{H}_2\text{SiF}_6]=0.74 \text{ M}$  
$\alpha = 1 \times 10^{-2} \text{ mm}$  
$\beta = 5 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$  

$cd = 139 \text{ A m}^{-2}$. Derived ratios: $\Phi_e = 72.0 \text{ mV}$, $[\text{Pb}^{2+}]=3.48$, $[\text{SiF}_6^{2-}]=1.38$, and $[\text{H}^+]=0.57$

1 The predicted mean ionic concentrations within the slimes layer can be made to match those experimentally measured by changing the eddy diffusion parameters $\alpha$ and $\beta$. 

[222]
Anodic overpotential values derived from the mathematical model

Fig. 14 Variation in physico-chemical properties of the slimes electrolyte as a function of the distance from the slimes/bulk electrolyte interface.

(A) Variation in electrical conductivity \( \kappa \)  
(B) Variation in density \( \rho \), and in kinematic viscosity, \( \nu \).
The migration potential and concentration profiles shown in Fig. 13 were obtained for the initial bulk electrolyte composition and current density used in the case study presented in Chapter 4 (Exp. LC2). To simulate the presence of eddy diffusion, the following values were assumed: \( \alpha = 1 \times 10^{-2} \text{ mm} \) and \( \beta = 5 \times 10^{-4} \text{ cm}^2 \text{ sec}^{-1} \).

From the data presented in Fig. 13, changes in \( \kappa, \rho, \) and \( v \), as a function of the distance from the slimes/bulk electrolyte interface were obtained (see Fig. 14).\(^1\)

As shown in Fig. 14A, \( \kappa \) decreases continuously as the slimes electrolyte gets depleted in \( \text{H}^+ \) and enriched in \( \text{Pb}^{2+} \) and \( \text{SiF}_6^{2-} \). From these data, the total ohmic drop across the slimes layer was computed using the following equation:

\[
\eta_{\text{ohm}} = I \int_0^\delta \frac{1}{\kappa(x)} dx
\]

The results of the numerical integration of the data presented in Fig. 14A, according to Eq. 32, are shown in Fig. 15. The concentration overpotential shown in this figure was computed according to the following equation:

\[
\eta_c = \frac{RT}{Z_{\text{Pb}^{2+}}F} \ln \frac{a_{\text{Pb}^{2+}}(x)}{a_{\text{Pb}^{2+}}(\text{bulk})}
\]

Using Eqs. 32 and 33, and the computed \( \Phi \) values, the total anodic overpotential can be obtained as follows:

\[
\eta_a = \eta_c + \eta_{\text{ohm}} + \Phi
\]

As shown in Fig. 15, the computed anodic overpotential, \( \eta_a^* \), is smaller than that experimentally measured, \( \eta_A \). The difference in potential between \( \eta_a^* \) and \( \eta_A \) decreases as the slimes layer thickens until it practically disappears towards the end of the electrorefining cycle (at \( \sim 14 \text{ mm} \) of slimes). The smaller \( \eta_a^* \) values with respect to \( \eta_A \) at smaller slimes thicknesses, are due to the fact that \( \eta_A \) was measured as a function of time, (i.e. with respect to a moving interface) whereas \( \eta_a^* \) was obtained from concentration gradients computed at a fixed time (i.e. with respect to a fixed interface). That is, the model predicts anodic overpotentials only after a pseudo-steady state has been established. Thus, the lowest experimental \( \eta_A \) values shown in Fig. 9 (those obtained at the end of the electrorefining cycle) are nearly equal to the computed \( \eta_a^* \) shown in Fig. 15. The small differences between

---

1 Changes in \( \kappa, \rho, \) and \( v \) were computed from the local ionic concentration changes using Eqs. 19 to 21.
the computed and experimental overpotentials can be related to variations in the corrosion potential of the lead anode as the slimes layer becomes exposed to wide ranges of electrolyte compositions.

Fig. 15 Comparison between the experimental (unsteady-state) and predicted (steady-state) anodic overpotentials.

- Experimental anodic overpotential from Exp. LC2 (outer reference electrode measurements corrected for uncompensated ohmic drop).
- Predicted anodic overpotential from the solution of the Nernst-Planck flux equation and from the data presented in Fig. 13.

The computed overpotential contains contributions from ohmic resistance, concentration overpotential (of Pb\(^{2+}\)), and migration potential (caused by unequal diffusivities of anions and cations). The ohmic and concentration overpotentials are shown.
Summary

The Betts electrorefining process (BEP) for lead is successful because it retains most noble impurities in adherent anode slimes while depositing rather pure (>99.99%) lead cathodes. The anode slimes account for only 1 to 4% of the weight of dissolved lead, and so represent an enrichment of a factor of 25 to 100 in the noble impurities (particularly precious metals) present in lead bullion.

A review of the Betts Process as described in the literature was presented in Chapter 1. From this review, important attributes of the Betts process were identified:

1) The anode slimes formed upon selective removal of lead from the impure bullion electrodes are adherent and thick (> 1 cm). X-ray diffraction on these slimes has identified mainly oxides and lead fluoride, but these results may have been compromised by accidental oxidation of samples. The actual (in-situ) slimes are more likely electrically conducting filaments of noble metals and intermetallic compounds, sometimes supplemented by precipitated PbF$_2$ and SiO$_2$ (both of which have been detected in anode slimes precipitates).

2) It is well known that anode polarization must be limited to less than 200 mV to avoid bismuth dissolution and transfer to the cathodic deposit. This, together with the reported X-ray diffraction data provides evidence that in-situ slimes contain metallic bismuth.

3) Electrolyte extracted from within slimes layers shows that it is markedly enriched in lead fluosilicate and somewhat depleted in fluosilicic acid. The change in the inner slimes electrolyte concentration is more abrupt towards the slimes/anode interface and accounts for the hydrolysis of SiF$_6^{2-}$ ions:

\[
3Pb^{2+} + SiF_6^{2-} + 3H_2O \rightarrow 3PbF_2 + H_2SiO_3 + 4H^+
\]

4) Fundamental electrochemical studies have evaluated the effects of additives such as lignin sulphonates, glue, and aloes extracts as levelling agents in cathode deposition. The presence of these additives in the electrolyte for lead refining may affect both the cathodic and the anodic overvoltages.

Among the most important processes in Betts refining are those which take place within the slimes layer. Thus, across this layer, ionic concentration gradients become established and depending on the electrolysis conditions (anode composition, current density, electrolyte properties) secondary reactions
(hydrolysis, secondary products precipitation, dissolution of noble impurities) can take place. This research studied these processes from a fundamental perspective in order to get a better understanding of the industrial operation of the BEP. Some of the fundamental questions this study addressed were:

a) What are the components of the anodic polarization and how do they relate to the hydrolysis of the acid and the precipitation of secondary products?

b) Under which thermodynamic conditions can noble compounds present in the slimes layer dissolve?

c) Are the filaments of noble metals in the slimes layer electrically conducting?

d) What effect do the addition agents have on the anodic process?

Furthermore, this study was directed to the formulation of a mathematical model to describe the changes in concentration and potential across the slimes layer.

In Chapters 2 and 3 the experiments designed to address some of these questions were presented. In the electrochemical experiments, the use of a high purity lead wire as a reference electrode was rationalized based on the high reversibility of lead in $\text{H}_2\text{SiF}_6$-$\text{PbSiF}_6$ electrolytes and the absence of a liquid junction. Also the components of the anodic polarization were individually analyzed and the use of transient electrochemical techniques was proposed to assess their magnitude and impact on the anodic processes.

The electrochemical processes taking place at open circuit or during anodic dissolution of lead electrodes were studied using "in-situ" transient techniques which include:

- a) Single potential and current step (i.e. potentiostatic and galvanostatic dissolution including chronopotentiometry).
- b) Current interruption.
- c) AC impedance in the presence and in the absence of a net Faradaic current.
- d) A variation of the Small Amplitude Cyclic Voltammetry (SACV) technique: during the AC impedance measurements the transient variations of potential and current were measured simultaneously.
The results obtained from electrochemical measurements were supplemented with physico-chemical data on experimentally measured electrolyte properties (electrical conductivity, kinematic viscosity, and density) and with data from "in-situ" and "industrially recovered" slimes electrolyte compositions. Also, scanning electron microscopy and X-ray diffraction were used to analyze the phases and compounds present in the slimes obtained during dissolution of lead bullion electrodes as used in the Betts refining process.

**Chapter 4** is a case study in which a lead bullion electrode was galvanostatically dissolved. Reference electrodes within the lead anode were incorporated to follow the difference in potential between the slimes electrolyte and the lead anode. Measurements on the slimes electrical conductivity were made by following the difference in potential between a bare Pt wire inserted in the slimes layer and the lead anode. In these measurements, it was found that the difference in potential between the Pt wire and the lead anode was negligible. The Pt wire and the anode appeared to be short-circuited indicating the high electrical conductivity of the slimes filaments.

Samples of the slimes electrolyte were withdrawn *in-situ*, and their composition was related to the transport processes across the slimes layer. Chemical analysis of Si and F at a fixed point in the slimes electrolyte, show that their total concentration decreases as the slimes layer thickens. These decreases were related to time dependent processes such as changes in convection due to movement of the anode/slimes interface and/or gradual precipitation of secondary products. The noble impurity concentrations was very small ($\text{SbO}^+ \sim 0.2\text{mM}$, $\text{AsO}^+ \sim 0.2\text{mM}$, and $\text{BiO}^+ \sim 0.01\text{mM}$) and did not change significantly during the refining cycle.

Upon galvanostatic dissolution, ionic concentration gradients become established and the anodic overpotential increases as the slimes layer thickens. On the other hand, upon current interruption the anodic overpotential decays, first abruptly, (as the uncompensated ohmic drop, $\eta_\text{oh}$, disappears) and then slowly (due to the presence of a back E.M.F. created by ionic concentration gradients that decay slowly). The uncompensated ohmic drop is caused by ohmic resistance of the mixed electrolyte between the reference electrodes and the solution within the slimes layer. Across the slimes layer there is not any measurable uncompensated ohmic drop because of the presence of ionic concentration gradients.
Current interruption measurements showed that (A) concentration gradients exist across the slimes layer, (B) inner solution potentials within the slimes layer can be larger than those measured from reference electrodes located in the bulk electrolyte (C) secondary products can shift the inner solution potential to negative values which reverse upon re-dissolution (D) ionic diffusion is seen upon current interruption but it is complex and difficult to model due to the presence of processes that can support the passage of internal currents.

X-ray diffraction and scanning electron microscopy analysis on the slimes layer indicated that secondary reactions took place: near the anode/slimes interface the "cellular" microstructure was infiltrated with silica-containing products.

In **Chapter 5** further studies on the components of the anodic polarization were performed by using "pure" lead (>99.99%) working electrodes. When pure lead dissolves, the uncompensated ohmic drop increases as the electrode/interface retreats. Concentration overpotential accounts for the remaining polarization (activation overpotential is negligible) and it is a function of the electrolysis time and the current density. On the other hand, in the presence of a net anodic current, dissolution of Pb\(^{+2}\) does not proceed unhindered when addition agents are incorporated in the bulk electrolyte. Because of the addition agents, a finite activation overpotential (\(\eta_{ac}<10\) mV), was observed using chronopotentiometry. The DC results were confirmed by AC impedance measurements which indicated unambiguously that addition agents have an impact on the anodic and rest potential behaviour of lead electrodes.

In **Chapter 6** the components of the anodic polarization measured upon dissolution of lead bullion electrodes were resolved. The polarization components were obtained by analyzing the potential and current dependance upon application of a small amplitude sinusoidal waveform. This dependance was found to be linear in the low overpotential region (< 250mV). Thus, upon subtraction of the uncompensated ohmic drop, the remaining polarization is due to the "apparent" ohmic drop of the slimes electrolyte and to liquid junction and concentration overpotentials. These components are directly linked to the electrolysis conditions and to the slimes layer structure. Furthermore, the ratio of these terms can be used to obtain the point at which secondary products precipitation starts. Changes in this ratio can also be related to the anodic effects caused by the presence of addition agents.
AC impedance measurements performed in the presence of a net Faradaic current showed that the impedance increases uniformly as the slime layer thickens up to the point at which noble impurities start to react.

The difference in the magnitudes of the impedance arcs measured under galvanostatic and potentiostatic conditions was attributed to the presence of secondary products blocking the anode/slimes interface and the ionic transport. After a certain electrolysis time under potentiostatic conditions, secondary products precipitate continuously. This significantly increases the impedance of the system which can reach values as high as 1000 Ω cm$^2$. Under galvanostatic conditions concentration gradients are not as steep and this results in smaller impedances (of the order of 10 Ω cm$^2$).

Under current interruption conditions the impedance decreases as the concentration gradients relax and secondary products re-dissolve. The change in shape of the impedance curves as compared to those obtained while in the presence of current, permits a distinction to be made between the contribution from the slime filaments and that from ionic concentration gradients and charge transfer at the anode/slimes interface. It was found that charge transfer and capacitative phenomena related to the slime filaments do not contribute significantly to the impedance of the system.

Three electrical analogue models were used to describe the AC impedance measurements. Two of these analogues were used to model the impedance changes observed while in the presence of a net Faradaic current while the third was found useful in describing the phenomena observed upon current interruption. These models were derived from a proposed analogue representation of a lead bullion electrode covered by a layer of slime, as developed from a set of assumptions. Each of the components in the derived electrical circuits has a reasonable physical meaning. Changes in the analogue parameters present in the electrical circuits were related to: (A) the DC conductivity of the slime electrolyte, (B) the charge transfer resistances associated with the lead dissolution process, (C) the distributed nature of the anode/slimes and the slime/slimes electrolyte interface, and (D) the distributed capacitance generated by concentration gradients present in the slime electrolyte.

1 A "distributed element" in an analogue model represents properties of the system distributed over macro distances, such as ionic gradients in solution across the slime layer, or such as slime filament/electrolyte interfaces distributed from the anode/slimes to the bulk electrolyte/slimes interface.
Overall, AC impedance measurements were found useful in describing the presence of concentration gradients and the onset of the precipitation of secondary products.

In Chapter 7 a thermodynamic analysis of the processes that can take place across the slimes layer was presented. Thus, Eh-pH diagrams for the quaternary systems Pb-Si-F-H₂O, Sb-Si-F-H₂O, As-Si-F-H₂O, and Bi-Si-F-H₂O were found useful in describing the sequence of reactions that can take place across the slimes layer. In the recirculating electrolyte for lead refining and in the electrolyte samples extracted from the slimes layer, the compositions of the noble impurities agree with the predictions of the Eh-pH diagrams ([Sb]>[As]>[Bi]). The nature of these elements and related secondary products (such as PbF₂ and SiO₂) can be assessed experimentally only if the slimes are properly washed and then kept in a dry atmosphere.

From changes in \( K \) as a function of composition for pure H₂SiF₆ and PbSiF₆ solutions, individual equivalent conductivities \( (\lambda_i) \) in H₂SiF₆-PbSiF₆ mixtures were obtained by assuming that \( \lambda_{\text{SiF}_6^2^-} = \lambda_{\text{Pb}^{2+}} \). From the \( \lambda_i \) values and ionic concentrations, transference numbers were obtained. Changes in transference numbers as the slimes layer thickens can then be derived from local ionic concentrations. Moreover, the diffusion coefficient for \( \text{Pb}^{2+} \) obtained from \( \lambda_{\text{Pb}^{2+}} \) values \( (D_{\text{Pb}^{2+}} = 5.0 \times 10^{-6} \text{ cm}^2/\text{sec}) \) agrees with that obtained from chronopotentiometric measurements \( (D_{\text{Pb}^{2+}} = 5.3 \pm 0.8 \times 10^{-6} \text{ cm}^2/\text{sec}) \).

Finally, based on the experimental and thermodynamic findings, a mathematical model based on the Nernst-Planck flux equations was developed. The resulting set of simultaneous differential equations was solved using a finite interval algorithm so that adjustments in \( \lambda_i, \gamma_i, \) and \( D_i \) can be incorporated. The model predicts steady state ionic concentrations and potential gradients across the slimes layer (i.e. it does not predict local concentration changes as the slimes thicken). Experimentally, this steady state is not observed, with the result that a convective (eddy diffusion) component must be invoked in order to account for an unsteady state, that is, for decreasing local lead concentrations and polarization at a fixed point in the slimes electrolyte as the anode/slimes interface retreats.

---

1 \( D_i \) is the overall diffusion coefficient for species \( i \), and includes the contributions of molecular and eddy diffusion.
The inclusion of mixing due to eddy diffusion (equal for all ions) accounts for the unsteady-state observations if the eddy diffusion contribution increases at a fixed distance from the slimes/electrolyte interface as the anode/slimes interface retreats. The form of the proposed eddy-diffusion component $D^e = | \beta \cdot \ln \frac{x_i + \alpha}{x_{i_{out}}} |$ contains this provision even though it is a simple empirical equation. If $\alpha$ and $\beta$ in this equation are adjusted so that the model fits the polarization across the whole slimes layer, it also predicts quite accurately the polarization of intermediate sections, even though these polarizations decline (i.e. are in unsteady state) with respect to the outer reference electrode measurements.

The mathematical model can be used to predict (a) ionic concentration gradients (b) total polarization values across anode slimes. The thermodynamics of the system can be incorporated to predict the onset of hydrolysis and the dissolution of noble elements.

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Table 1 Summary of information that can be derived from using transient electrochemical techniques

<table>
<thead>
<tr>
<th>Addition Agents</th>
<th>DC Faradaic Current</th>
<th>Slimes</th>
<th>Secondary Products</th>
<th>DC/AC Analysis</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>AC</td>
<td>Nearly reversible Pb/Pb(^{2+}) equilibrium ((\eta_{\text{ac}} \rightarrow 0)): (R_a) and (C_{\text{dl}}) not measurable. Impedance can be described by a CPE analogue. Diffusion coefficients cannot be obtained unless the electrode surface is smooth and the hydrodynamic conditions are controlled.</td>
</tr>
<tr>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>AC</td>
<td>Under rest potential conditions and in the absence of concentration gradients within the slimes electrolyte: (\eta_{\text{ac}} \rightarrow 0) for the Pb/Pb(^{2+}) equilibrium. The analogue parameters derived from analysis of the impedance spectrum were similar to those obtained when pure lead was being studied. The slimes layer does not appear to contribute significantly to the measured impedance.</td>
</tr>
<tr>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>AC</td>
<td>Addition agents decrease the (\eta_{\text{ac}}) values for the Pb/Pb(^{2+}) equilibrium. (R_a) and (C_{\text{dl}}) can be obtained from analysis of the impedance curve.</td>
</tr>
<tr>
<td>Yes/No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes/No</td>
<td>DC</td>
<td>The components of the anodic overpotential (\eta_{\text{a}} = b + IR_m ) were obtained by superimposing a low amplitude sinusoidal waveform at preset slimes thickness. Changes in the resistivity of the entrained electrolyte and of the liquid junction and corrosion potentials were used to analyze the conditions under which hydrolysis can take place. In the absence of addition agents (\frac{a}{R_m}) values remain nearly constant whereas in the presence of addition agents (\frac{a}{R_m}) decreases. This indicates that addition agents can enhance the concentration gradients within the slimes electrolyte.</td>
</tr>
<tr>
<td>Yes/No</td>
<td>No</td>
<td>Yes</td>
<td>Yes/No</td>
<td>DC</td>
<td>Upon current interruption concentration gradients relax and secondary products re-dissolve. Changes in (\eta_{\text{a}}) as a function of time were complemented with (b) and (IR_m) data obtained at preset current times. Upon current interruption the entrained electrolyte resistivity decreases monotonically with the corrosion (or &quot;rest&quot; potential).</td>
</tr>
<tr>
<td>Yes/No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes/No</td>
<td>AC</td>
<td>The impedance in the whole frequency range increases as the slimes layer thicken. These increases are uniform only up to the point at which noble compounds dissolve. (R_a) obtained from the high frequency end of the impedance spectrum is nearly equal to that obtained from current interruption measurements. Two electrical circuits were used to fit the experimental data. These circuits were derived from a general analogue model that was based on a set of assumptions derived from empirical data. The derived electrical analogue parameters were linked to the resistance of the entrained electrolyte, the charge transfer resistance for the Pb(^{2+}) dissolution process, and to the capacitative phenomena associated to the slimes filaments and the slimes electrolyte. The extent to which ionic concentration gradients become established and their relationship to the hydrolysis point were analyzed using these electrical analogues.</td>
</tr>
<tr>
<td>Yes/No</td>
<td>No</td>
<td>Yes</td>
<td>Yes/No</td>
<td>AC</td>
<td>Upon current interruption the impedance decreases. These decreases were modelled by a modified Randles circuit. (R_a) and (C_{\text{dl}}) were small indicating that capacitative phenomena associated to the slimes filaments can be neglected.</td>
</tr>
</tbody>
</table>
Conclusions

1) A thermodynamic analysis of the system indicates that the slimes electrolyte being depleted in acid and enriched in PbSiF$_6$ can cross a threshold which marks the onset of precipitation of secondary products, namely PbF$_2$ and SiO$_2$.

2) Addition agents **significantly** affect the **anodic** processes within the slimes layer (In lead electrowinning addition agents are added for **cathodic** purposes and ideally should have no **anodic** effect).

3) The filaments contained within the slimes layer are highly conductive and are grounded to the anode.

4) Upon galvanostatic dissolution, ionic concentration gradients become established and the anodic overpotential increases as the slimes layer thickens. Abrupt increases in overpotential can be observed when hydrolysis and precipitation of secondary products (such as PbF$_2$ and SiO$_2$) occur. Overpotential increases of sufficient magnitude are accompanied by dissolution of noble impurities present in the proximity of the slimes/bulk electrolyte interface.

5) Upon current interruption the anodic polarization decays first abruptly (as the uncompensated ohmic drop disappears) and then slowly (due to the presence of a back E.M.F. created by ionic concentration gradients that decay slowly).

6) The anodic polarization has four contributions that can be obtained experimentally using transient electrochemical techniques:
   1) Uncompensated ohmic drop
   2) "Apparent" ohmic drop of the slimes electrolyte.
   3) Liquid Junction or "Migration" potential
   4) Concentration Overpotential

7) A mathematical model based on the Nernst-Planck flux equations was developed. This model can be used to predict (a) ionic concentration gradients (b) total polarization values across anode slimes. The thermodynamics of the system can be incorporated to predict the onset of hydrolysis and the
dissolution of noble elements. Thus, the mathematical model could be used industrially as a control criterion for modifying the current density as the slimes layer thickens.

8) These studies show that the process could be "improved" (in a performance sense) if precipitation of secondary products were prevented or limited. To do this, the current density could be adjusted as the slimes layer thickens and the $\text{H}_2\text{SiF}_6$ content of the electrolyte could be increased. Further, methods of decreasing the final slimes thickness might be devised, such as casting thinner or corrugated anodes.
Recommendations for Further Work

1) The Nernst-Planck model should be tested and modified to make it predict the concentration and potential gradients observed in the industrial operation of the Betts electrorefining process.

2) The eddy diffusion coefficient within the slimes layer is a function of the electrode height, as well as slimes permeability and slimes thickness. Its value should be measured and related to electrode polarization for various electrode heights, especially practical heights found in the industry.

3) The experimental procedures generated in Chapters 4 to 6 can be used to expand the applicability range of the mathematical model here proposed. An experimental separation of the parameters accounted for in the model calls for the use of a horizontal anode (below the cathode) configuration. The immediate effect of this change will be the presence of large ionic concentrations approximating those computed from the model in the absence of natural convection. Furthermore, current interruption decays will have time constants related strictly to molecular diffusion and migration without the confusion introduced by natural convection. Vertical electrolysis using electrodes of different height should also provide information on the presence of natural convection and its relationship to the establishment of concentration gradients. Studies using rotating disk electrodes at very low rotation speeds (to avoid detachment of slimes) can also be used to improve the predictions of the model. All these studies can be complemented by measuring, at preset times, the resistance of the slimes electrolyte and the liquid junction and concentration overpotentials (e.g. by using a superimposed small amplitude cyclic waveform as described in Chapter 6, section III). These values can be compared directly with those predicted by the mathematical model.

4) The transport processes within the slimes layer could be related to the Navier-Stokes equation as an ultimate goal in modelling.

5) The extent to which concentration gradients become established across the slimes layer can be further studied by adjusting the flow of current to avoid precipitation of secondary products and impurities dissolution. Periodic interruption of current together with periodic current reversal can be used to accomplish those objectives.

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6) In the industrial operation of the BEP the components of the anodic overpotential could be determined "in-situ" using superimposed low amplitude AC currents at preset slimes thickness. This should provide with enough information for modulating the current density or changing the bulk electrolyte composition (including concentration and nature of addition agents).
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[245]
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BIBLIOGRAPHY Chapter 3


**BIBLIOGRAPHY Chapter 4**


**BIBLIOGRAPHY Chapter 5**


BIBLIOGRAPHY Chapter 6


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**BIBLIOGRAPHY Appendix 1**


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Appendix 1 Numerical Solution of the Nernst-Planck Flux Equations and Its Application to The Betts Process

I. Objective:

To introduce an algorithm to solve numerically the Nernst-Planck flux equations. From the solution of this equation the concentration of ionic species and the potential profile throughout the slimes layer will be obtained as a function of the electrolysis conditions.

II. Assumptions:

1) The Nernst-Planck flux equations can be applied in concentrated solutions when they are solved in their fundamental form.

2) Dissolution of lead is the only Faradaic reaction. This reaction takes place exclusively at the anode/slimes interface and proceeds without kinetic limitations (i.e. $i_o \rightarrow \infty$ for $\text{Pb} \rightarrow \text{Pb}^{2+} + 2e^-$).

3) Noble impurities originally present in the lead anode report to the slimes and remain unreacted during the whole electrorefining cycle (i.e. $i_o \rightarrow 0$ for the dissolution of Sb, Bi, As, and other noble impurities).

4) Hydrolysis and secondary products precipitation can be neglected.

5) Mixing of electrolytes within the slimes layer can be accounted for by incorporating the eddy diffusion component, $D^e$, in the overall diffusion term, $D$, (i.e. $v=0$) [1,2].

---

1 This assumption implies that the cross coefficients in the Onsager phenomenological equations can be neglected. Interrelationships between the involved ions can be incorporated within the absolute value of activities and mobilities.

2 Assumptions 2 and 3 are based on the fact that upon dissolution of lead bullion electrodes, lead dissolution at the anode/slimes interface is the main reaction. Furthermore, under normal operation of the BEP the slimes remain unreacted and polarized.

3 Dissolution of noble impurities is a function of the potential gradient across the slimes layer. Once the potential gradient is known, the point at which noble compounds start to react can be predicted.

4 Assumption 4 implies that the concentration gradients across the slimes layer do not depend on the presence of secondary products or hydrolysis. This assumption can be relaxed once changes in activities as a function of position are known. This will allow the hydrolysis point to be predicted.

5 Eddy diffusion will be used to incorporate mixing due to natural convection within the slimes electrolyte. Natural convection arises due to concentration differences that are created by the electrolysis itself. Forced convection takes place in regions in which the velocity field is not influenced by the concentration field around the electrode, and the density of the solution is constant [1,2]. Within the slimes electrolyte, large concentration gradients exist and natural convection is perceived to be much larger than forced convection.
6) Steady state, unidimensional model

7) Electrical neutrality is observed within the electrolyte entrapped in the slimes layer.

8) Only three ionic species are present (i.e. the PbSiF$_6$ and H$_2$SiF$_6$ molecules are completely dissociated):

Species a: Pb$^{+2}$
Species b: SiF$_6^{-2}$
Species c: H$^+$

III. Fundamental Equations

Given the previous assumptions, the Nernst-Planck flux equations that need to be solved simultaneously are as follows [9-6]:

\[ \frac{1}{N_a} D_a C_a \frac{d \ln a_a}{dx} + \mu_a C_a \frac{d \Phi}{dx} = -\frac{I(t)}{Z_a F} \] \hspace{1cm} \text{[i]}

\[ \frac{1}{N_b} D_b C_b \frac{d \ln a_b}{dx} + \mu_b C_b \frac{d \Phi}{dx} = 0 \] \hspace{1cm} \text{[ii]}

\[ \frac{1}{N_c} D_c C_c \frac{d \ln a_c}{dx} + \mu_c C_c \frac{d \Phi}{dx} = 0 \] \hspace{1cm} \text{[iii]}

\[ Z_a C_a + Z_b C_b + Z_c C_c = 0 \] \hspace{1cm} \text{[iv]}

where:
Species a = Pb$^{+2}$ Species b = SiF$_6^{-2}$ Species c = H$^+$

$C_i = \text{concentration of species } i, \text{ [mol cm}^{-3}\text{]}.

Z_i = \text{charge number of species } i, \text{ [eq mol}^{-1}\text{].}

$D_i = \text{overall diffusion coefficient of species } i, \text{ [cm}^2\text{ sec}^{-1}] : D_i = D_i^m + D^E$

$D_i^m = \text{molecular diffusion coefficient [cm}^2\text{ sec}^{-1}]$

$D^E = \text{eddy diffusion constant [cm}^2\text{ sec}^{-1}]$ [7].

1 The electrolyte composition for a fixed position across the slimes layer may change as a result of hydrolysis, precipitation of secondary products and natural convection. Depending on the height of the electrode (among other electrolysis parameters) local ionic concentrations may show gradients in both the vertical and horizontal coordinates.

2 Electrical neutrality rules out the presence of charge imbalance at any point throughout the slimes layer.

3 H$_2$SiF$_6$, PbSiF$_6$ are strong electrolytes and their dissociation is expected to be very high.

4 $D^E$ can be considered to be equal for all the ions. Furthermore, it can be modified so as to incorporate changes in porosity and tortuosity of the ionic flow across the slimes layer for different anode compositions and/or electrolysis conditions.

5 Notice that when the molecular diffusion coefficient is smaller than the eddy diffusion constant, the overall diffusion coefficient is nearly the same for all the components. In this case, eddy diffusion practically equalizes the effective diffusivities for all the components.
\( N_i = \text{water mol fraction with respect to species } i: \)
\[
N_i = 1 - \frac{C_i}{C_{\text{total}}} \quad \text{and} \quad C_{\text{total}} = \Sigma C_i + C_{\text{water}}
\]

\( a_i = \text{molar activity coefficient of species } i: a_i = \gamma_i C_i \)

\( \gamma_i = \text{individual molar activity coefficient}. \)

\( \Phi = \text{migration potential, [volt]} \)

\( \mu_i = \text{ionic mobility of species } i, [\text{cm}^2 \text{sec}^{-1} \text{volt}^{-1}]. \)

\( I(t) = \text{net current density as a function of the electrolysis time}, [\text{Amp cm}^{-2}]. \)

\( F = \text{Faraday's constant}, [96487 \text{ C eq}^{-1}]. \)

\( R = \text{universal gas constant, } 8.3114 \text{ J mol}^{-1} \text{ deg}^{-1}. \)

\( x = \text{distance from the slimes/electrolyte interface (as defined in Fig. 1), [cm]}. \)

Eq. \( i \) states that the only species being generated at the anode is \( \text{Pb}^{+2} \), whereas Eqs. \( ii \) and \( iii \) indicate that \( \text{H}^+ \) and \( \text{SiF}_6^{2-} \) do not react and their equilibrium concentration is only a function of the migration and diffusion gradients. Eq. \( iv \) is the electroneutrality condition.

---

1 \( D_i^m \) and \( \mu_i \) can be linked using the Nemst-Einstein relation:

\[
D_i^m = \frac{\mu_i RT}{Z_i^* F}
\]

where \( Z_i^* \) is the effective charge of species \( i \) exposed to the electric field, \( Z_i^* \leq Z_i \).

2 The Betts electorefining process for lead is normally carried out under nearly galvanostatic conditions (i.e. \( I(t) = \text{constant} \)).
IV. Derived Equations

Equation iv can be differentiated using the following relationship:

$$C_i = \frac{a_i}{\gamma_i}$$

then,

$$\frac{d}{dx} (c_i) = \frac{d}{dx} \left( \frac{a_i}{\gamma_i} \right) = \frac{\gamma_i \frac{d a_i}{dx} - a_i \frac{d \gamma_i}{dx}}{\gamma_i^2} = \frac{1}{\gamma_i} \frac{da_i}{dx} - \frac{a_i d \gamma_i}{\gamma_i^2}$$

rearranging terms:

$$\frac{d}{dx} \left( \frac{a_i}{\gamma_i} \right) = \frac{a_i}{\gamma_i} \left( \frac{d \ln a_i}{dx} - \frac{d \ln \gamma_i}{dx} \right)$$

By incorporating this relationship in equation (iv) and assuming that $Z_i = Z_i^{*}$ the following relationship is obtained:

$$\frac{d}{dx} \left[ \Sigma Z_i C_i \right] = \Sigma Z_i C_i \left[ \frac{d \ln a_i}{dx} - \frac{d \ln \gamma_i}{dx} \right] = 0$$

Thus, the electrical neutrality equation (Eq. iv) can be equivalently expressed as follows:

$$Z_a C_a \left[ \frac{d \ln a_a}{dx} - \frac{d \ln \gamma_a}{dx} \right] + Z_b C_b \left[ \frac{d \ln a_b}{dx} - \frac{d \ln \gamma_b}{dx} \right] + Z_c C_c \left[ \frac{d \ln a_c}{dx} - \frac{d \ln \gamma_c}{dx} \right] = 0 \quad ...[v]$$

By making the following substitutions in equations i, to v:

$$\frac{D_a}{N_a} = D_a \quad \frac{D_b}{N_b} = D_b \quad \frac{D_c}{N_c} = D_c$$

$$\frac{d \ln \gamma_a}{dx} = \gamma_a \quad \frac{d \ln \gamma_b}{dx} = \gamma_b \quad \frac{d \ln \gamma_c}{dx} = \gamma_c$$

$$\frac{d \ln a_a}{dx} = a_a \quad \frac{d \ln a_b}{dx} = a_b \quad \frac{d \ln a_c}{dx} = a_c$$

$$\frac{d \Phi}{dx} = \Phi \quad \frac{I(t)}{2FC_a} = \Pi$$

Eqs. i, ii, iii, and v can be represented by the following equations:

$$D_a a_a + \mu_a \Phi = -\Pi \quad ...1$$

$$D_b a_b + \mu_b \Phi = 0 \quad ...2$$
Formulation of the Equations to be Solved Numerically

\[ D_e \bar{a}_e + \mu_c \Phi = 0 \quad \ldots 3 \]

\[ 2C_a(\bar{a}_a - \bar{\gamma}_a) - 2C_b(\bar{a}_b - \bar{\gamma}_b) + C_c(\bar{a}_c - \bar{\gamma}_c) = 0 \quad \ldots 4 \]

Equations 1 to 4 constitute a set of simultaneous differential equations that have to be solved subject to the following initial conditions:

at \( x = 0 \) (i.e. at the slimes/bulk electrolyte interface): \( ^1 \)

\[ C_i = C_i^o \]

\[ a_i = a_i^o \]

\[ \gamma_i = \gamma_i^o \]

\[ \Phi = 0 \]

Eqs. 1 to 4 have to be solved for 7 unknowns \((\bar{a}_a, \bar{a}_b, \bar{a}_c, \bar{\gamma}_a, \bar{\gamma}_b, \bar{\gamma}_c, \Phi)\) using three additional equations of the form:

\[ \frac{d \ln a_i}{dx} = \frac{d \ln C_i}{dx} + \frac{d \ln \gamma_i}{dx} \]

These equations can be used to obtain either \( \gamma_i \) or \( a_i \) once the concentrations of all the species are known.

V. Formulation of the Equations to be Solved Numerically

Eqs. 1 to 4 constitute a system of differential simultaneous equations that have to be solved in order to yield the values for the four unknowns as a function of the distance from the slimes/electrolyte interface: \( \bar{a}_a(x), \bar{a}_b(x), \bar{a}_c(x), \Phi(x) \). By performing the following transformations, the differential equations are combined in such a way that they can be solved by a finite difference numerical technique.

This transformation is accomplished as follows:

Multiplying Eq. 1 times \( \mu_c \) minus Eq. 3 times \( \mu_c \):

\[ D_a \mu_c \bar{a}_a - D_c \mu_c \bar{a}_c = -\Pi \mu_c \]

rearranging and solving for \( \bar{a}_a \):

\[ \bar{a}_a = \frac{1}{D_e} \left( \frac{D_c \mu_c}{\mu_c} \bar{a}_c - \Pi \right) \quad \ldots 5 \]

---

1 For a fixed electrolyte concentration, the individual activity coefficients, \( \gamma \), and the individual activities can be derived from theoretical and experimental information [8-12].
Multiplying Eq. 1 times $\mu_b$ minus Eq. 2 times $\mu_a$:

$$D_a\mu_b\bar{a}_a - D_b\mu_a\bar{a}_b = -\Pi\mu_b$$

rearranging and solving for $\bar{a}_a$

$$\bar{a}_a = \frac{1}{D_a\mu_b}(D_b\mu_a\bar{a}_b - \Pi\mu_b) \quad \ldots 6$$

Eqs. 5 and 6 are equivalent, thus:

$$\frac{1}{D_a}\left(\frac{D_c\mu_a}{\mu_c}a_c - \Pi\right) = \frac{1}{D_a\mu_b}(D_b\mu_a\bar{a}_b - \Pi\mu_b)$$

and

$$\frac{\bar{a}_b}{\bar{a}_c} = \frac{D_c\mu_b}{D_b\mu_c}a_c \quad \ldots 7$$

Incorporating Eqs. 5 and 7 into eq. 4:

$$2C_a\left[\frac{1}{D_a}\left(\frac{D_c\mu_a}{\mu_c}a_c - \Pi\right) - \bar{y}_a\right] - 2C_b\left(\frac{D_c\mu_b}{D_b\mu_c}a_c - \bar{y}_b\right) + C_c(\bar{a}_c - \bar{y}_c) = 0$$

rearranging and solving for $\bar{a}_c$:

$$\bar{a}_c\left(C_c + 2C_a\frac{D_c\mu_a}{D_a\mu_c} - 2C_b\frac{D_c\mu_b}{D_b\mu_c}\right) = 2C_a\bar{y}_a - 2C_b\bar{y}_b + C_c\bar{y}_c + 2\frac{C_c\Pi}{D_a}$$

$$\bar{a}_c = \frac{2C_a\bar{y}_a - 2C_b\bar{y}_b + C_c\bar{y}_c + 2\frac{C_c\Pi}{D_a}}{C_c + 2C_a\frac{D_c\mu_a}{D_a\mu_c} - 2C_b\frac{D_c\mu_b}{D_b\mu_c}} \quad \ldots 8$$

Thus if initial values for the $\bar{y}_i$ and other variables are provided, a finite interval numerical approach could be used to solve for $\bar{a}_c$. Once $\bar{a}_c$ is known, $\bar{a}_b$ and $\bar{a}_a$ can be obtained from Eqs. 7 and 5 respectively. The fourth unknown, $\phi$, can be obtained from either Eq. 2 or from Eq. 3.

**VI. Finite Difference Equations**

The differential terms presented in the previous equations can be approximated using a first-order Taylor expansion.
Thus, $\bar{a}_i$ can be represented as:

$$\bar{a}_i = \frac{1 \, d a_i}{a_i \, dx} = \frac{1 \, a_{i+1}^j - a_i^j}{\Delta x}$$

from which:

$$a_{i+1}^j = a_i^j + \Delta x \cdot a_i^j \cdot \bar{a}_i$$

where the superscripts $j$ and $j+1$ refer to different nodal positions (see Fig. 1) and $\Delta x$ is the finite difference distance.

A similar equation can be written for the change in the activity coefficients:

$$\gamma_i = \frac{1 \, d \gamma_i}{\gamma_i \, dx} = \frac{1 \, \gamma_{i+1}^j - \gamma_i^j}{\Delta x}$$

from which the value of the activity coefficient at the next nodal point can be obtained:

$$\gamma_{i+1}^j = \gamma_i^j + \Delta x \cdot \gamma_i^j \cdot \bar{\gamma}_i$$

Local ionic concentrations can also be put in a finite difference form by using the following equations:

$$\bar{a}_i = \frac{d \ln a_i}{dx} = \frac{d \ln C_i}{dx} + \frac{d \ln \gamma_i}{dx}$$

$$\frac{d \ln C_i}{dx} = \bar{a}_i - \frac{d \ln \gamma_i}{dx}$$

$$\frac{d C_i}{dx} = C_i [\bar{a}_i - \bar{\gamma}_i]$$

From the previous equation, the local values of the ionic concentrations can be obtained as follows:

$$C_i^{j+1} = C_i^j + C_i^j \cdot \Delta x \cdot [\bar{a}_i - \bar{\gamma}_i]$$

The migration potential can also be expressed in finite difference form:

$$\Phi^{j+1} = \Phi^j + \Delta x \cdot \bar{\Phi}$$

$\Delta x$ is a negative quantity (see Fig. 1).
Finally, the values of the $D_t$, $\mu_i$, $C_i$, and $\Pi$ parameters in equations 1 to 4 all refer to their values at position $j$.

**VII. Algorithm for the Numerical Solution**

Given the equations presented in the previous section the numerical problem consists in finding the values of the activities and potential at the next nodal point given their initial values $(a_i^j \Rightarrow a_i^{j+1}$, $\Phi_i^j \Rightarrow \Phi_i^{j+1})$. To obtain these values, the following variables have to be known at the following position:

$$D_i^j, \mu_i^j, N_i^j, a_i^j, \gamma_i^j, \gamma_i^{j+1}$$

The concentrations at point $j$ are known and the values of the above parameters can be easily computed at that position. On the other hand the concentrations at the next nodal point are not known in advance and an estimate has to be used to compute the $\gamma_i^{j+1}$ values. The values for the $\gamma_i^{j+1}$ parameters can be improved by repeating the iteration procedure until the assumed and computed concentrations in the next nodal point are nearly equal. In the following paragraphs the algorithm to solve such iteration problem will be outlined.

**A. Input data**

To solve the Nernst-Planck flux equations in their finite difference form, the following information has to be known in advance:

at $x=0$ (i.e. in the bulk electrolyte):

$$C_a = C_a^*$$
$$C_b = C_b^*$$
$$C_c = C_c^*$$

and

$$\Phi = \Phi^* = 0$$

For a fixed value of the concentration of the ionic species, the following variables have to be computed according to pre-established relationships:\

\[1\] $D_i^j$ values have to be provided also as a function of the slimes thickness, $x^j$, because of the presence of eddy diffusion.
The current density, \( I \), has to be given as a function of the electrolysis time: \( I = f(t) \). In addition, the total electrolysis time, \( T \), and the number of uniform time intervals in which it will be divided, \( NT \), have to be provided (\( \Delta t = \frac{T}{NT} \)). Given these values, the movement of the anode/slimes interface can be computed from the following equations:

\[
I(t) \text{ has to be integrated during the time interval } \Delta t, \text{ to obtain the differential amount of coulombs passed per unit area }, \ Q_{\Delta t}^{i+1} 3,4:
\]

\[
Q_{\Delta t}^{i+1} = \int_{t}^{t+\Delta t} I(t) \cdot dt \left[ \frac{Cm}{cm^2} \right] \ldots 9
\]

From this value, the amount of lead dissolved can be obtained, \( \Delta x \), 5:

\[
\Delta x^{i+1}[cm] = Q_{\Delta t}^{i+1} \left[ \frac{Cm}{cm^2} \right] \times \frac{103.8gPb}{96487gPb} \times \frac{1cm^3}{11.2gPb} 
\]

Thus, at any point, \( j \), the distance from the anode/slimes interface, \( x_j \), can be computed from:

\[
x_j [cm] = \sum_{j=0}^{i \leq j} \Delta x^j
\]

**B. Algorithm**

1) From the function \( I(t) \) obtain the time interval, \( \Delta t \). From this value obtain the changes in slimes thickness, \( \Delta x \), for the different nodes. Set \( j = 0 \)

2) Set the node number to \( j=j+1 \)

---

1 Even though the time intervals, \( \Delta t \) are equal and uniformly spaced, depending on the shape of the current waveform, \( I(t) \), the distance intervals, \( \Delta x \), may not be equal or uniformly spaced.

2 For any time interval \( \Delta t = t^{i+1} - t^i, \Delta t > 0 \).

3 This value is an exact quantity as the shape of the \( I(t) \) waveform is known precisely.

4 The value for the current at the first nodal point (\( x=0 \)) is given by: \( I^1 = I(0) \)

5 \( \Delta x \) and \( x \) are negative quantities according to the frame of reference shown in Fig. 1. Thus both values have to be multiplied by -1 before using them in their respective equations.
3) Assume that for the next interval\(^1\) \(\gamma_a = \gamma_b = \gamma_c = 0\)

4) Given the initial electrolyte composition obtain the values of the following parameters:
\[
C_a^i = C_a^* \\
C_b^i = C_b^* \\
C_c^i = C_c^*
\]
the value of migration potential at this point is also known:
\[
\Phi' = \Phi^*
\]
From these values compute the following parameters:
\[
\begin{align*}
D_a^i & \quad D_b^i & \quad D_c^i \\
\mu_a^i & \quad \mu_b^i & \quad \mu_c^i \\
\gamma_a^i & \quad \gamma_b^i & \quad \gamma_c^i \\
a_a^i & \quad a_b^i & \quad a_c^i \\
N_a^i & \quad N_b^i & \quad N_c^i \\
D_a^i & \quad D_b^i & \quad D_c^i
\end{align*}
\]

Obtain the value of the \(\Pi\) parameter:
\[
\Pi' = \frac{\Pi^i}{Z_a F C_a^i}
\]

5) Compute \(\overline{a}_c\) from Eq. 8:
\[
\overline{a}_c = \frac{2C_a^i \gamma_a^i - 2C_b^i \gamma_b^i + C_c^i \gamma_c^i + 2 \frac{C_c^i \Pi^i}{\nu_a^i}}{C_c^i + 2C_a^i \frac{D_a^i \mu_a^i}{D_a^i \mu_a^i} - 2C_b^i \frac{D_b^i \mu_b^i}{D_b^i \mu_b^i}}
\]

6) Compute \(\overline{a}_a\) and \(\overline{a}_b\) from Eqs. 6 and 7 respectively:
\[
\begin{align*}
\overline{a}_b &= \frac{D_c^i \mu_c^i}{D_b^i \mu_b^i} \overline{a}_c \\
\overline{a}_a &= \frac{1}{D_a^i \mu_a^i} (D_b^i \mu_a^i \overline{a}_b - \Pi' \mu_b^i)
\end{align*}
\]

7) Obtain the value of \(\overline{\Phi}\) from Eq. 3:

---

\(1\) Notice that this assumption implies that for the first interval the activity coefficients do not change: \(\gamma' = \gamma^*\).
Algorithm

\[ \Phi = \frac{D_c}{\mu_c} \mathcal{A}_c \]

8) Obtain the concentration and potential values for the node \( j+1 \):

\[
\begin{align*}
C_a^{j+1} &= C_a^j + C_a^j \cdot \Delta x^j \cdot [a_a - \bar{\gamma}_a] \\
C_b^{j+1} &= C_b^j + C_b^j \cdot \Delta x^j \cdot [a_b - \bar{\gamma}_b] \\
C_c^{j+1} &= C_c^j + C_c^j \cdot \Delta x^j \cdot [a_c - \bar{\gamma}_c] \\
\Phi^{j+1} &= \Phi^j + \Delta x^j \cdot \Phi
\end{align*}
\]

9) From these concentration values obtain \( \gamma_a^{j+1}, \gamma_b^{j+1}, \gamma_c^{j+1} \) and from these values obtain:

\[
\begin{align*}
\bar{\gamma}_a &= \frac{1}{\gamma_a^j} \frac{\gamma_a^{j+1} - \gamma_a^j}{\Delta x^j} \\
\bar{\gamma}_b &= \frac{1}{\gamma_b^j} \frac{\gamma_b^{j+1} - \gamma_b^j}{\Delta x^j} \\
\bar{\gamma}_c &= \frac{1}{\gamma_c^j} \frac{\gamma_c^{j+1} - \gamma_c^j}{\Delta x^j}
\end{align*}
\]

10) Repeat steps 3 to 8 using the "new" \( \bar{\gamma} \) values ¹.

11) Continue the iteration until:

\[
\frac{C_i^{j+1}(\text{new}) - C_i^{j+1}(\text{old})}{C_i^{j+1}(\text{new})} \leq 0.01 \quad \text{(or any other tolerance value)}
\]

12) Once the convergence criteria have been fulfilled, go back to step 2 and compute the concentrations and potentials for the next step.

¹ The convergence criteria have to be fulfilled by two of the three computed concentrations (the third is obtained from electrical neutrality). A successful convergence criterion was found by averaging the assumed and computed concentrations and using the new value to improve the solution:

\[
C_i^{j+1}(\text{next iteration}) \leftarrow \frac{C_i^{j+1}(\text{new}) + C_i^{j+1}(\text{old})}{2}
\]

[275]
Appendix 2 Analytical Solution of the Nernst-Planck Flux Equations

I. Objective:

To solve analytically the Nernst-Planck Flux equations. This solution is to be obtained for the case in which activities are equal to concentrations and eddy diffusion is not present. From this solution the migration/diffusion ratio is derived. Also an equation that describes local changes in resistivity of the entrained electrolyte is obtained.

II. Assumptions:

1) Dissolution of lead is the only Faradaic reaction. This reaction takes place exclusively at the anode/slimes interface and proceeds without kinetic limitations (i.e. $i_a \rightarrow \infty$ for $Pb \rightarrow Pb^{2+} + 2e^-$).

2) Noble impurities originally present in the lead anode report to the slimes and remain unreacted during the whole electrorefining cycle (i.e. $i_v \rightarrow 0$ for the dissolution of Sb, Bi, As, and other noble impurities).

3) Hydrolysis and secondary products precipitation can be neglected.

4) Mixing of electrolytes within the slimes layer is neglected (i.e. $D^2 = 0$ and $v = 0$).

5) Activities are equal to concentrations.

6) The water mol fraction is the same for all the ions and is equal to 1.

7) Steady state, unidimensional model.

8) Electrical neutrality is observed within the electrolyte entrapped in the slimes layer.

9) Only three ionic species are present (i.e. the $PbSiF_6$ and $H_2SiF_6$ molecules are completely dissociated):

   - Species a: $Pb^{2+}$
   - Species b: $SiF_6^{-2}$
   - Species c: $H^+$

---

1 These assumptions are similar to those used to obtain the numerical solution (see Appendix 1) except for assumptions 4 to 6.

2 It can be shown that the solution here presented is also valid when individual activity coefficients are constant (see Appendix 1).
III. Fundamental Equations

Given the previous assumptions, the Nernst-Planck flux equations that need to be solved simultaneously are as follows [1-3]:

\[-D_a\left[ \frac{dC_a}{dx} + C_a \frac{Z_aF}{RT} \frac{d\phi}{dx} \right] = \frac{I}{Z_aF} \quad \ldots 1\]
\[-D_b\left[ \frac{dC_b}{dx} + C_b \frac{Z_bF}{RT} \frac{d\phi}{dx} \right] = 0 \quad \ldots 2\]
\[-D_c\left[ \frac{dC_c}{dx} + C_c \frac{Z_cF}{RT} \frac{d\phi}{dx} \right] = 0 \quad \ldots 3\]
\[Z_aC_a + Z_bC_b + Z_cC_c = 0 \quad \ldots 4\]

where:
Species a = Pb^{2+}  Species b = SiF_6^{2-}  Species c = H^+
C_i = concentration of species i, [mol cm^{-3}].
Z_i = charge number of species i, [eq mol^{-1}].
D_i = molecular diffusion coefficient [cm^2 sec^{-1}]
\(\phi\) = migration potential, [volt]
\(\mu_i\) = ionic mobility of species i, [cm^2 sec^{-1} volt^{-1}] ^1.
I = current density [Amp cm^{-2}].
F = Faraday’s constant, [96487 C eq^{-1}]
R = universal gas constant, \(8.3114 \text{ J mol}^{-1} \text{ deg}^{-1}\)
x = distance from the slimes/electrolyte interface (as defined in Fig. 1), [cm]

Eq. i state that the only species being generated at the anode is Pb^{2+} whereas Eqs. ii and iii indicate that H^+ and SiF_6^{2-} do not react and their equilibrium concentration is only a function of the migration and diffusion gradients. Eq. iv is the electroneutrality condition.

IV. Boundary Conditions

Eqs. 1 to 4 constitute a set of simultaneous differential equations that have to be solved subject to the following boundary conditions (see Fig. 1):
Fig. 1 Coordinate system used to obtain the analytical solution of the Nernst-Planck flux equations.

Eqs. 1 to 4 are to be rearranged so that the concentration and potential profiles can be obtained as a function of the distance from the slimes/bulk electrolyte interface, \( x \). This is done as follows:

Dividing Eqs. 1, 2, and 3 by \( D_A \), \( D_B \), and \( D_C \) respectively and substituting the corresponding \( Z_i \) values in these three equations and in Eq. 4, the following relationships are obtained:

\[
\frac{dC_a}{dx} + 2C_a \frac{F}{RT} \frac{d\Phi}{dx} = - \frac{I}{2FD_a} \quad \ldots 9
\]
\[ \frac{dC_b}{dx} - 2C_b \frac{F}{RT} \frac{d\Phi}{dx} = 0 \] ...

\[ \frac{dC_c}{dx} + C_c \frac{F}{RT} \frac{d\Phi}{dx} = 0 \] ...

\[ 2C_a + C_e = 2C_b \] ...

adding Eqs. 9, 10, and 11:

\[ \frac{dC_a}{dx} + \frac{dC_b}{dx} + \frac{dC_c}{dx} + (2C_a + C_e - 2C_b) \frac{F}{RT} \frac{d\Phi}{dx} = - \frac{I}{2FD_a} \] ...

substituting Eq. 12 in Eq. 13:

\[ \frac{dC_a}{dx} + \frac{dC_b}{dx} + \frac{dC_c}{dx} = - \frac{I}{2FD_a} \] ...

separating variables and integrating using b.c. 1 5, 6, and 7:

\[ C_a + C_b + C_c = C_a^0 + C_b^0 + C_c^0 + \frac{Ix}{2FD_a} \] ...

Eq. 15 can be expressed in dimensionless form by dividing it by \( C^0 \):

\[ \frac{\bar{C}_a + \bar{C}_b + \bar{C}_c}{\bar{C}_a^0 + \bar{C}_b^0 + \bar{C}_c^0} = \frac{Ix}{2FD_a C^0} \] ...

where \( \bar{C}_i \) is the dimensionless concentration defined as follows:

\[ \bar{C}_i = \frac{C_i}{C^0} \] ...

and

\( C^0 = \) total bulk electrolyte concentration, \( C^0 = C_1 + C_2, [\text{mol cm}^{-3}] \) ...

\( C_1 = \) PbSiF\(_6\) concentration in the bulk electrolyte, [mol cm\(^{-3}\)].

\( C_2 = H_2SiF_6\) concentration in the bulk electrolyte, [mol cm\(^{-3}\)].

Eq. 16 can be simplified by defining a new constant, \( K_1 \):

\[ K_1 = \bar{C}_a^0 + \bar{C}_b^0 + \bar{C}_c^0 \] ...

Thus, Eq. 16 can be expressed as follows:

\[ \bar{C}_a + \bar{C}_b + \bar{C}_c = K_1 + \frac{Ix}{2FD_a C^0} \] ...

1 "boundary conditions" is abbreviated as b.c.
VI. Analytical Solution

All the terms to the right of the equal sign in Eq. 20 are known or can be assumed. Thus, the problem consists in finding algebraic relationships between the \( \bar{C}_a \), \( \bar{C}_b \), and \( \bar{C}_c \) terms. These relationships were obtained as follows:

rearranging Eq. 10 and separating variables:

\[
\frac{dC_b}{dx} = 2C_b F \frac{d\Phi}{RT \, dx} \quad \ldots 21
\]

\[
\frac{dC_b}{C_b} = 2F \frac{d\Phi}{RT \, dx} \quad \ldots 22
\]

Eq. 22 can be integrated using b.c. 6 and 8:

\[
\ln \frac{C_b}{C_0} = \frac{-2F}{RT} \Phi \quad \ldots 23
\]

rearranging:

\[
C_b = C_0 \exp \left( \frac{-2F}{RT} \Phi \right) \quad \ldots 24
\]

Eq. 24 can be expressed in dimensionless form by dividing it by \( C_0 \):

\[
\bar{C}_b = \bar{C}_0 \exp \left( \frac{-2F}{RT} \Phi \right) \quad \ldots 25
\]

Eq. 25 provides a relationship between \( \bar{C}_b \) and \( \Phi \). A similar relationship between \( \bar{C}_c \) and \( \Phi \) can be obtained from Eq. 11 using b.c. 7 and 8:

\[
(\bar{C}_c)^2 = (\bar{C}_0)^2 \exp \left( \frac{-2F}{RT} \Phi \right) \quad \ldots 26
\]

A relationship between \( \bar{C}_b \) and \( \bar{C}_c \) can be found by multiplying Eqs. 25 and 26:

\[
\bar{C}_b (\bar{C}_c)^2 = \bar{C}_0^2 (\bar{C}_0^2)^2 \quad \ldots 27
\]

the \( \bar{C}_b (\bar{C}_c)^2 \) term in Eq. 27 can be equaled to a new constant, \( K_2 \):

\[
K_2 = \bar{C}_0^2 (\bar{C}_c)^2 \quad \ldots 28
\]

Thus, \( \bar{C}_b \) can be expressed as follows:

[280]
\[ \overline{C}_s = \frac{K_2}{(\overline{C}_c)^2} \]  

...29

Eq. 29 can be substituted in Eq. 12 to obtain the following relationship:

\[ 2\overline{C}_a + \overline{C}_c = \frac{2K_2}{(\overline{C}_c)^2} \]  

...30

this equation can be rearranged to obtain:

\[ \overline{C}_a = \frac{K_2}{(\overline{C}_c)^2} - \frac{\overline{C}_c}{2} \]  

...31

Finally, substituting Eqs. 29 and 31 in Eq. 20 and rearranging:

\[ (\overline{C}_c)^3 + (\overline{C}_c)^2 \left[ -2K_1 - \frac{I_x}{FD_aC^0} \right] + 4K_2 = 0 \]  

...32

Eq. 32 is a cubic equation that has to be solved for \( \overline{C}_c \) given \( K_1, K_2, \) and \( \frac{I_x}{FD_aC^0} \).

From the obtained \( \overline{C}_c \) values, \( \overline{C}_a \), \( \overline{C}_s \), and \( \Phi \) values can be obtained from Eqs. 29, 31, and 25 respectively.

Eq. 32 was used to obtain changes in the dimensionless concentrations and in the migration potential as a function of the bulk electrolyte composition and of the dimensionless parameter \( \Theta \) (see Figs. 2 to 4):

\[ \Theta = \frac{I_x}{FD_aC^0} \]  

...33
Fig. 2 Effect of the variable $\Theta$ on the potential difference, $\Phi$, and on the dimensionless ionic concentrations, $\overline{C}_i$, ($C^0=0.4 \text{ M}$, $C_1=0.2 \text{ M}$, $C_2=0.2 \text{ M}$).
Fig. 3 Effect of the variable $\Theta$ on the potential difference, $\Phi$, and on the dimensionless ionic concentrations, $\overline{C}_i$.

(A) $C^0 = 1.0$ M, $C_1 = 0.2$ M, $C_2 = 0.8$ M.  
(B) $C^0 = 1.0$ M, $C_1 = 0.8$ M, $C_2 = 0.2$ M.
Fig. 4 Effect of the variable $\Theta$ on the potential difference, $\Phi$, and on the dimensionless ionic concentrations, $\bar{C}_i$.

(A) $C^0=1.6 \text{ M}$, $C_1=0.8 \text{ M}$, $C_2=0.8 \text{ M}$.  
(B) $C^0=1.6 \text{ M}$, $C_1=0.1 \text{ M}$, $C_2=1.5 \text{ M}$. 

\[ \Theta = \frac{I}{FD_{Pb} C^0} \]
VII. Changes in the Specific Resistivity of the Entrained Electrolyte

The specific resistivity of dilute electrolytes can be expressed as follows:

\[
\rho_i = \frac{1}{F} \sum_i Z_i \mu_i C_i = \frac{RT}{F^2} \frac{1}{\sum_i Z_i^2 D_i C_i}
\]

where:

\( \rho_i \) = specific resistance, \([\Omega cm]\).

The dimensionless ratio between the resistivity of the bulk electrolyte and that of the entrained electrolyte, \( \bar{\rho}(I) \), is given by the following equation:

\[
\bar{\rho}(I) = \frac{\rho(\Theta = \Theta)}{\rho(\Theta = 0)} = \frac{\sum_i Z_i^2 D_i C_i (\text{Bulk Electrolyte})}{\sum_i Z_i^2 D_i C_i (\text{Slimes Layer})}
\]

Changes in \( \bar{\rho}(I) \) as a function of \( \Theta \) are given in Fig. 5 for the indicated constant diffusion coefficient values. \( \bar{\rho}(I) \) decreases as \( \Theta \) increases indicating that the entrained electrolyte is more conductive than the bulk electrolyte.\(^1\)

---

\(^1\) Electrical conductivities within the slimes electrolyte are likely to decrease rather than increase (see Appendix 1 and Chapter 7).
Changes in the specific resistivity of the entrained electrolyte

Fig. 5 Effect of the variable $\Theta$ on the dimensionless resistivity, $\rho(l)$, for different bulk electrolyte compositions.
VIII. Computation of the Diffusion Flux

As shown by Eq. 1, the ionic flux has two contributions:

\[ -D_a \frac{dC_a}{dx} = \text{Diffusion Flux} \quad -D_a C_a \frac{Z_a F}{RT} \frac{d\Phi}{dx} = \text{Migration Flux} \]

Thus, the diffusion flux can be obtained once the \( \frac{dC_a}{dx} \) changes are known.

The \( \frac{dC_a}{dx} \) term was obtained using the following algebraic procedure:

The derivative of Eq. 12 with respect to \( x \) is given by:

\[ 2 \frac{dC_a}{dx} + \frac{dC_c}{dx} = 2 \frac{dC_b}{dx} \quad \ldots 34 \]

Eqs. 10 and 11 can be rearranged to obtain a relationship between \( C_a \) and \( C_b \):

\[ \frac{F}{RT} \frac{d\Phi}{dx} = -\frac{1}{C_c} \frac{dC_c}{dx} = \frac{1}{2C_b} \frac{dC_b}{dx} \]

\[ \frac{dC_a}{dx} = \frac{2C_b dC_c}{C_c} \quad \ldots 35 \]

Thus, Eqs. 34 and 35 can be used to obtain \( \frac{dC_a}{dx} \), \( \frac{dC_b}{dx} \), and \( \frac{dC_c}{dx} \) as a function of \( \frac{dC_a}{dx} \):

\[ 2 \frac{dC_a}{dx} + \frac{dC_c}{dx} = -4 \frac{C_b dC_c}{C_c} \]

\[ \frac{dC_c}{dx} \left[ 1 + \frac{C_b}{C_c} \right] = -2 \frac{dC_a}{dx} \]

\[ \frac{dC_c}{dx} = -\frac{2C_c dC_a}{C_c + 4C_b} \quad \ldots 36 \]

\[ \frac{dC_b}{dx} = \frac{4C_b dC_a}{C_c + 4C_b} \quad \ldots 37 \]

Incorporating Eqs. 36 and 37 in Eq. 14, and solving for \( \frac{dC_a}{dx} \):

\[ \frac{dC_a}{dx} \left[ 1 + \frac{4C_b}{C_c + 4C_b} - \frac{2C_c}{C_c + 4C_b} \right] = \frac{dC_a}{dx} \left[ \frac{C_c + 4C_b + 4C_b - 2C_c}{C_c + 4C_b} \right] = -\frac{I}{2FD_a} \]
\[
\frac{dC_a}{dx} = -\frac{I}{2FD_a} \left[ \frac{C_c + 4C_b}{8C_b - C_c} \right] \quad ...38
\]

Eq. 38 can be expressed in dimensionless form by multiplying it by \( \frac{c^*}{C} \)

\[
\frac{dC_a}{dx} = -\frac{I}{2FD_a} \left[ \frac{\bar{C}_c + 4\bar{C}_b}{8\bar{C}_b - \bar{C}_c} \right] \quad ...38.a
\]

The bracketed term in Eq. 38.a can be further simplified by using Eq. 29:

\[
\frac{\bar{C}_c + 4\bar{C}_b}{8\bar{C}_b - \bar{C}_c} = \frac{C_c + \frac{4K_2}{(c_f)^2}}{8K_2 - (C_c)^3} = \frac{(C_c)^3 + 4K_2}{8K_2 - (C_c)^3}
\]

Thus, Eq. 38.a can be expressed as follows:

\[
\frac{dC_a}{dx} = -\frac{I}{2FD_a} \left[ \frac{(C_c)^3 + 4K_2}{8K_2 - (C_c)^3} \right]
\]

From which the diffusion flux can be obtained:

\[
-D_a \frac{dC_a}{dx} = -\frac{I}{2F} \left[ \frac{(C_c)^3 + 4K_2}{8K_2 - (C_c)^3} \right] \quad ...39
\]

**IX. Computation of the Migration Flux**

The migration flux can easily be derived once the diffusion flux is known. This can be inferred by rearranging Eq. 1:

\[
-D_a \frac{dC_a}{dx} = -\frac{I}{2F} \left[ \frac{(C_c)^3 + 4K_2}{8K_2 - (C_c)^3} \right]
\]

The left hand terms in this equation can be simplified by using Eq. 39:

\[
\frac{I}{2F} + D_a \frac{dC_a}{dx} = \frac{I}{2F} \frac{1}{2F} \left[ \frac{(C_c)^3 + 4K_2}{8K_2 - (C_c)^3} \right] = \frac{1}{2F} \left[ \frac{(C_c)^3 + 4K_2}{8K_2 - (C_c)^3} \right] = \frac{1}{2F} \left[ \frac{4K_2 - 2(C_c)^3}{8K_2 - (C_c)^3} \right]
\]

From which the migration flux can be obtained as follows:

\[
-D_a \frac{dC_a}{dx} = -\frac{I}{2F} \left[ \frac{4K_2 - 2(C_c)^3}{8K_2 - (C_c)^3} \right] \quad ...40
\]
X. Computation of the Migration/Diffusion Ratio

Both the migration and diffusion fluxes can be obtained once the $\overline{C}_c$ values are known (see Eq. 32). The migration/diffusion ratio, $R(l)$, can be obtained by dividing Eq. 40 by Eq. 39:

$$\frac{\text{Migration Flux}}{\text{Diffusion Flux}} = R(l) = \frac{4K_2 - 2(C_c)^3}{(C_c)^3 + 4K_2}$$ ...

As shown in Fig. 6, the diffusional flux is always larger than the migrational flux. Migration becomes increasingly more important at large values of the dimensionless parameter $\Theta$ (e.g. at large slimes thicknesses and/or current densities).
Fig. 6 Effect of the variable $\Theta$ on the migration/diffusion ratio, $R(I)$, for different bulk electrolyte compositions.
Appendix 3  Time Domain To Frequency Domain Transformation: The Fourier Transform In Current Step Electrochemical Techniques

I. Introduction

The theoretical foundations of the Laplace transformation are described extensively in the literature [1-4]. Laplace plane domain techniques are widely used in the analysis of electrical circuits [5-7]. Particularly, in the area of system analysis Laplace analysis is extremely valuable [8]. The availability of personal computers with high processing power has boosted the use of this technique in almost every scientific field. Among other advantages, the power of the technique resides in its ability to decompose any signal into its fundamental components. Furthermore, the possibility of obtaining the transfer function of the system is a strong driving force for the implementation of this technique. Electrochemists have applied Laplace techniques to the study of a variety of electrochemical systems [9-19].

In this appendix, the one-sided Laplace transformation (or Fourier transform) will be used to analyze a simple electrical circuit. The circuit here chosen follows the electrical analogue of the electrode/solution interface proposed by Gerischer [20] and Grahame [21]. The response of this circuit to a pulse of current will be analyzed both in the time and in the frequency domains. The transfer function of the system will be obtained by Fourier transformation of the input and the output signals. The differences between the values obtained by the numerical (using the FFT algorithm \(^1\)) and the analytical Fourier transformations will be stressed.

II. Response of a Simple RC Circuit to Current Pulses

In the analysis of electrochemical systems the use of electrical analogues is widespread [22-27]. The advantages and limitations of this approach are discussed in the literature [28-30]. Fig. 1 shows the analogue that has been extensively used to model the behavior of electrochemical cells. In this circuit \(R_1\) represents the uncompensated ohmic resistance, \(R_2\) the Faradaic resistance for charge transfer, and \(c\) the capacity of the electrical double layer. The quantification of each of this parameters can be done using a wide array of electrochemical techniques [24,31,32].

\(^1\) FFT stands by Fast Fourier Transformation.
For this simple analogue, the study of the decay in potential upon current interruption provides accurate information on these parameters. However, as the system becomes more complex, analysis of the time-domain transients is extremely difficult and the amount of information that can be obtained is limited. Very often information on $\eta_0$ is the only value sought [33-38] but sometimes kinetic and mass transport data are also required. Usually a "trial and error" procedure has to be conducted in order to find an electrical analogue that matches the response of the experimental system. That is, the configuration of the electrical circuit is not usually known and experimental data have to be provided to create an analogue circuit. The use of the Fourier transformation is a strong aid in such an analysis. More complex circuits can be analyzed following the same technique.

**A. Analytical solution**

The problem here consists in finding for a known configuration of the electrical circuit, the response (potential as a function of time) given the input (a current pulse). This circuit is depicted in Fig. 1.a.

The response of the circuit shown in Fig. 1 to two different input functions will be analyzed both in the time and in the frequency domains.

Figs. 2.a and 2.b describe the input functions used to exemplify the analytical procedure. Fig. 2.a describes a current step with zero decay and rise times whereas Fig. 2.b sketches a similar current step but with a non-zero rise time $^1$.

The analytical procedure to obtain the output of the system is as follows:

---

$^1$ In Fig. 2, $t_r$ represents the time that has elapsed since the current step was first applied.

[292]
1) Obtain the Laplace transform of each one of the components of the electrical circuit (i.e. \(i(t)\), \(R_1\), \(R_2\), \(C\)).

The Laplace transform is defined as:

\[
L[f(t)] = \int_0^\infty f(t)e^{-St}dt = F(S) \quad t \geq 0 \quad \ldots 1
\]

where:

- \(L[f(t)] = F(S)\) = Laplace transform of the time-dependent function, \(f(t)\).
- \(S\) = new algebraic variable which is independent of time.

2) Obtain the transfer function of the system:

In this case, the transfer function is known as the impedance, \(Z(S)\). For the circuit shown in Fig. 1, \(Z(S)\) can easily be obtained using nodal analysis. The general form of \(Z(S)\) is given by the following relationship\(^1\):

\[
Z(S) = \frac{E(S)}{I(S)} \quad \ldots 2
\]

where:

- \(I(S)\) = Laplace transform of the current, \(i(t)\)
- \(E(S)\) = Laplace transform of the potential, \(e(t)\).

3) Obtain the value of \(E(S)\) from Eq. 2 \(^2\).

4) Obtain the inverse Laplace transform of \(E(S)\), which is:

\[
L^{-1}[E(S)] = e(t) \quad \ldots 3
\]

Thus, given \(i(t)\) and the configuration of the electrical analogue, the response of the system, \(e(t)\), is obtained by following the 4 steps previously described. In the following section these steps will be performed one by one for each current step waveform (cases A and B).

**Case A:**

\(^1\) Notice the relationship between Eq. 2 and Ohm's Law: \(R = \frac{V}{I}\)

\(^2\) Notice that this step can be performed because both \(Z(S)\) and \(I(S)\) are known precisely.
Current step functions used to analyze the circuit described in Fig. 1
(a) Current step with zero decay and rise times
(b) Current step with zero decay but with a finite rise time.

**Step 1:**
The input function, $i(t)$, can be described by the following relationship:

$$i(t) = k_1 [1(t) - \frac{1}{t} - t_a] + [1(t) - t_b]$$

where $1(t)$ is the unit step function:

$$1(t) = \begin{cases} 0 & \text{for } t < 0 \\ 1 & \text{for } t > 0 \end{cases}$$

The Laplace transformation of the $R_1$, $R_2$, $C$ components is described by the following equations:

$$L[R_1] = R_1$$
$$L[R_2] = R_2$$
$$L[C] = \frac{1}{cS}$$
while the Laplace transform of the time dependent function, \( i(t) \) can be expressed as follows:

\[
I(S) = \frac{k_1}{S} \left[ 1 - e^{-\lambda S} + e^{-\gamma S} \right] \quad ...9
\]

**Step 2:**

The Laplace domain representation of the electrical circuit shown in Fig. 1.a is shown in Fig. 1.b. Applying nodal analysis the impedance of the system is obtained:

\[
Z(S) = Z_1(S) + Z_2(S) \quad ...10
\]

where:

\[
Z_1(S) = R_1 \quad ...11
\]

\[
Z_2(S) = \left( \frac{1}{R_2 + cS} \right)^{-1} = \frac{R_2}{1 + R_2 c S} \quad ...12
\]

thus,

\[
Z(S) = R_1 + \frac{R_2}{1 + R_2 c S} \quad ...13
\]

rearranging:

\[
Z(S) = \frac{R_1 S + \frac{R_1 + R_2}{R_c}}{S + \frac{1}{R_c}} \quad ...14
\]

**Step 3:**

\( E(S) \) is obtained by multiplying Eq. 14 times Eq. 9:

\[
E(S) = I(S)Z(S) = \frac{k_1}{S} \left[ 1 - e^{-\lambda S} + e^{-\gamma S} \right] \left( \frac{R_1 S + \frac{R_1 + R_2}{R_c}}{S + \frac{1}{R_c}} \right) \quad ...15
\]

rearranging:

\[
E(S) = \frac{k_1 R_1}{S + \frac{1}{R_c}} \left[ 1 - e^{-\lambda S} + e^{-\gamma S} \right] + \frac{k_1 \frac{R_1 + R_2}{R_c}}{S \left( S + \frac{1}{R_c} \right)} \left[ 1 - e^{-\lambda S} + e^{-\gamma S} \right] \quad ...16
\]
Step 4:
The inverse Laplace transformation of Eq. 16 gives

\[
e(t) = k_1 R_1 \left[ e^{-\frac{1}{k_2} t} - e^{-\frac{1}{k_2} (t-t_a)} \frac{1}{2} (t-t_a) + e^{-\frac{1}{k_2} (t-t_b)} \right] +
\]
\[
+ k_1 [R_1 + R_2] \left[ 1 - e^{-\frac{1}{k_2} t} - \left[ 1 - e^{-\frac{1}{k_2} (t-t_a)} \right] \frac{1}{2} (t-t_a) + \left[ 1 - e^{-\frac{1}{k_2} (t-t_b)} \right] \frac{1}{2} (t-t_b) \right] \quad \ldots 17
\]

Eq. 17 is the pursued analytical solution for the input function shown in Fig. 2.a.

Case B:

Step 1:
The function \( i(t) \) can be described by

\[
i(t) = k_1 \left\{ \frac{1}{2} (t - t_a) + m \left[ r(t - t_b) - r(t - t_c) \right] \right\} \quad \ldots 18
\]

where \( r(t) \) is the unit ramp function:

\[
r(t) = \begin{cases} 
0 & \text{for } t < 0 \\
1 & \text{for } t > 0 
\end{cases} \quad \ldots 19
\]

and \( m \) is the slope of the rise time curve which is defined as:

\[
m = \frac{k_1}{t_c - t_b} \quad \ldots 20
\]

The Laplace transform of the time-invariant components is given by Eqs. 6 to 8 and the Laplace transform of \( i(t) \) is given by:

\[
L[i(t)] = I(S) = \frac{k_1}{S} \left[ 1 - e^{-S} \right] + \frac{m S^2 e^{-S}}{S^2} - e^{-S} \quad \ldots 21
\]

Step 2:
The impedance of the system is independent of the input and output functions and is given by Eq. 14.

Step 3:
E(S) can be described as follows:
Step 4:

Taking the inverse Laplace transform of Eq. 22, \( e(t) \) is obtained as follows:

\[
e(t) = k_1 R_1 \left[ e^{\frac{-R_1}{R_2} t} - e^{\frac{-R_2}{R_1} (t-t_0)} \right] \frac{1}{S} (t-t_0) + m R_1 R_2 c \left[ 1 - e^{\frac{-R_1}{R_2} (t-t_0)} \right] \frac{1}{S} (t-t_0) + \left[ 1 - e^{\frac{-R_1}{R_2} (u-t_0)} \right] \frac{1}{S} (t-t_0) \]

\[
+ k_1 (R_1 + R_2) \left[ 1 - e^{\frac{-R_1}{R_2} (u-t_0)} \right] \frac{1}{S} (t-t_0)
+ m (R_1 + R_2) R_2 c \left[ 1 - e^{\frac{-R_1}{R_2} (u-t_0)} + \frac{1}{R_2 c} (t-t_0) - 1 \right] \frac{1}{S} (t-t_0) - \left[ e^{\frac{-R_1}{R_2} (u-t_0)} + \frac{1}{R_2 c} (t-t_0) - 1 \right] \frac{1}{S} (t-t_0) \]

\]

B. Analysis of the data generated in the time domain

The response of the circuit shown in Fig. 1.a to the input signals expressed by Eqs. 4 and 18 is described by Eqs. 17 and 23 respectively. The time dependance of the input and output signals is presented in Fig. 3 assuming the indicated parameters. Analysis of the response of the system in specific windows of time can provide the unknown values of some of the parameters present in the circuit. For instance, considering the time interval between \( t^- \) (i.e. after the capacitor is fully charged but before current is interrupted) and \( t^- \) (i.e. just before current is applied back), Eqs. 24 to 26 are derived from Eqs. 17 and 23:
Analysis of the data generated in the time domain

Fig. 3  Response of the circuit described in Fig. 1 to the input functions described in Fig. 2 assuming the indicated system parameters. Figs. (a.1) and (a.2) correspond to Eqs. 4 and 17 respectively. Figs. (b.1) and (b.2) comply with Eqs. 18 and 23 respectively.

A) At t = t:\n
\[ e(t) = k_1(R_1 + R_2) \] ...

B) at t = t:\n
steep potential decay = \[ k_1R_1 \] ...

C) between t and t:\n
\[ e(t) = k_1R_2e^{-\frac{1}{k_2}(t-t)} \] ...

[298]
Thus, $R_1$ and $R_2$ can be obtained by solving simultaneously Eqs. 24 and 25. Knowing $R_2$, $c$ is computed using Eq. 26. Analysis of other windows of time should provide with equivalent values for the resistors and the capacitor.

For this particular example, the computation of the value of the electrical parameters was straightforward. On the other hand, when the number of analogue elements increases and/or time-dependant components are involved, this analysis is overwhelmingly difficult. Thus, the use of Fourier analysis is encouraged.

The Fourier transform is defined as [38-41]:

$$F(f) = \int_{-\infty}^{\infty} f(t)e^{-j\omega t} dt = F(j\omega)$$ ...27

where $\omega$ is the frequency (in rad/sec) and $j$ is the imaginary number ($\sqrt{-1}$). The functions used in electrochemistry are only defined for times greater than zero, therefore Eq. 27 can be expressed as

$$F(f) = \int_{0}^{\infty} f(t)e^{-j\omega t} dt = F(j\omega)$$ ...28

Eq. 28 resembles closely Eq. 1 when the variable $S$ is substituted by the variable $j\omega$. Eq. 28 can be called the one-sided or imaginary part expression of the Laplace transformation. Thus, the Fourier and Laplace transformations which themselves are two separate mathematical entities, can be linked through changes in the $S$ algebraic variable. A real part representation of the Laplace transform can also be obtained. However, for the following analysis this particular representation is not explicitly required.

The Fourier transform of the impedance of the circuit described in Fig. 1 can be obtained in the same way its Laplace transform was derived. Thus, by analogy with Eq. 13, the following equation is obtained:

$$Z(j\omega) = R_1 + \frac{R_2}{1 + R_2c_j\omega}$$ ...29

The variation of $Z(j\omega)$ with frequency is sketched in Fig. 4.a. In this plot, the real part of the impedance is the abscissa and the negative of the imaginary part of the impedance is plotted as the ordinate. Analysis of this plot (so-called Argand diagram) can provide the value of the elements of the analogue circuit. Plotting of log ($\omega$) vs. $|Z(j\omega)|$ (so-called Bode plot) complements the overall information.
required to analyze the system. The Bode plot for this circuit is shown in Fig. 4.b. Information on the values and characteristics of the electrical parameters likely to be present, can be derived from these plots [28,42,43].

The value of the real part of the total impedance can be obtained as the low frequency interception of the impedance curve in the Argand diagram. In addition, at high frequencies the value of $R_1$ is attained:

$$Z(j\omega) = R_1 + R_2 \quad \text{when} \quad \omega = 0$$  \hspace{1cm} \text{...30}

$$Z(j\omega) = R_1 \quad \text{when} \quad \omega \rightarrow \infty$$  \hspace{1cm} \text{...31}

Eq. 29 can also be written as:

$$Z(j\omega) = R_1 + \frac{1}{\frac{1}{R_2} + \frac{c}{j\omega}}$$  \hspace{1cm} \text{...32}

Thus, at $\omega = \omega_c = \frac{1}{r_c}$ a maximum in the Argand diagram is found. This maximum is marked in Fig. 4.a and corresponds to the value of $\frac{1}{r_c}$. Thus, to obtain the value of $c$, $|Z(j\omega)|$ is computed at this point and the frequency at which it takes place is obtained from the Bode plot (Fig. 4.b). Complex non-linear regression analysis [44,45] and deconvolution techniques [42,43] can also be applied in the analysis of impedance data.

At this point, it is worth noting the fact already stated in the literature [28,29] that the impedance obtained by Fourier transformation of data generated in the time domain is also in character an AC impedance. That is, the results obtained from the study of a time-invariant system should be equivalent in both cases.
Numerical Solution

The relationship between the Laplace and Fourier transformations expressed by Eq. 28, produce the following representation of the impedance in the frequency domain:

\[ Z(j\omega) = \frac{E(j\omega)}{I(j\omega)} \]
By knowing the configuration of the electrical circuit the frequency
dependance of the impedance was found (Fig. 4). As Eq. 33 shows, the impedance
can also be obtained by Fourier transforming the input and output functions and
taking their ratio. In the previous section the system response was derived
analytically from the knowledge of the circuit configuration and of the time
dependance of the input function. The approach in this section is to obtain the
transfer function given the input and output functions in discrete form. Details
of the configuration of the electrical analogue and evaluation of its components
are to be derived from the analysis of the frequency spectrum of the transfer
function.

The numerical representation of the transfer function is obtained by finding
the zero-order approximation of Eq. 27. This approximation to the Fourier integral
is known as the discrete Fourier transformation (DFT). The DFT is defined as [46]:

\[
\hat{F}_m = \hat{F}(j\omega) = \sum_{n=-\infty}^{\infty} f_n(t)e^{-j\omega n\Delta t} \quad \ldots 34
\]

where:
\( f_n(t) = \) value of the digitized time dependent signal \( f(t) \) taken at the nth time interval.
\( N = \) total number of sampled points taken
\( \Delta t = \) sampling interval, sec

Assuming that \( f(t) \) is only defined for \( t > 0 \) and that it has a finite number of
points, the following relationship is derived from Eq. 34:

\[
\hat{F}_m = \hat{F}(j\omega) = \sum_{n=0}^{N-1} f_n(t)e^{-\frac{j2\pi mn}{N}} \quad m = 0, 1, \ldots, N - 1 \quad \ldots 35
\]

where \( m \) is an integral value known as the frequency index.

The frequency index is related to the frequency, \( \omega \), through the following
relationship:

\[
\omega = \frac{2\pi m}{N\Delta t} \quad m = 0, 1, \ldots, N - 1 \quad \ldots 36
\]

The period, \( T \), of the function \( f(t) \) is given by the product \( N\Delta t \). For a single
period, Eq. 36 shows that \( \omega \Delta t \) spans in values comprehended between 0 and \( 2\pi \)
rad. It also shows that the frequency representation of the data generated in the
time-domain is given in multiples of the fundamental frequency \( \omega_f \):

\[
\omega_f = \frac{2\pi}{N\Delta t} \quad \ldots 37
\]
Accurate results can only be obtained by "matching" $\omega_t$ so that an integral number of waveform periods is covered. If this condition is not fulfilled, "leakage" [46] will be present and incorrect spectra will be attained. Another phenomenon that can significantly alter the frequency spectrum is known as "aliasing" [46]. This can be avoided by limiting the value of the highest frequency that can be precisely known. This is done by applying the sampling theorem [46] which can be expressed by the following relationship:

$$\omega_{hi} \leq \frac{2\pi}{2\Delta t} \left( \frac{\text{rad}}{\text{sec}} \right)$$

Thus, even though $\omega \Delta t$ values as high as $2\pi$ can be obtained (Eq. 36) the highest meaningful $\omega \Delta t$ value is $\pi$ rad. In practice, this value is reduced even further to avoid as much as possible the presence of aliasing.

By applying the definition of the DFT given in Eq. 35 to Eq. 33, the discrete Fourier transformation of the impedance can be expressed as follows:

$$\hat{Z}_m = \frac{\hat{E}_m}{\hat{I}_m}$$

where the DFT of the different functions involved has been incorporated.

Thus, the problem reduces to find the Fourier coefficients $\hat{F}_m$ for the $e(t)$ and $i(t)$ functions and taking their ratio. This transformation has to account for the restrictions imposed by leakage and aliasing and the $\hat{F}_m$ coefficients must be computed from Eq. 35 using the FFT algorithm.

One of the requirements for the implementation of the FFT algorithm is that the $f(t)$ functions have to be given as sets of $2^q$ ($q$ being a positive integer number) equally spaced data points. A large amount of easy-to-use programs are available in the literature to implement this algorithm [1,46-48]. In this particular work, use of a built-in FFT routine present in a commercial software package was employed.

When the numerical time-domain to frequency-domain transformation is to be performed, important consideration should be given to the values that the sampling interval, $\Delta t$, and the function period, $T$, can adopt. To assure that the maximum spectral content is to be obtained, $\Delta t$ has to be chosen as small as possible (see Eq. 37). In addition to this, the extent to which information in the lower frequency range can be attained is regulated by the total number of points sampled, $N$ (see Eq. 36). Thus, the use of very small $\Delta t$ values and a large number...
Numerical Solution of data points is advantageous to obtain the full frequency spectrum. However, due to instrumental and experimental constraints, there is a limit as to how small or large these parameters can be. Moreover, choice of the signal period is not an easy task and a "cut" and "try" approach has to be undertaken.

In the numerical analysis of the potential and current transients here conducted, \( \omega_{hi} \) values were restricted even further than indicated by Eq. 36 because a large amount of aliasing was found when the frequencies considered went as high as Eq. 36 indicates. Thus, by using a "trial and error" procedure the maximum allowable value of \( \omega_{hi} \) was found to be:

\[
\omega_{hi} = \frac{1}{2\Delta t} \left( \frac{rad}{sec} \right) \quad \ldots 40
\]

Table 1, hypothetical values for \( N\Delta t \) were introduced to illustrate how changes in this parameter can affect the characteristics of the frequency spectrum. In this table, \( \omega_f \) and \( \omega_{hi} \) were calculated according to Eqs. 37 and 40 respectively. For a fixed \( N\Delta t \) value, increases in the number of sampled points are reflected in a wider frequency region. Reduction in the \( N\Delta t \) values for a fixed sampling rate produces an increase in the frequency range but at the cost of decreased resolution (by increasing \( \omega_f \)). Thus, changes in \( \omega_f \) can only be introduced through modifications in \( N\Delta t \). Small \( \omega_f \) values are helpful as the lower they are the better resolved the spectrum and the lower the possibility of "leakage". If the fundamental frequency is to be decreased, the easiest way of doing it is by extending the period of the waveform.

| Table 1 Changes in the maximum and fundamental frequencies for different waveform periods and number of sampled points |
|---|---|---|---|---|---|
| \( N\Delta t=1 \text{ sec}, \omega_f=2\pi \) | \( \Delta t \) | \( \omega_{hi} \) | \( \Delta t \) | \( \omega_{hi} \) | \( \Delta t \) | \( \omega_{hi} \) |
| 128 | 0.00781 | 64 | 0.01563 | 32 | 0.03125 | 16 |
| 256 | 0.00391 | 128 | 0.00781 | 64 | 0.01563 | 32 |
| 512 | 0.00195 | 256 | 0.00391 | 128 | 0.00781 | 64 |
| 1024 | 0.00098 | 512 | 0.00195 | 256 | 0.00391 | 128 |
| 2048 | 0.00049 | 1024 | 0.00098 | 512 | 0.00195 | 256 |

1 Use of filters can help in obtaining frequencies as high as the ones implied by Eq. 36.
Numerical Solution

The interaction of the previous parameters will be further exemplified by analyzing the numerical representation of the frequency spectrum of the transfer function given in Figs. 5 to 8. The effect that \( \Delta t \) and \( N \) have on \( \omega_r \) and \( \omega_m \) is shown in the respective captions. The impedance was obtained by applying the FFT algorithm to the theoretical discrete and uniformly spaced input and output functions. These functions were generated by using the equations developed in the previous section. The numerical representation of the frequency spectrum of the impedance was compared with its analytical counterpart. As can be observed, good agreement exists between the analytical and numerical solutions. The large number of data points considered together with small \( \Delta t \) values contributed to this correspondence.

One of the most critical choices in the FFT transformation is the one concerning the point at which the waveform starts. The logic behind this is that the input and output waveforms have to be considered as a trend, that is, as if they repeat themselves periodically. Thus, in this case, the time \( t_o \) was chosen so as to avoid the influence of the initial charging of the double layer. By doing this, truncation errors were avoided and a "clean" frequency spectrum was obtained. If time \( t_o \) is to be considered equal to zero, the waveform period has to be selected between zero and \( t_b \). In addition to this, \( t_b \) has to be chosen as large as possible so that the double layer is fully discharged before current is applied back. By imposing these limits the waveform can be considered to repeat itself afterwards.

Figs. 5 and 6 show the frequency spectrum obtained when different input functions and system parameters are employed. By comparing the Argand diagrams in these figures it can be seen that they are similar. This is to be expected as the only electrical parameter that was changed was the capacitor value. The decrease in this value is observed in the Bode plots as a displacement of the frequency towards higher values. As can be observed, an order of magnitude decrease in the capacitor value reflected in a tenfold frequency increase required to define the frequency spectrum.
Fig. 5 Frequency response of the circuit depicted in Fig. 1 obtained assuming the parameters shown in (a).

The input (a) and output (b) functions were calculated according to Eqs. 4 and 17 respectively. These functions were digitized using N=2048, Δt=5.127×10^-4 sec.

Plots (c) and (d) describe the analytical (Eq. 33) and numerical (Eq. 37) frequency spectra. For this set of data ω=5.98 rad/sec, ωm=975 rad/sec (Eqs. 37 and 40 respectively)
Fig. 6 Frequency response of the circuit depicted in Fig. 1 obtained assuming the parameters shown in (a).

The input (a) and output (b) functions were calculated according to Eqs. 4 and 17 respectively. These functions were digitized using $N=2048$, $\Delta t=4.883\times10^{-3}$ sec. Plots (c) and (d) describe the analytical (Eq. 33) and numerical (Eq. 37) frequency spectra. For this set of data $\omega_1=62.83$ rad/sec, $\omega_m=10240$ rad/sec (Eqs. 37 and 40 respectively)
Figs. 7 and 8 show the effect that a different waveform period and sampling interval have on the definition of the frequency spectrum at lower frequencies. Increasing the waveform period from 0.03 to 0.10 sec decreased the value of $\omega_m$ but increased $\omega_c$ due to the fact that $\Delta t$ was increased. Better resolution of the frequency spectrum at lower frequencies is reflected in a well defined Bode plot shown in Fig. 8.d.

Figs. 5, 7, and 8 were obtained using the same electrical analogue parameters and only changes in the characteristics of the input function were studied. Plots c and d in these figures show that regardless of the shape and magnitude of the input and output functions, the transfer function remains identical provided the same system is being analyzed.

The advantages of the Fourier transformation in the analysis of time-domain transients can be visualized by inspecting plots c and d in Figs. 5 to 8. The numerical transfer function obtained matches the one derived analytically. If the electrical circuit analogue had not been not known in advance, it could be inferred from analysis of this frequency spectrum. Different circuits could be proposed and their frequency spectrum calculated so as to match the numerical frequency response. The numerical frequency response could then be curve fitted to the theoretical circuit leading to the derivation of the values of the electrical parameters.

Plots c and d of Figs. 6 to 9 also show that the information that AC impedance and current interruption can provide is equivalent. This equivalence is due to the fact that "lumped" time-invariant electrical parameters were considered. The presence of distributed and/or time dependant parameters may give different information from each technique as different systems may be analyzed. If systems where these parameters are present are to be studied, careful experimental planning is required. Also, the information provided by each technique may be used jointly to better characterize the system.
Fig. 7 Frequency response of the circuit depicted in Fig. 1 obtained assuming the parameters shown in (a).

The input (a) and output (b) functions were calculated according to Eqs. 18 and 23 respectively. These functions were digitized using N=2048, ∆t=4.883×10⁻⁵ sec.

Plots (c) and (d) describe the analytical (Eq. 33) and numerical (Eq. 37) frequency spectra. For this set of data ω₁=209.44 rad/sec, ω₂=34133 rad/sec (Eqs. 37 and 40 respectively)
Fig. 8 Frequency response of the circuit depicted in Fig. 1 obtained assuming the parameters shown in (a).

The input (a) and output (b) functions were calculated according to Eqs. 18 and 23 respectively. These functions were digitized using $N=2048$, $\Delta t=1.465 \times 10^{-5}$ sec. Plots (c) and (d) describe the analytical (Eq. 33) and numerical (Eq. 37) frequency spectra. For this set of data $\omega_0=62.80$ rad/sec, $\omega_n=10240$ rad/sec (Eqs. 37 and 40 respectively).
IV. Summary

Equations were derived to describe the time domain response to a current step for a simple RC electrical circuit. These equations were used to generate theoretical time-dependant discrete functions that were subject to DFT by using the FFT algorithm. The complex process of analyzing electrochemical data in the time domain was simplified by analyzing it in the frequency domain. The practical implementation of the FFT algorithm was discussed. The limitations and application range of the time domain to frequency domain transformation were also explored. It was stressed that provided the same system is analyzed, current interruption and AC impedance can provide the same information.
Appendix 4 Analytical Chemistry of Electrolyte Solutions Containing PbSiF$_6$-H$_2$SiF$_6$

I. Objectives:

A) To describe the different techniques that have been reported in the literature to analyze solutions containing H$_2$SiF$_6$.

B) To explain how a modified technique for analyzing H$_2$SiF$_6$ solutions was developed.

C) To describe the analytical technique used in the present study to analyze H$_2$SiF$_6$-PbSiF$_6$ electrolytes.

A. Chemical analysis of H$_2$SiF$_6$ solutions

1. Overview of the acid properties

The different techniques reported in the literature [1-8] for the analysis of H$_2$SiF$_6$ solutions are based on the very special properties of this acid. Upon dissociation, H$_2$SiF$_6$ behaves like a strong acid, its strength being close to that of H$_2$SO$_4$ solutions [9]. By potentiometric titration of H$_2$SiF$_6$ solutions in water and in various organic solvents, the first and second dissociation constants of the acid were determined [9]:

$$
\begin{align*}
H_2SiF_6 & \rightleftharpoons HSiF^- + H^+ & pK_1 & = -0.13 \\
HSiF^- & \rightleftharpoons SiF^-_2 + H^+ & pK_2 & = 1.79
\end{align*}
$$

The H$_2$SiF$_6$ molecule is known to exist only in aqueous solutions [1,7,10-13]. On evaporation, H$_2$SiF$_6$ solutions decompose into SiF$_4$ (g) and HF (g) [7,10]$^1$. The maximum concentration of the acid that has been found in liquid solutions is 61% [3,10].

$^1$ Solutions with more than 13.3% H$_2$SiF$_6$ become enriched with HF due to preferential evaporation of SiF$_4$. Reciprocally, SiF$_4$ solution enrichment takes place upon evaporation of solutions with less than 13.3% H$_2$SiF$_6$ [7,10].
The fluorine to silica ratio \(^1\) in \(\text{H}_2\text{SiF}_6\) solutions is not always equal to six \([11,14-16]\). \(\frac{F}{Si}\) ratios larger than 6 are observed in solutions in which HF is present. Solutions with \(\frac{F}{Si}\) ratios lower than 6 are observed when the acid has an excess of \(\text{SiO}_2\cdot n\text{H}_2\text{O}\). A large variety of compounds containing silica can be present under these conditions. Among these, conductometric and cryoscopic measurements have shown that the solubility of \(\text{SiO}_2\) in \(\text{H}_2\text{SiF}_6\) is due to the formation of \(\text{SiF}_4\cdot 2\text{H}_2\text{O}\) \([15]\). This compound behaves like a strong acid \([16]\). The \(\frac{F}{Si}\) number depends on the technique used to produce the acid \([11,14,17]\). \(\frac{F}{Si}\) ratios can also be changed by dilution \([18]\).

In dilute solutions, hydrolysis of \(\text{SiF}_6^{2-}\) takes place in different steps which involve intermediate splitting of one \(F^-\) and formation of \(\text{SiF}_5[\text{H}_2\text{O}]^-\) (reaction 3). This compound loses its \(F^-\) atom in a second step forming \(\text{SiF}_4\) which then hydrolyses towards \(\text{H}_2\text{SiO}_3\) (reactions 4 and 5) \([5,14,19-21]\):

\[
\begin{align*}
\text{SiF}_6^{2-} + 2\text{H}_2\text{O} &\rightleftharpoons \text{SiF}_5[\text{H}_2\text{O}]^- + F^- \quad \ldots 3 \\
\text{SiF}_5[\text{H}_2\text{O}]^- + \text{H}_2\text{O} &\rightleftharpoons \text{SiF}_4 + F^- + 2\text{H}_2\text{O} \quad \ldots 4 \\
\text{SiF}_4 + 3\text{H}_2\text{O} &\rightleftharpoons \text{H}_2\text{SiO}_3 + \text{HF} \quad \ldots 5
\end{align*}
\]

In very dilute solutions, \(\text{SiF}_6^{2-}\) is completely dissociated \([20,22]\). This has lead to the use of fluorosilicates (i.e. \(\text{Na}_2\text{SiF}_6\)) for the fluoridation of water supplies \([23,24]\). Data on the physico-chemical properties of \(\text{H}_2\text{SiF}_6\) solutions are reported extensively in the literature \([18,22,24-30]\).

2. Techniques for the analysis of \(\text{H}_2\text{SiF}_6\) solutions

\(\text{H}_2\text{SiF}_6\) solutions have been analyzed using titrimetric techniques \([3,6,8]\). The acid is titrated against alkaline solutions such as \(\text{NaOH}\) or \(\text{LiOH}\). During the titration, two equivalence points can be observed. The first equivalence point corresponds to the neutralization of the acid and the second equivalence point corresponds to the hydrolysis of the hexafluorosilicate ion. The two equivalence points can be described by the following reactions:

---

1 In \(\text{H}_2\text{SiF}_6\) solutions the fluorine to silica ratio is defined as:

\[
\frac{F}{Si} = \frac{6 \cdot [\text{H}_2\text{SiF}_6] + [\text{HF}]}{[\text{H}_2\text{SiF}_6] + [\text{SiO}_3]}
\]

2 \(\text{SiF}_6^{2-}\) is an octahedral ion.
Techniques for the analysis of H$_2$SiF$_6$ solutions

\[
H_2SiF_6 + 2NaOH \rightarrow Na_2SiF_6 + H_2O \quad \ldots 6
\]

\[
Na_2SiF_6 + 4NaOH \rightarrow 6NaF + H_2SiO_3 + H_2O \quad \ldots 7
\]

Reactions 6 and 7 indicate that the amount of alkali required in the second equivalence point should be equal to twice the amount used for the neutralization of the acid. Disagreement in these values indicates the presence of other species in solution. The presence of HF and soluble SiO$_2$ compounds in H$_2$SiF$_6$ solutions have accounted for these discrepancies. In addition to this, it has been found, that the hydrolysis of SiF$_6^{2-}$ is kinetically slow [20]. To circumvent these limitations, various analytical techniques have been proposed [3,8]. In these techniques, a two-step titration routine has been used to analyze the acid for H$_2$SiF$_6$, and either SiO$_2$ or HF. The first step in this routine consists in adding a suitable salt to precipitate the hexafluorosilicate ions. When this salt is chosen to be a fluoride salt, SiO$_2$ can be determined in the same titration. Thus, if NaF is added to the H$_2$SiF$_6$ solution, the following reactions take place:

\[
H_2SiF_6 + 2NaF \rightarrow Na_2SiF_6 \downarrow +2HF \quad \ldots 8
\]

\[
6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O \quad \ldots 9
\]

Reactions 8 and 9 show that by adding an excess of NaF, all the hexafluorosilicate ions are present as Na$_2$SiF$_6$. If any SiO$_2$ were present, it would react with HF according to reaction 9. The total amount of HF is obtained by titrating the solution at low temperatures [10]$^1$ using NaOH:

\[
HF + NaOH \rightarrow NaF + H_2O \quad \ldots 10
\]

Reaction 10 reaches completion at a pH close to 8.

Once this first step is completed, the sample is diluted with hot water and titrated near its boiling point$^2$. This dilution and solution warming brings all the hexafluorosilicate ions into solution allowing reaction 7 to take place. This reaction reaches completion near pH 10. From the stoichiometry of reactions 7 to 10, the acid composition can be found. If the amount of alkali spent during

---

$^1$ This titration has to be carried out at low temperatures (near 0 °C) to avoid dissolution of sodium hexafluorosilicate. The solubility of Na$_2$SiF$_6$ is: 6.52 g/l at 17°C and 24.54 g/l at 100°C.

$^2$ Titration of the solution near its boiling point aids in the kinetics of the hydrolysis reaction.

[314]
the second titration was larger than twice as much the amount spent in the first titration, HF was present in the sample. A reciprocal relation will indicate that SiO₂ was present in the solution.

Experimentally this two-step titration technique is difficult to perform. The main difficulties in the implementation of the technique are the cooling and heating operations which have to be performed carefully. Dilution of the samples can be a source of error as some unaccounted fluorosilicate hydrolysis can occur. Additionally, any alkali added in excess during the first titration will react with the hexafluorosilicate ions. Jacobson [3] points out that in addition to the temperature of the solution during the first titration being very low, the solution has to be concentrated so that the reaction products of the first stage do not pass into the second stage before the first stage reactions are completed. Notwithstanding these difficulties, this technique provides accurate acid analysis and its use is frequently reported in the literature [5,18].

3. Analysis of H₂SiF₆-PbSiF₆ electrolytes

Analysis of the electrolyte used in lead refining has been carried out by modifying the two-stage titration previously described [7,31]. In the analysis of H₂SiF₆-PbSiF₆ electrolytes, Pb has to be removed before the acid is titrated. Use of Na₂SO₄ to separate Pb from the electrolyte was discarded due to potential co-precipitation of Na₂SiF₆ with PbSO₄ [31]. To avoid this loss of SiF₆⁻², known amounts of H₂SO₄ are added to the sample to remove Pb⁺² as PbSO₄ (see reaction 11). The precipitation of PbSO₄ releases an equivalent amount of H₂SiF₆ that can be subsequently titrated using the two-stage titration previously described.

\[
PbSiF₆ + H₂SO₄ \rightarrow H₂SiF₆ + PbSO₄ \downarrow \quad \ldots 11
\]

B. Modification of existing experimental procedure

1. Background

The two-step titration technique was modified so as to determine, in a single step, H₂SiF₆, and either SiO₂ or HF. The approach that was taken was to titrate
the acid against LiOH adding LiF and/or HF. $H_2SiF_6$ solutions were titrated at room temperature using an automatic titration system\(^1\). The same $H_2SiF_6$ solution (sample S1\(^3\)) was titrated under the following conditions:

- **Case A:** Straight titration against LiOH in the presence of excess SiO\(_2\).
- **Case B:** Titration against LiOH in the presence of excess HF.
- **Case C:** Titration against LiOH in the presence of excess HF and LiF.
- **Case D:** Titration against LiOH when LiF is added previous to the titration.

Each of these routines is explained in the following paragraphs.

**(A) Straight titration against LiOH in the presence of excess SiO\(_2\).**

When $H_2SiF_6$ solutions are titrated against LiOH, the following reactions take place:

\[
\begin{align*}
H_2SiF_6 + 2LiOH & \rightarrow Li_2SiF_6 + H_2O \quad \ldots 12 \\
Li_2SiF_6 + 4LiOH & \rightarrow 6LiF + H_2SiO_3 + H_2O \quad \ldots 13
\end{align*}
\]

$Li_2SiF_6$ is the most soluble of all the alkali fluosilicates\(^3\). Thus, upon neutralization of the acid (reaction 12), all the $SiF_6^{2-}$ remains in solution. As these ions are already in solution, heating and dilution preceding hydrolysis via reaction 13, are not required. On the other hand, the hydrolysis reaction has to be carried out very slowly to circumvent its kinetic limitations. Fig. 1.A shows the titration curve\(^4\) obtained under these conditions\(^5\). Two equivalence points are present during the titration of the acid. The first equivalence point takes place at a pH between 3.5 and 4 and corresponds to reaction 12. The second equivalence point takes place at pH values between 7.7 and 8.4 and corresponds to reaction 13. While $[H_2SiF_6]$ can be calculated from the total amount of LiOH spent in the titration, $[SiO_2]$ cannot be quantified using this technique\(^6,7\).

---

1 Radiometer end-point titration system model ETS 822.
2 Acid composition 2.03 $M$ $H_2SiF_6$ and 0.40 $M$ SiO\(_2\). All samples were titrated against 0.8657 $M$ LiOH.
3 The solubility of LiSiF\(_6\) $2H_2O$ is 730 g/l, $T=17^\circ C$.
4 Titration curves are shown primarily to indicate where equivalence points are observed. Particular characteristics of these curves may vary depending on the experimental conditions.
5 0.5 ml of the acid sample S1 was diluted to 20 ml with deionized water and titrated using 0.8657 $M$ LiOH.
6 The presence of SiO\(_2\) in the sample will be indicated by the difference in alkali volumes spent during the first and second equivalence points.
7 $[H_2SiF_6]$, $[PbSiF_6]$, [HF], [SiO\(_3\)] = concentrations of the indicated species in mol/l, [M].
(B) Titration against LiOH in the presence of excess HF.

The sample analyzed in Case A showed that SiO₂ was present. To quantify it, a known amount of HF was added to the sample:\(^1\)

HF reacts with SiO₂ according to reaction 9 producing H₂SiF₆. Upon titration of the acid, any HF in solution is neutralized according to:

\[
HF + LiOH \rightarrow LiF + H₂O
\] \(\ldots14\)

Fig. 1.B shows the titration curve obtained in a sample containing H₂SiF₆ and HF. This curve shows that reactions 12 and 14 take place very close to each other (at a pH between 3.1 and 3.8). Furthermore, hydrolysis of SiF₆²⁻ takes place at a pH between 7.7 and 8.4 (reaction 13). From the alkali volumes spent to reach the first and second equivalence points, [H₂SiF₆] and [HF] can be calculated. By deducting the amount of H₂SiF₆ released during reaction 9, [SiO₂] could be obtained.

(C) Titration against LiOH in the presence of excess HF and LiF.

To differentiate between reactions 12 and 14 during the first neutralization reaction, LiF was added to the original acid sample. Additionally, HF was added to this solution:\(^2\)

LiF reacts with H₂SiF₆ according to the following relationship:

\[
H₂SiF₆ + 2LiF \rightarrow Li₂SiF₆ + 2HF
\] \(\ldots15\)

As reaction 15 shows, by adding LiF to the sample, only HF and Li₂SiF₆ are present in solution. Thus, only two well-defined equivalence points are expected upon titration of this sample. As Fig. 1.C shows, these points are well defined, and agree with reactions 13 and 14. Accurate acid analysis can be obtained by analyzing this titration curve.

---

1 2 ml of 1.127 M HF were added to 0.5 ml of the acid sample S1. Afterwards the solution was diluted to 20 ml using deionized water.

2 2 ml of 1.127 M HF were added to 0.5 ml of the acid sample S1. Afterwards the solution was diluted to 20 ml using deionized water. To this solution = 0.5 g of CP LiF was added.
Fig. 1 Changes in pH during the titration of a H$_2$SiF$_6$ solution against LiOH (Sample S1, Table 1).

(A) Case A: Straight titration
(B) Case B: Added HF
(C) Case C: Added HF + LiF
(D) Case D: Added LiF (LiF-LiOH Technique).
**Titration against LiOH when LiF is added previous to the titration.**

To the original acid sample, LiF was added and the solution was titrated against LiOH\(^1\). The two equivalence points described by reactions 13 and 14 can be observed in Fig. 1.D. As in the previous case, accurate analysis of the solution can be obtained by analyzing the titration curve.

**Comparison of the different analytical routines:**

The results obtained by analyzing the same acid sample using the routines previously described are shown in Table 1. Similar concentrations can be found by either of these techniques. The technique described in **Case D** (LiF-LiOH technique) proved to give accurate acid analysis and was used extensively in this work. This technique was used to analyze \(H_2SiF_6\) within \(\pm 1.5\) g/l, SiO\(_2\) within \(\pm 1\) g/l, and HF within \(\pm 1\) g/l. When PbSiF\(_6\)-H\(_2\)SiF\(_6\) solutions were analyzed by this technique, Pb was removed prior to the acid analysis by using Li\(_2\)SO\(_4\):

\[
PbSiF_6 + Li_2SO_4 \rightarrow Li_2SiF_6 + PbSO_4 \downarrow \quad \ldots 16
\]

The amount of Li\(_2\)SiF\(_6\) released by Li\(_2\)SO\(_4\) can be calculated by knowing the Pb content of the sample. Pb is quantified in a separate sample by using EDTA complexometric analysis [32].

<table>
<thead>
<tr>
<th>Table 1 Comparison of the different analytical techniques.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technique</td>
</tr>
<tr>
<td>----------------------------</td>
</tr>
<tr>
<td>Two-step titration:</td>
</tr>
<tr>
<td>Cold-Hot titration</td>
</tr>
<tr>
<td>One Step LiOH Titrations:</td>
</tr>
<tr>
<td><strong>Case A:</strong> Straight titration</td>
</tr>
<tr>
<td><strong>Case B:</strong> HF added.</td>
</tr>
<tr>
<td><strong>Case C:</strong> HF and LiF added.</td>
</tr>
<tr>
<td><strong>Case D:</strong> LiF added.</td>
</tr>
</tbody>
</table>

1. 0.5 ml of the acid sample S1 was diluted to 20 ml using deionized water. To this solution = 0.5 g of CP LiF was added.

[319]
C. $H_2SiF_6$ and HF or SiO$_2$ analysis in $H_2SiF_6$-$PbSiF_6$ electrolytes (LiF-LiOH Technique)

1. Analytical routine

Pipette a 2-ml aliquot of the sample into a plastic centrifuge tube$^1$, add approximately 10-ml of $\approx 0.2$ M Li$_2$SO$_4$$^2$. Mix well, then centrifuge for 5 minutes. Decant the supernatant liquor into a 50-ml beaker. Wash the solid residue in the centrifuge twice with 2-3 ml of distilled water, and add the washings to the solution in the beaker. Add $\approx 0.5$ g of powdered CP LiF. Stir well and titrate the mixture with LiOH$^3$ up to a pH of 3-4 (first equivalence point). Record this volume as $V_1$. Continue the titration adding LiOH at a very slow rate$^4$ up to a pH of 6.8-7.3. Record this volume as $V_2$ (second equivalence point).

To titrate the acid sample, use of an automatic titration system is highly recommended. In this set-up LiOH addition rates can be set to very low speeds. Also, the equivalence points can be easily determined by obtaining the derivative of the titration curve.

2. Reactions

As described previously, the reactions that take place during the LiF-LiOH titration are as follows$^5$:

(a) Neutralization of the lead salt:

$$PbSiF_6 + Li_2SO_4 \rightarrow Li_2SiF_6 + PbSO_4 \downarrow \quad \ldots \ldots 16$$

(b) Addition of LiF and reaction of HF with SiO$_2$ (if present):

$$H_2SiF_6 + 2LiF \rightarrow Li_2SiF_6 + 2HF \quad \ldots \ldots 15$$

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O \quad \ldots \ldots 9$$

(c) First neutralization point pH= 3-4:

$$HF + LiOH \rightarrow LiF + H_2O \quad \ldots \ldots 14$$

---

1 Plastic tube volume larger than 10 ml.
2 Add enough Li$_2$SO$_4$ so as to neutralize all the lead salt present in the electrolyte (reaction 15).
3 LiOH = 0.9 M, known titer.
4 LiOH addition rates smaller than 0.5 ml/min.
5 $[Pb]$ = Lead concentration in the sample as obtained in a separate analytical routine, M.

$V_{\text{sample}}$ = Volume of the acid sample, ml.
Record the volume of LiOH spent as \( V_1 \) and obtain the moles of LiOH required in this titration: 
\[
m_1 = V_1 \times [\text{LiOH}]
\]

(d) Second neutralization point pH = 6.8-7.3

\[
Li_2SiF_6 + 4LiOH \rightarrow 6LiF + H_2SiO_3 + H_2O
\]

Record the volume of LiOH spent as \( V_2 \) and obtain the moles of LiOH required in this titration: 
\[
m_2 = V_2 \times [\text{LiOH}]
\]

3. Calculation of results

HF is present when: 
\( 2V_1 > V_2 \). Compute \([HF]\) and \([H_2SiF_6]\) as follows:

\[
[H_2SiF_6] = \frac{m_2}{V_{\text{sample}}} - \frac{1}{4}[Pb]
\]

\[
[HF] = \frac{m_1}{V_{\text{sample}}} - 2[H_2SiF_6]
\]

SiO_2 is present when: 
\( 2V_1 < V_2 \). Compute \([SiO_2]\) and \([H_2SiF_6]\) as follows:

\[
[H_2SiF_6] = \frac{(m_1 + m_2) - 4[Pb]V_{\text{sample}}}{6V_{\text{sample}}}
\]

\[
[SiO_2] = \frac{2[H_2SiF_6] - \frac{m_1}{V_{\text{sample}}}}{4}
\]

The total fluorine to silica ratio is derived from the following relationship:

\[
\frac{F}{Si} = \frac{6[H_2SiF_6] + [PbSiF_6] + [HF]}{[H_2SiF_6] + [PbSiF_6] + [SiO_2]}
\]
Appendix 5 Computer Interfacing of the Wenking Potentiostat: Calibration of the Routines used to Interrupt the Current

I. Objectives:

A) To explain some of the details involved in the computer interfacing of the Wenking potentiostat.

B) To describe the algorithm used to interrupt the current.

C) To demonstrate how by using "dummy" cell circuits the current interruption routines were checked.

D) To analyze the experimental results obtained in the time domain in the frequency domain by using the FFT algorithm.

A. Current interruption using the Wenking potentiostat

In Chapter 3 the various connections required to interface the computer to the potentiostat were described (see Fig. 3.6). Current was halted by using a mercury wetted relay activated by the computer. This relay short circuits the battery that controls the amount of current that goes through the electrochemical cell. To activate this relay, a DC voltage of at least 3.5 V is required. Voltages smaller than 0.5 V deactivate the relay allowing current to flow back to the cell. The easiest and fastest way of controlling the relay operations was found to be through the use of the digital output of the DT2805 board\(^1\).\(^2\). By setting the output value of the digital bits to 1, the relay was activated and the current halted\(^3\). Accordingly, resetting this value to zero opened the short circuit imposed by the relay, allowing the re-establishment of the current flow.

During the galvanostatic experiments, at least two data acquisition channels were used\(^4\). One of these channels was used to record the difference in potential between the reference and working electrodes. The other was used to monitor the current flow to the cell. As Fig. 3.6 shows, all the data logger channels were

---

1 When a digital value of 1 ("high" bit status), is output a voltage of \(\approx 2.5\) volts is generated, and when its value is zero ("low" bit status), the voltage output value drops to \(\approx 0.2\) V. This signal goes back and forth in the shape of a pulse.

2 To generate the required voltages to activate the relay three digital output bits were connected in series.

3 Oscilloscope readings showed that current was halted within 10 \(\mu\)sec.

4 Additional channels were used when the difference in potential between the inner slimes electrolyte and the working electrode was measured.
grounded with respect to the working electrode. This aided in preventing common mode voltages. Additionally, common mode voltages were avoided by not making direct connections between the counter electrode and the DT2805 board.

**B. Algorithm used to interrupt the current.**

Concurrent interruption of current at preset times under galvanostatic conditions was implemented by the hardware connections shown in Fig. 3.6. In addition, appropriate software programs were developed. The characteristics of these programs varied according to the number of channels sampled, the length of the experiment, and the extent and frequency of the current interruptions.

The computer programs were written so as to handle up to a maximum of 8 analogue input channels. Additionally, control of the digital bits used to generate the voltages required to control the relay's functions was incorporated in these programs. Thus, data acquisition and setting and resetting of digital bits were the tasks considered in the program's algorithm. In this algorithm, the speed at which these operations took place was the most important parameter accounted for.

The different operations performed by the computer were programmed by using the "foreground/background" operation mode. In this mode, all the tasks performed by the DT2805 board are executed in the "background" while the computer is free to do other operations in the "foreground". The rate at which the background operations run is set by fixing the **task period**. Additionally, the frequency at which each task runs is controlled by fixing the **task modulo**. Moreover, tasks may start synchronously but they may not be instantaneously activated. The **task phase** controls how many task periods have to take place before the task is first executed. Furthermore, completion of a specific task may activate/deactivate other tasks. The state of each task may also be altered from the "foreground" operating mode. Also, tasks become idle, once the number of times the task has been executed equals a preset value. This preset value is defined as the **number of iterations**.

Table 1 shows the task set-up used to control the DT2805 operations. Typical values for the task modulo, task phase, and number of times the task is executed are provided in this table. The order in which each task is defined is important as tasks are executed sequentially rather than simultaneously. Every task period, the status of each task is checked. If the task status is idle, the task is skipped and the next task is executed.
Algorithm used to interrupt the current.

### Table 1: Tasks description and typical parameter values.

<table>
<thead>
<tr>
<th>Task</th>
<th>Function</th>
<th>Description</th>
<th>Task Modulo</th>
<th>Task Phase</th>
<th>Number of Iterations</th>
<th>Task Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Set bits</td>
<td>Halts flow of current to the cell</td>
<td>9</td>
<td>9</td>
<td>1</td>
<td>Typical values when task period = 4 msec</td>
</tr>
<tr>
<td>2</td>
<td>Reset bits</td>
<td>Re-establishes flow of current to the cell</td>
<td>50</td>
<td>50</td>
<td>1</td>
<td>Tasks simultaneously activated by Task 4</td>
</tr>
<tr>
<td>3</td>
<td>Acquire data</td>
<td>&quot;Transient Recorder Mode&quot;. Logs data continuously before, after, and during current interruption.</td>
<td>1</td>
<td>1</td>
<td>100</td>
<td>These tasks control the current interruption cycle</td>
</tr>
<tr>
<td>4</td>
<td>No operation</td>
<td>Once activated it starts the current interruption routine by starting Tasks 1, 2, and 3.</td>
<td>1</td>
<td>1</td>
<td>(\infty)</td>
<td>&quot;Foreground&quot; activated once Task 5 buffer is filled. &quot;Background&quot; deactivated once Task 3 is completed</td>
</tr>
<tr>
<td>5</td>
<td>Acquire data</td>
<td>&quot;Data Logger Mode&quot;. Logs data during normal galvanostatic conditions. This task controls the current interruption frequency and the experiment length. Every certain number of acquired points Task 4 is activated.</td>
<td>25000</td>
<td>25000</td>
<td>3900</td>
<td>Always active</td>
</tr>
</tbody>
</table>

As was previously described, all tasks run at the same rate. This rate is fixed by the value of the task period which for most of the programs was set to 4 msec. The frequency at which tasks are executed is fixed by the task modulo. Thus, for example, Task 5 was used to acquire a set of data points every 100 sec (i.e. 25000 times 4 msec). These data were sequentially put in a buffer array. The size of this array was selected to control the current interruption frequency. Thus, every time the buffer array was filled, data were saved in the computer's hard drive, and Task 4 was activated. Once Task 4 is activated, Tasks 1, 2, and 3 start simultaneously. These three tasks are executed sequentially. However, Tasks 1 and 2 start only after a certain number of tasks periods (or clock-ticks) have gone by, whereas Task 3 is executed immediately. Task 3 acquires data at the highest acquisition rate set by the task period (in this case at 250 Hz). As Table 1 shows, 100 data points are collected at this acquisition rate (i.e. during 400 msec). After 9 data points have been collected, Task 1 sends a high bit and halts the flow of
current. As this task is executed first, there is a time lag between the current interruption and the acquisition of the tenth set of data points. This time lag is due to the fact that the computer has to check Task 2 status before executing Task 3 (i.e. there is a software overload). This time lag was measured with an oscilloscope and was of the order of 1 msec. The current interruption length is controlled by Task 2. Task 2 phase is 50, thus, current was interrupted during 41 clock-ticks (i.e. during 164 msec). After this time, Task 2 sends a low bit and re-establishes the flow of current. One millisecond after the short circuit is opened, data are recorded. Subsequently, samples are taken every 4 msec during a period of 196 msec. Once Task 3 is completed, Task 4 is deactivated and the data are saved in the computer's hard drive. As Task 5 is active all the time, the previous process repeats as often as Task 5 buffer is filled. The data acquisition program ends when task 5 becomes idle (i.e. after 3900 data points or 108.33 Hrs.).

During the data acquisition run, an interactive procedure for changing the A/D gain was incorporated in the computer program. Thus, the DT2805 board measured potentials lower than 100 mV with an accuracy of ±0.3 mV. Potentials between 100 and 1000 mV were measured within ±1 mV.

C. Calibration of the routines used to interrupt the current

In addition to using an oscilloscope to check the input-output operations performed by the DT2805 board, "dummy" cell circuits were also used. A typical RC circuit equal to the one shown in Fig. A3.1.A was assembled out of commercial components. Capacitors and resistors of known values were used to test the current interruption routines. The nominal value of the components was compared with the obtained empirically.

Fig. 1 shows the empirical potential and current waveforms obtained by current interruption. The theoretical values of the elements of the circuit are shown in the figure. Also, the points at which samples were taken are marked in the plots. In all the cases, current was interrupted after applying current to the circuit for several minutes. Thus, the initial charging of the capacitor is not shown.

---

1 The DT2805 board performs analogue to digital (A/D) conversions at a 12-bit resolution. Four input voltage ranges are available in the board: -20 to 20 mV, -100 to 100 mV, -1000 to 1000 mV, and -10000 to 10000 mV. These ranges can be interactively changed by software control improving the resolution of the acquired data.

2 Resistors were measured independently by using a Tech-300 digital voltmeter. Capacitor values were obtained by using AC impedance techniques (see Appendix 6).

[325]
Calibration of the routines used to interrupt the current

![Diagram](image)

Fig. 1 Transients obtained upon current interruption using a dummy cell

Experimental data: $R_1 = 15.1 \, \Omega$, $R_2 = 10.2 \, \Omega$, $c = 3147 \, \mu F$.
Theoretical data derived from analysis of the potential decay: $R_1 = 15.1 \, \Omega$, $R_2 = 10.1 \, \Omega$, $c = 3140 \, \mu F$.

(A) Current as a function of time
(B) Potential as a function of time

in these transient curves. As Fig. 1.A shows, current is interrupted almost immediately after sending a "high" bit from the computer. On the other hand, several milliseconds are required for the current to recover its previous value once the short circuit is opened.

The response of RC circuit upon current interruption was studied using the equations developed in Appendix 3. Eqs. A3.24 to A3.26 were used to obtain the values of the components of the electrical circuit. The potential upon current interruption was fitted to Eq. A3.26. From this equation the $R_2$ and $c$ values were obtained. Extrapolation of this curve at time zero provided the $R_1$ value.
Table 2: Comparison between experimental and theoretical RC component values obtained by the interruption technique

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<tr>
<th>mAmp</th>
<th>Theoretical values</th>
<th>Experimental Values</th>
<th>Regression</th>
<th>No. points Considered</th>
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<td>$R_2$, $\Omega$</td>
<td>$c$, $\mu F$</td>
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<td>24.63</td>
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<td>***</td>
<td>-0.500</td>
</tr>
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</table>
Table 2 shows the values of resistors and capacitors obtained for different current levels. The theoretical and experimental values of the components of the electrical circuit are shown in this table. The first two rows of data show the circuit parameters obtained when a single resistor is used as a dummy cell. In all the other cases, the circuit shown in Fig. A3.1.A was used. The number of points upon current interruption used to fit the data to Eq. A3.26 is also presented in Table 2. The parameters used in the current interruption routine to obtain these data sets were the same in all the cases (Table 1).

Table 2 shows that as long as the time constant of the electrical circuit is larger than 10 msec, accurate values of the parameters of the circuit can be obtained. These large time constants are present in the sets where the 3147 and 1117 μF capacitors were used. Circuits in which smaller time constants were used did not provide accurate parameter values. In these circuits, only the total resistance value \( R_1 + R_2 \) can be obtained. In both cases, the amount of steady state current going through the circuit does not seem to have an effect on the calculation of the parameters of the circuit.

**D. Time domain to frequency domain transformation: experimental results**

In Appendix 3 the fundamentals behind the time domain to frequency domain transformation were presented. Here, FFT techniques will be used to Fourier transform the time domain transients presented in Fig. 1.

The FFT algorithm requires the data to be given as sets of \( 2^q \) (\( q \) being a positive integer number) equally spaced data points. Thus, to satisfy these requirements, the transient functions shown in Fig. 1 were modified. This was done by curve fitting these functions using high order polynomials over different time intervals. Once the transients were curve fitted, they were reconstructed using a uniform sample interval equal to 1 msec. By doing this, the functions shown in Fig. 1 were represented by 400 points rather than by the original 100 points. To increase the range of the frequency spectrum and to have the required \( 2^q \) data points, the transient functions were extended. Thus, a total of 4096 points were Fourier transformed. The impedance of the system was obtained by Fourier transforming

---

1 The time constant for the RC circuit shown in Fig. A3.1.A can be expressed by: \( \tau(\text{sec}) = R \cdot C \)
the output (potential transient) and the input (current transient) functions and taking their ratio. The results of this transformation are shown in Fig. 2. The theoretical impedance spectrum is also shown in this figure.

![Diagram of circuit](A)

Fig. 2 Frequency domain representation of the time domain data presented in Fig 1.

The analytical solution was computed using the known parameter values: \( R_1 = 15.1 \, \Omega, R_2 = 10.2 \, \Omega, c = 3147 \, \mu\text{F} \).

The numerical solution was obtained by applying the FFT algorithm to the experimental data presented in Fig. 1, from which the following values were obtained: \( R_1 = 15.3 \, \Omega, R_2 = 9.9 \, \Omega, c = 2864 \, \mu\text{F} \).

(A) Argand Plot
(B) Bode Plot

Fig. 2 shows that the circuit parameters derived from the experimental data are within 10% of the theoretical values. These values are not as good as the ones obtained by time domain analysis. However, if the electrical analogue had not been known in advance, Fourier transformation would have shown some of the characteristics of the circuit. Thus, time domain and frequency domain analysis can be used concurrently to study and verify experimental data. As the information provided by each technique is given by only changing the frame of reference (time \( \Rightarrow \) frequency), the data can be interpreted from different perspectives.
Appendix 6 Current Interruption and AC Impedance Measurements using the Solartron Devices

I. Objectives:

A) To describe how the Solartron Electrochemical Interface (SEI) performs the "sampled" current interruption procedure.

B) To describe the implementation of the AC impedance measurements using the SEI and the Frequency Response Analyzer (FRA).

A. Current interruption using the SEI

The SEI offers three ways of compensating for the value of IRg * 1. Two of them (Feedback and Real Part Correction) require the value of the uncompensated ohmic resistance, Rg, to be known in advance. The third of these procedures, the "sampled" IRg drop compensation, determines Rg by using a current interruption routine. Use of this routine involved the quantification of the potential and current values during current interruption conditions. These values are different from the ones observed under steady state conditions as the SEI interrupts the current continuously at frequencies as high as 18.5 KHz. Thus, by executing the "sampled" interruption routine, the following parameters are obtained:

a) P_actual: This is the value of the potential actually being applied to the cell under current interruption conditions.

b) C_actual: This is the value of the current actually being applied to the cell under current interruption conditions.

C) P_sample+hold: This is the value of the potential 5 µsec before current is applied back to the cell.

From these parameters the value of the uncompensated resistance is obtained using the following equation:

\[ R_s = \frac{(P_{actual} - P_{sample + hold})}{C_{actual}} \]

The current interruption procedure was tested by using the dummy cell provided by Solartron 2. The routine was applied under potentiostatic and under galvanostatic conditions. A 18.5 KHz current interruption frequency was found

---

1 This IRg value corresponds to \( \eta_{in} \) described in Chapters 2 and 4.
2 Dummy Cell circuit 12861 ECI test module
to give the best results. The $R_s$ values obtained from this technique were within 5% of the theoretical values. Table 1 shows some of the $R_s$ values obtained under potentiostatic conditions using the Solartron dummy cell.

| Values obtained under steady-state conditions | Values obtained under current interruption conditions | Experimental value
|---------------------------------------------|----------------------------------------------------|-----------------
| Potential mV | Current $\mu$Amp | $P_{\text{actual}}$ mV | $P_{\text{sample+hold}}$ mV | $C_{\text{actual}}$ $\mu$Amp | $R_s$, $\Omega$
|----------------|------------------|---------------------|------------------------|------------------------|-----------------
| 200            | 20.86            | 234.0               | 192.3                  | 24.32                  | 1714
| 500            | 52.04            | 593                 | 483                    | 61.67                  | 1784

**B. Implementation of the AC measurements**

In a typical AC experiment, a low amplitude sinusoidal voltage waveform is generated by the FRA and sent to the SEI. Depending on whether the SEI is set to operate under potentiostatic or galvanostatic conditions, the waveform is superimposed either on the DC potential or on the DC current being applied to the cell\(^1\). The variation in current and potential measured by the SEI is fed back to the FRA which obtains the transfer function of the system. This is obtained by repeating this process for a range of frequencies. From this information, plots such as those shown in Figs. 1 and 2 are obtained. In these plots, imaginary numbers are required to express the transfer function of the system. In a Bode plot (Figs. 1.B and 2.B) the frequency of the sinusoidal waveform is plotted on the abscissa, whereas the absolute value of the impedance is plotted on the ordinate. In an Argand diagram, the real and the negative parts of the imaginary impedance are plotted on the ordinate and in the abscissa respectively (Figs. 1.A and 2.A). From the analysis of these plots, kinetic and mass transfer parameters can be deduced when electrochemical systems are studied.

---

\(^1\) If the system is controlled under galvanostatic conditions, the voltage waveform input by the FRA is converted to a current waveform by the SEI. This current signal is superimposed on the DC current being applied to the cell. The amplitude of this superimposed signal is obtained by dividing the sinusoidal voltage amplitude by the value of the resistor used in the SEI to measure current.
To illustrate the use of the AC impedance technique dummy cells were assembled. The impedance of these circuits was measured using the experimental set-up shown in Figs. 3.7 and 3.8. The frequency spectrum was obtained under potentiostatic control using 5 mV R.M.S. sinusoidal waveforms. Frequency was swept between 1 and 60000 Hz. Figs. 1 and 2 show the Argand and Bode plots obtained experimentally. These curves were analyzed following the procedure described in Appendix 3, Fig. A3.4.

The curves shown in Fig. 1 correspond to the frequency spectrum of the Solartron dummy cell. This circuit has two RC components connected in series. As the time constants of these RC components are far from each other, two well resolved humps are obtained. By analyzing each hump separately, the values of the parameters of the circuit were obtained. The magnitude of these parameters was within 0.1% of the expected values.
Fig. 1 Impedance diagrams generated using a RC Dummy cell

\[ R_1 = 10.2 \, \Omega, \, R_2 = 10.2 \, \Omega, \, c = 3147 \, \mu F \]

(A) Argand Plot  (B) Bode Plot

Fig. 2 shows the frequency spectrum for a dummy cell with only one RC component. Only one hump is obtained in the Argand diagram. The \( R_1 \) and \( R_2 \) values obtained were within 1.0% of the expected values. Capacitor values measured by this technique were within 5% of the nominal value (i.e. the value provided by the manufacturer) \(^1\).

\[^1\] The capacitor measurements done by AC impedance were used as standards for calibrating the current interruption routines presented in appendix 5.
Appendix 7 Solubility of PbSiF$_6$·4H$_2$O

I. Objective:

To obtain the solubility of PbSiF$_6$·4H$_2$O in water and in H$_2$SiF$_6$ as a function of temperature and acid composition. Solubility changes are computed from data available in the literature.

II. Solubility of pure PbSiF$_6$·4H$_2$O as a function of temperature

The solubility of pure PbSiF$_6$·4H$_2$O solutions in terms of the anhydrous mole fraction is given by the following relationship [1]:

$$\log x_2 = -62.56499 + \frac{2464.4418}{T} + 21.54633 \log T \quad \ldots 1$$

where:

$x_2$ = anhydrous mole fraction (number of moles of the i-th component divided by the number of moles of the mixture).

$T$ = Temperature, K

From the $x_2$ value at a fixed temperature, the $W_{\text{anhyd}}$ value can be obtained from the following relationship:

$$W_{\text{anhyd}} = \frac{x_2 M_{\text{anhyd}}}{x_2 M_{\text{anhyd}} + (1 - x_2) M_i} \quad \ldots 2$$

where:

$W_{\text{anhyd}}$ = weight of the anhydrous component contained in 1 Kg of solution [Kg of component/ Kg solution].

$M_{\text{anhyd}}$ = molecular weight of the anhydrous component (For PbSiF$_6$, $M_{\text{anhyd}}$ is equal to 349.34 g/mol)

$M_i$ = molecular weight of the solvent (for water $M_i = 18$ g/mol)

From the $W_{\text{anhyd}}$ value obtained in Eq. 2, the $W_{\text{hydr}}$ value can be obtained as follows:

$$W_{\text{hydr}} = \left( \frac{M_{\text{anhyd}}}{M_{\text{hydr}}} \cdot \frac{1}{W_{\text{anhyd}}} - 1 \right)^{-1} \quad \ldots 3$$

where:

$W_{\text{hydr}}$ = weight of the hydrated component contained in 1 Kg of solution [Kg of component/ Kg solution].

$M_{\text{hydr}}$ = molecular weight of the hydrated component (For PbSiF$_6$·4H$_2$O, $M_{\text{hydr}}$ is equal to 421.34 g/mol)

$M_i$ = molecular weight of the solvent
Once $W_{\text{anh}}$ and $W_{\text{anh}}$ are obtained, the solubility of the salt can be obtained from any of the following relationships:

\[ m_2 = \frac{1000W_{\text{anh}}}{M_{\text{anh}}(1-W_{\text{anh}})} \] \hspace{1cm} \ldots 4

\[ P_i = \frac{100x_2M_{\text{anh}}}{x_2M_{\text{anh}} + (1-x_2)M_1} \] \hspace{1cm} \ldots 5

\[ c_2 = \frac{1000W_{\text{anh}} \rho}{M_{\text{anh}}} \] \hspace{1cm} \ldots 6

where:
- $m_2$ = molality of the solution [mol/Kg of solvent]
- $c_2$ = molarity of the solution [mol/l]
- $P_i$ = weight percent : Kg of anhydrous $i$-th component contained in 100 Kg of solution.
- $\rho$ = solution density, [g/cm$^3$]

Table 1 shows the solubility changes as a function of the temperature for pure PbSiF$_6$·4H$_2$O solutions obtained from Eqs. 1 to 6.

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<td>7.58</td>
<td>72.58</td>
<td>5.05</td>
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<td>0.7515</td>
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<td>8.66</td>
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</tr>
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<td>0.1474</td>
<td>0.7704</td>
<td>13.13</td>
<td>9.61</td>
<td>77.04</td>
<td>5.36</td>
</tr>
</tbody>
</table>

* $c_2$ values obtained using a density value $\rho = 2.43$ g/cm$^3$ [2].

III. Solubility of PbSiF$_6$·4H$_2$O in the presence of H$_2$SiF$_6$ at T=20 °C

Table 2 shows the solubility of PbSiF$_6$·4H$_2$O as a function of the H$_2$SiF$_6$ concentration as reported in the literature[3].
Table 2 Solubility of PbSiF$_6$.4H$_2$O as a function of the H$_2$SiF$_6$ concentration at T=20 °C [3].

<table>
<thead>
<tr>
<th>$P_i$ [H$_2$SiF$_6$] ,%</th>
<th>$P_i$ [PbSiF$_6$] ,%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>68.97</td>
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<tr>
<td>0.98</td>
<td>67.96</td>
</tr>
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<td>7.34</td>
<td>56.5</td>
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<td>13.93</td>
<td>43.1</td>
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<td>25.82</td>
<td>23.95</td>
</tr>
<tr>
<td>39.65</td>
<td>10.38</td>
</tr>
</tbody>
</table>

$P_i$ = weight percent : Kg of anhydrous i-th component contained in 100 Kg of solution.
Appendix 8 Solution of Fick's Second Law Equation Under Current Interruption Conditions

I. Objective:

To solve analytically Fick's Second Law equation in the presence and in the absence of a net Faradaic current. This solution will be used to predict local concentrations from which the concentration overpotential across the hypothetical Nernst diffusion layer will be derived.

II. Assumptions:

1) Dissolution of lead is the only Faradaic reaction and proceeds without kinetic limitations (i.e. \( i_o \to \infty \) for \( \text{Pb} \to \text{Pb}^{2+} + 2e^- \)).

2) Mixing of electrolytes within the hypothetical Nernst diffusion layer is neglected (\( D_e = 0 \) and \( v = 0 \)).

3) Migration is absent.

4) Activities are equal to concentrations.

5) Dissolution of lead takes place under semi-infinite, unidimensional conditions.

III. Fundamental Equations

Unsteady state diffusion can be described by Fick's second law \[1,2\]^1:

\[
D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} \quad \text{...[i]}
\]

where:

- \( C \) = concentration of species \( i \) [in this case \( \text{Pb}^{2+} \)], [mol cm\(^{-3}\)].
- \( D \) = \( \text{Pb}^{2+} \) molecular diffusion coefficient [cm\(^2\) sec\(^{-1}\)]
- \( t \) = time, [sec]
- \( x \) = distance from the electrode/solution interface, [cm]

For any problem the initial concentration, \( C' \), is known\(^2\):

---

1 In this appendix the equations presented by Bushrod et al. \[2\] are re-derived and explained in greater detail. Furthermore, a relationship between concentration overpotential and local concentrations (not included in Bushrod's derivation) is obtained.

2 i.e. \( C = C' \) for \( t = 0 \) at any point \( x \).
Eqs. [i] and [ii] can be expressed in a general form by substituting the variable $C$ for the variable $u$:

$$D \frac{\partial^2 u}{\partial x^2} = \frac{\partial u}{\partial t} \quad \ldots 1$$

$$u^* = u(x,0) \quad \ldots 2$$

The general solution of Eq. 1 subject to the initial condition 2 can be obtained from their Laplace transform.

The Laplace transform, $L$, of the left and right terms of Eq. 1, is as follows:

$$L \left[ D \frac{\partial^2 u}{\partial x^2} \right] = D \frac{\partial^2 u^*}{\partial x^2} \quad \quad \quad L \left[ \frac{\partial u}{\partial t} \right] = S \tilde{u} - u^*$$

where $\tilde{u} = \tilde{u}(x,S)$ is the Laplace transform of $u = u(x,t)$. Thus, Eq. 1 can be expressed as follows:
\[
\frac{\partial^2 u}{\partial x^2} - \frac{S}{D} u = \frac{u^*}{D}
\]  
...3

Eq. 3 can also be expressed by the following relationship:

\[
\frac{\partial^2 y}{\partial x^2} + \beta y = -\frac{C^*}{D}
\]  
...3.a

in which \( y(x) = \tilde{u}(x, S) \) and \( \beta = -\frac{S}{D} \).

The solution of Eq. 3.a can be obtained from the complementary (homogeneous) and the particular (nonhomogeneous) solutions:

The complementary solution satisfies the source free equation:

\[
\frac{\partial^2 y}{\partial x^2} = 0
\]  
...4

Eq. 4 can be solved by assuming a trial solution:

\[ y(x) = k \exp[m x] \]  
...5

where \( m \) is a dummy variable. Substituting Eq. 5 in Eq. 4 and rearranging:

\[
m^2 + \beta = 0
\]  
...6

Eq. 6 is the characteristic or auxiliary equation. Thus, solving for \( m \), the following complex conjugate roots are obtained:

\[ m_{1,2} = \pm \sqrt{-\beta} = \pm \sqrt{\frac{S}{D}} \]

from which the complementary solution of Eq. 4 is obtained:

\[
y(x) = k_1 \exp[-x\sqrt{\frac{S}{D}}] + k_2 \exp[x\sqrt{\frac{S}{D}}]
\]  
...7

Similarly, the particular solution is obtained by assuming a trial solution:

\[ y(x) = k_3 \]  
...8

Incorporating Eq. 8 in Eq. 3.a and solving for \( k_3 \):

\[ \beta k_3 + \frac{u^*}{D} = 0 \]
Finally, the general solution is obtained by adding the complementary and particular solutions:

\[ \bar{u}(x, S) = M(S) \exp \left[ -x \sqrt{\frac{S}{D}} \right] + N(S) \exp \left[ x \sqrt{\frac{S}{D}} \right] + \frac{u^*}{S} \]  

\[ y(x) = k_1 \exp \left[ x \sqrt{\frac{S}{D}} \right] + k_2 \exp \left[ x \sqrt{\frac{S}{D}} \right] + \frac{u^*}{S} \]  

\[ k_3 = \frac{u^*}{S} \]  

IV. Boundary Conditions and Analytical Solution

For semi-infinite linear diffusion \( C(\infty, t) = C^* \) and \( u(\infty, S) = \frac{u^*}{S} \). Consequently, N(S)=0 and Eq. 10 is given by:

\[ \bar{u}(x, S) = M(S) \exp \left[ -x \sqrt{\frac{S}{D}} \right] + \frac{u^*}{S} \]  

Eq. 12 will be solved for three different cases (see Fig. 2):

A) Application of a galvanostatic step \((t_1 < t)\)

B) Current Interruption in the presence of concentration gradients in the Nernst-Boundary layer \((t_1 < t < t_2)\)

C) Application of constant current after current interruption \((t > t_2)\) .
A. Application of a galvanostatic step

The boundary condition that expresses the application of a galvanostatic anodic current step is as follows:

$$\frac{\partial u}{\partial x}(o,t) = -\frac{i_1}{ZFD}$$  ...13

where:

- \(i_1\) = current density, [Amp-m²].
- \(Z\) = Charge number of Pb^{2+} [eq-mol⁻¹]

The Laplace transform of Eq. 13 is given by:

$$\frac{\partial u}{\partial x}(o,S) = -\frac{i_1}{ZFDS}$$  ...14

Thus, Eq. 14 is to be incorporated in Eq. 12 to obtain \(M(S)\), from which the changes in concentration as a function of time can be obtained. This is done as follows:

Derivating Eq. 12, rearranging and solving for \(M(S)\):
\[
\frac{\partial \bar{u}}{\partial x} (x, S) = -\sqrt{\frac{S}{D}} M(S) \exp \left[ -x \sqrt{\frac{S}{D}} \right]
\]
\[
\frac{\partial \bar{u}}{\partial x} (0, S) = -\sqrt{\frac{S}{D}} M(S) = -\frac{i_1}{Z F D S}
\]

Incorporating Eq. 16 in Eq. 12:

\[
\bar{u}(x, S) = \frac{i_1}{Z F \sqrt{D} S^3} \exp \left[ -x \sqrt{\frac{S}{D}} \right] + \frac{u^*}{S}
\]

The inverse Laplace transformation of Eq. 17 can be obtained using the following relationship:

\[
L^{-1} \left\{ \frac{1}{S^3} \exp \left[ -k \sqrt{S} \right] \right\} = 2 \sqrt{\frac{t}{\pi}} \exp \left[ -\frac{k^2}{4t} \right] - k \text{erfc} \left[ \frac{k}{2\sqrt{t}} \right]
\]

with

\[
k = \frac{x}{\sqrt{D}}
\]

Thus,

\[
u(x, t_i) = \frac{i_1}{Z F \sqrt{D}} \left\{ 2 \sqrt{\frac{t_i}{\pi}} \exp \left[ \frac{-x^2}{4Dt_i} \right] - \frac{x}{\sqrt{D}} \text{erfc} \left[ \frac{x}{2\sqrt{D}t_i} \right] \right\} + u^*
\]

\[
u(0, t_i) = \frac{2i_1}{Z F} \sqrt{\frac{t_i}{\pi D}} + u^*
\]

From Eqs. 18.a and 18.b, the concentration overpotential can be obtained from the following relationship:

\[
\eta_c(x, t) = \frac{RT}{Z F} \ln \frac{u(x, t)}{u^*}
\]

from which:
\[ \eta_c(x, t_i) = \frac{RT}{ZF} \ln \left( 1 + \frac{i_i}{ZF \sqrt{D u^*}} \left( 2 \sqrt{\frac{t_i}{\pi}} \exp \left[ \frac{-x^2}{4D t_i} \right] - \frac{x}{\sqrt{D}} \text{erfc} \left[ \frac{x}{2\sqrt{D t_i}} \right] \right) \right) \] \quad \text{...20.a}

\[ \eta_c(0, t_i) = \frac{RT}{ZF} \left( 1 + \frac{2i_i}{ZF u^* \sqrt{\pi D}} \right) \] \quad \text{...20.b}

**B. Current interruption**

After applying current for \( t_i \) sec, a concentration profile that follows Eq. 18.a is present. Thus, Eq. 12 is to be solved for the current interruption case using Eq. 18.a as initial condition and Eq. 21 as boundary condition:

\[ \frac{\partial u}{\partial x} (0, t) = 0 \]

\[ \frac{\partial u}{\partial x} (0, S) = 0 \] \quad \text{...21}

Thus, Eq. 12 can be expressed as follows:

\[ \bar{u}(x, S) = M(S) \exp \left[ -x\sqrt{\frac{S}{D}} \right] + \frac{u^*(x, t_i)}{S} \] \quad \text{...22}

Incorporating Eq. 18.a in Eq. 22 and derivating:

\[ \frac{\partial \bar{u}}{\partial x} (x, S) = -\sqrt{\frac{S}{D}} M(S) \exp \left[ -x\sqrt{\frac{S}{D}} \right] + \]

\[ + \frac{i_i}{ZF \sqrt{D}} \left\{ \frac{-4x}{4D t_i} \sqrt{\frac{t_i}{\pi}} \exp \left[ \frac{-x^2}{4D t_i} \right] \frac{1}{\sqrt{D}} \text{erf} \left[ \frac{x}{2\sqrt{D t_i}} \right] + \frac{2x}{\sqrt{D}} \exp \left[ \frac{x^2}{2D t_i} \right] \right\} \] \quad \text{...23}

Evaluating Eq. 23 at (0,S) and solving for \( M(S) \):

\[ \frac{\partial \bar{u}}{\partial x} (0, S) = -\sqrt{\frac{S}{D}} M(S) - \frac{i_i}{ZF \sqrt{D}} \frac{1}{\sqrt{D}} \frac{1}{S} = 0 \] \quad \text{...24}

\[ M(S) = -\frac{i_i}{ZF \sqrt{D} S^2} \] \quad \text{...25}

Finally, incorporating Eqs. 25 and 18.a in Eq. 22, obtaining the inverse Laplace transform and rearranging:
Application of current back to the electrode

\[ u(x,t) = \frac{i_1}{ZF\sqrt{D}} \left[ 2\sqrt{\frac{D}{\pi}} \exp\left( -\frac{x^2}{4Dt_1} \right) - 2\sqrt{\frac{D}{\pi}} \exp\left( -\frac{x^2}{4Dt_2} \right) - \frac{x}{\sqrt{D}} \left( \text{erfc} \left( \frac{x}{2\sqrt{Dt_1}} \right) - \text{erfc} \left( \frac{x}{2\sqrt{Dt_2}} \right) \right) \right] + u^* \] \quad \text{(26.a)}

\[ u(0,t) = \frac{2i_1}{ZF\sqrt{\pi D}} (\sqrt{t_1} - \sqrt{t_2}) + u^* \] \quad \text{(26.b)}

The concentration overpotential can be obtained from Eq. 26.b:

\[ \eta_c(0,t) = \frac{RT}{ZF} \ln \left( 1 + \frac{2i_1}{ZF \sqrt{\pi D}} (\sqrt{t_1} - \sqrt{t_2}) \right) \] \quad \text{(27)}

C. Application of current back to the electrode

After time \( t_2 \) current is applied back (see Fig. 1). The initial concentration profile follows Eq. 26.a, and the boundary condition is given by Eq. 28:

\[ \frac{\partial u}{\partial x} (o,t) = -\frac{i_2}{ZF D} \]

\[ \frac{\partial u}{\partial x} (o,S) = -\frac{i_2}{ZF S} \] \quad \text{(28)}

Thus Eq. 12 can be expressed as follows:

\[ \bar{u}(x,S) = M(S) \exp \left[ -x\sqrt{\frac{S}{D}} \right] + \frac{u^*(x,t_2)}{S} \] \quad \text{(29)}

Incorporating Eq. 26.a in Eq. 29 and derivating:

\[ \frac{\partial \bar{u}}{\partial x} (x,S) = -\sqrt{\frac{S}{D}} M(S) \exp \left[ -x\sqrt{\frac{S}{D}} \right] + \]

\[ + \frac{i_1}{ZF \sqrt{D}} \left( \sqrt{\frac{D}{4Dt_1}} \exp \left[ -\frac{x^2}{4Dt_1} \right] + \sqrt{\frac{D}{4Dt_2}} \exp \left[ -\frac{x^2}{4Dt_2} \right] \right) \]

\[ + \frac{i_1}{ZF \sqrt{D}} \left( \frac{1}{\sqrt{\pi}} \left( \text{erf} \left[ \frac{x}{2\sqrt{D}t_1} \right] + \text{erf} \left[ \frac{x}{2\sqrt{D}t_2} \right] \right) \right) \]

\[ + \frac{2x}{\sqrt{D}} \left( \exp \left[ \frac{x^2}{4D_1} \right] + \exp \left[ \frac{x^2}{4D_2} \right] \right) \] \quad \text{(30)}

Evaluating Eq. 30 at (0,S) and solving for M(S):
Finally, incorporating Eqs. 32 and 26.a in Eq. 29, obtaining the inverse Laplace transform and rearranging:

\[
\frac{\partial u}{\partial x}(0,S) = -\sqrt{\frac{S}{D}} M(S) + \frac{i_2}{ZF \sqrt{D} S^2} \frac{1}{S} = 0
\] ...

\[
M(S) = \frac{i_2}{ZF \sqrt{D} S^2}
\] ...

\[
\eta_c(0, t_3) = \frac{RT}{ZF} \left(1 + \frac{2}{ZF u* \sqrt{\pi D}} (i_2 \sqrt{t_3} + i_1 \sqrt{t_1} - i_1 \sqrt{t_2})\right)
\] ...

Figs. 3 and 4 show the variation in concentration and overpotential for different step functions according to Eqs. 18.b, 20.b, 26.b, 27, 33.b, and 34.
Fig. 3  Changes in $u(0,t)$ and $\eta_c(0,t)$ upon application of the current step described in Fig. 2.

$C^\prime=C(x,0)=[Pb^{2+}]_{bulk}=0.8 \text{ mol/l}, \ i_1=I_2=50 \text{ Amp-m}^2, \ D=5 \times 10^6 \text{ cm}^2\text{sec}^{-1}, \ \tau_1^\prime = 16 \text{ sec}, \ \tau_2^\prime = 32 \text{ sec}.$

(A) Changes in $[Pb^{2+}]$  (B) Changes in $\eta_c$ corresponding to the data presented in Fig. A
Fig. 4 Changes in $\eta(t,0)$ upon application of the current step described in Fig. 2. 
$C=C(x,0)=[Pb^{2+}]_{\text{bulk}}=0.8 \text{ mol} \cdot \text{L}^{-1}$, $D=5\times10^{-6} \text{ cm}^2 \text{ sec}^{-1}$

<table>
<thead>
<tr>
<th>Fig.</th>
<th>$i_1$, Amp\text{m}^{-2}</th>
<th>$i_2$, Amp\text{m}^{-2}</th>
<th>$t_1^*$, sec</th>
<th>$t_2^*$, sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>50</td>
<td>100</td>
<td>16</td>
<td>32</td>
</tr>
<tr>
<td>B</td>
<td>200</td>
<td>100</td>
<td>16</td>
<td>32</td>
</tr>
<tr>
<td>C</td>
<td>200</td>
<td>200</td>
<td>100</td>
<td>800</td>
</tr>
<tr>
<td>D</td>
<td>200</td>
<td>200</td>
<td>200</td>
<td>600</td>
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</tbody>
</table>
Appendix 9 Extended Version of Tables Presented in Chapter 6.

Objective:

To present the complete set of tables presented in chapter 6 and their associated statistical regression parameters.

Foreword:

The abstracted tables presented in chapter 6 are shown in this appendix in their complete form. The names of the tables in this appendix were chosen to correspond to those presented in chapter 6. Furthermore, the regression parameters associated with the data shown in these tables are also presented in this appendix alongside the main tables.

The regression parameters shown in this appendix were obtained from ANOVA analysis. The square of the multiple regression coefficient, $r^2$, and the square of the residual errors, $|y_r|^2$, were obtained from such analysis. These quantities are defined by the following relationships:

\[
|r|^2 = \frac{|y_x|^2}{|y|^2}
\]
\[
|y_r|^2 = |Y - Y'|^2
\]

in which:

$Y$ = Experimental data

$Y'$ = Regressed data

$y_x$ = parameter related to the variations vector, $y$ with $y = y_r + y_x$.

$y_r$ = remaining residual error

$r$ = multiple regression coefficient.

The regression parameters $r^2$ and $|y_r|^2$ obtained from the curve fitting of the AC impedance data, are given with respect to the real, $Z_R$, the imaginary, $-Z_I$, and the absolute impedances, $|Z|$, ($|Z| = \sqrt{Z_R^2 + Z_I^2}$)

---

1 ANOVA stands for Analysis of Variance.
2 $y$ and $y_x$ are related through the following relationship: $|y_x|^2 = |y|^2 - |Y - Y'|^2$
Table 3 Summary of the values of the electrical analogue parameters obtained under rest potential conditions

<table>
<thead>
<tr>
<th>Experiment and Sweep Number</th>
<th>Addition Agents</th>
<th>Pot/Gal Control</th>
<th>(\omega_{\text{min}}), (\text{rad/sec})</th>
<th>(\omega_{\text{max}}), (\text{rad/sec})</th>
<th>(R_s), (\Omega\text{cm}^2)</th>
<th>(R_m), (\Omega\text{cm}^2)</th>
<th>(C_a), (\mu\text{F cm}^2)</th>
<th>(B_1), (\Omega\text{cm}^2\text{sec}^{-1})</th>
<th>(\psi_{zc})</th>
<th>(i_0), Amp/m²</th>
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<tbody>
<tr>
<td>CA2-1</td>
<td>yes</td>
<td>Gal</td>
<td>560</td>
<td>99588</td>
<td>1.42</td>
<td>0.501</td>
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<td>23.71</td>
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<tr>
<td>CA4-1</td>
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<td>315</td>
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<td>1.855</td>
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<td>12.45</td>
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</tr>
<tr>
<td>CA5-1</td>
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<td>Pot</td>
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<td>0.725</td>
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<td>-</td>
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<tr>
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<td>Gal</td>
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<td>-</td>
<td>-</td>
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<td>0.45</td>
<td>-</td>
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<tr>
<td>CC2-1</td>
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<td>560</td>
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<td>-</td>
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<td>560</td>
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<td>0.85</td>
<td>-</td>
<td>-</td>
<td>1.88</td>
<td>0.59</td>
<td>-</td>
</tr>
</tbody>
</table>

Values of statistical parameters related to the quality of the fit:

| Experiment and Sweep Number | \(|y_r|^2\), \(\Omega^2\text{cm}^4\) | \(r^2\) | \(|y_r|^2\), \(\Omega^2\text{cm}^4\) | \(r^2\) | \(|y_r|^2\), \(\Omega^2\text{cm}^4\) | \(r^2\) | \(|y_r|^2\), \(\Omega^2\text{cm}^4\) | \(r^2\) |
|-----------------------------|-----------------|-------|-----------------|-------|-----------------|-------|-----------------|-------|
| CA2-1                       | 4.99x10⁴        | 0.972 | 2.43x10³        | 0.977 | 4.75x10²        | 0.971 |
| CA4-1                       | 2.92x10³        | 0.995 | 4.74x10³        | 0.986 | 2.45x10¹        | 0.996 |
| CA5-1                       | 1.05x10¹        | 0.976 | 6.53x10³        | 0.967 | 9.81x10²        | 0.976 |
| CA5-4                       | 2.09x10¹        | 0.969 | 1.23x10²        | 0.955 | 1.96x10¹        | 0.970 |
| CA6-2                       | 3.10x10¹        | 0.995 | 5.06x10²        | 0.992 | 5.59x10¹        | 0.996 |
| CC1-5                       | 5.09x10⁴        | 0.876 | 2.19x10⁴        | 0.966 | 3.51x10⁴        | 0.967 |
| CC1-6                       | 1.02x10³        | 0.970 | 3.11x10⁴        | 0.987 | 1.03x10³        | 0.982 |
| CC2-1                       | 8.00x10⁴        | 0.944 | 6.39x10⁵        | 0.975 | 1.16x10⁴        | 0.971 |
| CC2-2                       | 1.48x10⁴        | 0.913 | 4.75x10⁵        | 0.984 | 1.60x10⁴        | 0.966 |
Table 4 Analysis of the spikes produced during the application of the AC waveform, in the presence of a net DC current (Exp. CA2, Figs. 6.32 to 35)

| Slimes Thickness mm | Slope $R_m$, $\Omega$cm$^2$ | Intercept, $b$, (mV) | $r^2$ | $|y_i|^2$, mV$^2$ | $\frac{b}{IR_m}$ | $\rho_m$, $\Omega$cm | IR$_m$, mV | IR$_m+b$, mV | $\eta_A$, mV |
|---------------------|----------------------------|----------------------|-------|-----------------|-----------------|-----------------|-------------|--------------|--------------|
| 0.80                | 0.62                       | 30.8                 | 0.850 | 6.8             | 2.54            | 7.78            | 12.1        | 42.9         | 41.9         |
| 1.61                | 1.19                       | 38.1                 | 0.983 | 5.1             | 1.65            | 7.37            | 23.1        | 61.2         | 60.4         |
| 2.23                | 1.45                       | 45.8                 | 0.986 | 6.4             | 1.63            | 6.48            | 28.1        | 73.9         | 73.3         |
| 3.10                | 2.15                       | 54.4                 | 0.988 | 12.6            | 1.30            | 6.93            | 41.8        | 96.1         | 95.5         |
| 3.72                | 2.50                       | 61.1                 | 0.992 | 8.8             | 1.26            | 6.72            | 48.6        | 109.7        | 109.3        |
| 4.72                | 3.16                       | 73.7                 | 0.952 | 86.0            | 1.20            | 6.70            | 61.5        | 135.2        | 133.5        |
| 5.33                | 3.93                       | 75.3                 | 0.981 | 59.8            | 0.98            | 7.38            | 76.5        | 151.8        | 150.4        |
| 5.95                | 4.57                       | 82.4                 | 0.961 | 163.7           | 0.93            | 7.68            | 88.8        | 171.2        | 170.0        |
| 6.56                | 5.23                       | 93.1                 | 0.920 | 375.1           | 0.92            | 7.98            | 101.7       | 194.8        | 193.3        |
| 7.18                | 5.71                       | 113.9                | 0.905 | 633.5           | 1.03            | 7.95            | 110.9       | 224.8        | 221.8        |
| 7.79                | 7.22                       | 124.9                | 0.888 | 1192.5          | 0.89            | 9.27            | 140.3       | 265.2        | 262.4        |
| 8.41                | 4.96                       | 361.0                | 0.051 | 4386.0          | 3.74            | 5.90            | 96.5        | 457.5        | 436.0        |
| 8.65                | 9.40                       | 360.6                | 0.558 | 5688.7          | 1.97            | 10.86           | 182.7       | 543.3        | 520.0        |

Between 18 and 20 experimental points were used to obtain the regression coefficient. These points were collected during ~55 min and correspond to digitized samples taken when the frequency of the applied AC waves was between 0.063 and 6.3 rad/sec.
Table 5.A Analysis of the spikes produced during the application of the AC waveform, in the presence of a net DC current (Exp. CA6)

<table>
<thead>
<tr>
<th>Slimes Thickness (mm)</th>
<th>Slope R_m, Ωcm^-1</th>
<th>Intercept, b, (mV)</th>
<th>r²</th>
<th></th>
<th>IR_m, mV</th>
<th>IR_m+b, mV</th>
<th>ηA, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.70</td>
<td>0.36</td>
<td>24.9</td>
<td>0.95</td>
<td>0.17</td>
<td>3.56</td>
<td>5.14</td>
<td>7.0</td>
</tr>
<tr>
<td>0.98</td>
<td>0.48</td>
<td>28.4</td>
<td>0.99</td>
<td>0.03</td>
<td>3.05</td>
<td>4.90</td>
<td>9.3</td>
</tr>
<tr>
<td>1.25</td>
<td>0.67</td>
<td>29.6</td>
<td>0.98</td>
<td>0.11</td>
<td>2.28</td>
<td>5.36</td>
<td>13.0</td>
</tr>
<tr>
<td>1.47</td>
<td>0.56</td>
<td>35.7</td>
<td>0.98</td>
<td>0.04</td>
<td>3.28</td>
<td>3.83</td>
<td>10.9</td>
</tr>
<tr>
<td>2.11</td>
<td>1.00</td>
<td>38.3</td>
<td>0.99</td>
<td>0.14</td>
<td>1.96</td>
<td>4.75</td>
<td>19.5</td>
</tr>
<tr>
<td>2.39</td>
<td>1.21</td>
<td>40.0</td>
<td>0.92</td>
<td>1.80</td>
<td>1.69</td>
<td>5.08</td>
<td>23.6</td>
</tr>
<tr>
<td>2.66</td>
<td>1.15</td>
<td>46.5</td>
<td>0.97</td>
<td>0.71</td>
<td>2.09</td>
<td>4.31</td>
<td>22.3</td>
</tr>
<tr>
<td>3.06</td>
<td>1.52</td>
<td>47.0</td>
<td>0.99</td>
<td>0.40</td>
<td>1.59</td>
<td>4.98</td>
<td>29.6</td>
</tr>
<tr>
<td>5.37</td>
<td>1.89</td>
<td>93.8</td>
<td>0.85</td>
<td>15.64</td>
<td>2.55</td>
<td>3.52</td>
<td>36.8</td>
</tr>
<tr>
<td>5.58</td>
<td>2.87</td>
<td>81.4</td>
<td>0.88</td>
<td>15.37</td>
<td>1.46</td>
<td>5.14</td>
<td>55.8</td>
</tr>
<tr>
<td>5.79</td>
<td>2.16</td>
<td>98.6</td>
<td>0.97</td>
<td>4.33</td>
<td>2.35</td>
<td>3.74</td>
<td>42.0</td>
</tr>
<tr>
<td>6.00</td>
<td>2.08</td>
<td>105.7</td>
<td>0.96</td>
<td>6.85</td>
<td>2.61</td>
<td>3.47</td>
<td>40.5</td>
</tr>
<tr>
<td>6.22</td>
<td>1.95</td>
<td>113.0</td>
<td>0.92</td>
<td>10.92</td>
<td>2.98</td>
<td>3.13</td>
<td>37.9</td>
</tr>
<tr>
<td>6.43</td>
<td>2.53</td>
<td>106.1</td>
<td>0.82</td>
<td>42.73</td>
<td>2.16</td>
<td>3.94</td>
<td>49.2</td>
</tr>
<tr>
<td>6.64</td>
<td>2.70</td>
<td>113.6</td>
<td>0.88</td>
<td>10.16</td>
<td>2.16</td>
<td>4.06</td>
<td>52.5</td>
</tr>
<tr>
<td>6.85</td>
<td>2.76</td>
<td>120.3</td>
<td>0.92</td>
<td>7.49</td>
<td>2.24</td>
<td>4.02</td>
<td>53.6</td>
</tr>
<tr>
<td>7.06</td>
<td>3.36</td>
<td>118.6</td>
<td>0.85</td>
<td>24.54</td>
<td>1.82</td>
<td>4.75</td>
<td>65.3</td>
</tr>
<tr>
<td>7.28</td>
<td>3.98</td>
<td>112.3</td>
<td>0.66</td>
<td>83.22</td>
<td>1.45</td>
<td>5.47</td>
<td>77.4</td>
</tr>
<tr>
<td>7.49</td>
<td>3.13</td>
<td>140.9</td>
<td>0.97</td>
<td>4.09</td>
<td>2.31</td>
<td>4.18</td>
<td>60.9</td>
</tr>
</tbody>
</table>

4 experimental points were used to obtain the regression coefficient. These points were collected during ~12 min and correspond to digitized samples taken when the frequency of the applied AC waves was between 0.63 and 6.3 rad/sec.

Table 5.B Analyses of the spikes produced during the application of the AC waveform, under current interruption conditions (Exp. CA6)

<table>
<thead>
<tr>
<th>Time, hrs</th>
<th>Slope R_m, Ωcm^-1</th>
<th>Intercept, b, (mV)</th>
<th>r²</th>
<th></th>
<th>IR_m, mV</th>
<th>IR_m+b, mV</th>
<th>ηA, mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.63</td>
<td>2.23</td>
<td>60.8</td>
<td>0.89</td>
<td>21.95</td>
<td>2.82</td>
<td>0.0</td>
<td>60.8</td>
</tr>
<tr>
<td>2.44</td>
<td>3.62</td>
<td>48.4</td>
<td>0.91</td>
<td>41.19</td>
<td>4.57</td>
<td>0.0</td>
<td>48.4</td>
</tr>
<tr>
<td>3.83</td>
<td>3.83</td>
<td>44.5</td>
<td>0.95</td>
<td>62.43</td>
<td>4.84</td>
<td>0.0</td>
<td>44.5</td>
</tr>
<tr>
<td>9.08</td>
<td>2.93</td>
<td>31.5</td>
<td>0.79</td>
<td>154.01</td>
<td>3.70</td>
<td>0.0</td>
<td>31.5</td>
</tr>
<tr>
<td>14.33</td>
<td>2.59</td>
<td>24.0</td>
<td>0.64</td>
<td>208.29</td>
<td>3.27</td>
<td>0.0</td>
<td>24.0</td>
</tr>
<tr>
<td>41.96</td>
<td>1.92</td>
<td>6.7</td>
<td>0.88</td>
<td>30.14</td>
<td>2.42</td>
<td>0.0</td>
<td>6.7</td>
</tr>
<tr>
<td>43.07</td>
<td>1.64</td>
<td>5.3</td>
<td>0.87</td>
<td>22.09</td>
<td>2.07</td>
<td>0.0</td>
<td>5.3</td>
</tr>
<tr>
<td>54.97</td>
<td>0.98</td>
<td>3.3</td>
<td>0.37</td>
<td>22.74</td>
<td>1.24</td>
<td>0.0</td>
<td>3.3</td>
</tr>
<tr>
<td>65.17</td>
<td>1.00</td>
<td>3.3</td>
<td>0.66</td>
<td>21.53</td>
<td>1.26</td>
<td>0.0</td>
<td>3.3</td>
</tr>
<tr>
<td>91.44</td>
<td>1.15</td>
<td>2.4</td>
<td>0.95</td>
<td>17.22</td>
<td>1.14</td>
<td>0.0</td>
<td>2.4</td>
</tr>
<tr>
<td>102.00</td>
<td>0.90</td>
<td>3.4</td>
<td>0.70</td>
<td>17.22</td>
<td>1.14</td>
<td>0.0</td>
<td>3.4</td>
</tr>
<tr>
<td>112.8</td>
<td>0.99</td>
<td>0.2</td>
<td>0.69</td>
<td>21.63</td>
<td>1.25</td>
<td>0.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>

9 experimental points were used to obtain the regression coefficient. These points were collected during ~27 min and correspond to digitized samples taken when the frequency of the applied AC waves was between 0.63 and 6.3 rad/sec.
Table 6 Analysis of the spikes produced during the application of the AC waveform, in the presence of a net DC current (Exp. CC1)

<table>
<thead>
<tr>
<th>Slimes Thickness (mm)</th>
<th>Parameters Derived from Regression Analysis Computations</th>
<th>From Eq. 4</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slope $R_m$, $\Omega$ cm$^2$</td>
<td>Intercept, $b$, (mV)</td>
<td>$r^2$</td>
</tr>
<tr>
<td>1.37</td>
<td>0.52</td>
<td>32.4</td>
<td>0.98</td>
</tr>
<tr>
<td>1.79</td>
<td>0.63</td>
<td>38.0</td>
<td>0.97</td>
</tr>
<tr>
<td>2.22</td>
<td>0.74</td>
<td>42.8</td>
<td>0.98</td>
</tr>
<tr>
<td>2.65</td>
<td>0.81</td>
<td>48.0</td>
<td>0.95</td>
</tr>
<tr>
<td>3.07</td>
<td>0.92</td>
<td>52.4</td>
<td>0.93</td>
</tr>
<tr>
<td>3.50</td>
<td>0.96</td>
<td>58.4</td>
<td>0.93</td>
</tr>
</tbody>
</table>

5 experimental points were used to obtain the regression coefficient. These points were collected during ~12 min and correspond to digitized samples taken when the frequency of the applied AC waves was between 0.63 and 6.3 rad/sec.
Table 7 Parameters derived from the fitting of the impedance data obtained in Exp. CA2 to the $Z_{ZARC}$-$Z_{ZARC}$ analogue (Circuit A.2, Figs. 6.38, 39)

<table>
<thead>
<tr>
<th>Slimes Thickness, mm</th>
<th>$R_1$, $\Omega cm^2$</th>
<th>$\Psi_{ZC1}$</th>
<th>$D_1$, $\Omega cm^2 sec^{-1}$</th>
<th>$b_1$, $\Omega cm^2 sec^{-1}$</th>
<th>$\tau_{\Psi_{ZC1}}$, sec</th>
<th>$R_2$, $\Omega cm^2$</th>
<th>$\Psi_{ZC2}$</th>
<th>$D_2$, $\Omega cm^2 sec^{-1}$</th>
<th>$b_2$, $\Omega cm^2 sec^{-1}$</th>
<th>$\tau_{\Psi_{ZC2}}$, sec</th>
<th>$R_{A, total}$, $\Omega cm^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.21</td>
<td>0.73</td>
<td>0.0062</td>
<td>33.50</td>
<td>0.0010</td>
<td>0.44</td>
<td>0.77</td>
<td>0.079</td>
<td>5.55</td>
<td>0.037</td>
<td>0.65</td>
</tr>
<tr>
<td>1.61</td>
<td>0.31</td>
<td>0.67</td>
<td>0.0165</td>
<td>18.76</td>
<td>0.0023</td>
<td>0.88</td>
<td>0.69</td>
<td>0.21</td>
<td>4.17</td>
<td>0.104</td>
<td>1.19</td>
</tr>
<tr>
<td>2.23</td>
<td>0.42</td>
<td>0.64</td>
<td>0.0296</td>
<td>14.09</td>
<td>0.0042</td>
<td>1.17</td>
<td>0.69</td>
<td>0.30</td>
<td>3.84</td>
<td>0.176</td>
<td>1.58</td>
</tr>
<tr>
<td>3.10</td>
<td>0.64</td>
<td>0.59</td>
<td>0.0683</td>
<td>9.39</td>
<td>0.0102</td>
<td>1.62</td>
<td>0.69</td>
<td>0.39</td>
<td>4.11</td>
<td>0.260</td>
<td>2.26</td>
</tr>
<tr>
<td>3.72</td>
<td>0.52</td>
<td>0.59</td>
<td>0.0503</td>
<td>10.34</td>
<td>0.0064</td>
<td>2.22</td>
<td>0.68</td>
<td>0.42</td>
<td>5.30</td>
<td>0.276</td>
<td>2.74</td>
</tr>
<tr>
<td>4.72</td>
<td>1.10</td>
<td>0.55</td>
<td>0.1511</td>
<td>7.25</td>
<td>0.0321</td>
<td>2.50</td>
<td>0.70</td>
<td>0.59</td>
<td>4.26</td>
<td>0.464</td>
<td>3.59</td>
</tr>
<tr>
<td>5.33</td>
<td>1.06</td>
<td>0.60</td>
<td>0.1045</td>
<td>10.19</td>
<td>0.0225</td>
<td>3.17</td>
<td>0.71</td>
<td>0.69</td>
<td>4.60</td>
<td>0.592</td>
<td>4.23</td>
</tr>
<tr>
<td>5.95</td>
<td>1.54</td>
<td>0.51</td>
<td>0.1866</td>
<td>8.27</td>
<td>0.0373</td>
<td>3.45</td>
<td>0.71</td>
<td>0.85</td>
<td>4.06</td>
<td>0.795</td>
<td>4.99</td>
</tr>
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<td>6.56</td>
<td>4.70</td>
<td>0.56</td>
<td>0.5415</td>
<td>8.68</td>
<td>0.3323</td>
<td>1.29</td>
<td>0.98</td>
<td>1.57</td>
<td>0.82</td>
<td>1.583</td>
<td>5.99</td>
</tr>
<tr>
<td>7.18</td>
<td>5.13</td>
<td>0.55</td>
<td>0.5671</td>
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<td>0.3593</td>
<td>2.08</td>
<td>0.96</td>
<td>1.94</td>
<td>1.07</td>
<td>1.992</td>
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</tr>
<tr>
<td>7.79</td>
<td>4.30</td>
<td>0.59</td>
<td>0.3873</td>
<td>11.11</td>
<td>0.2030</td>
<td>4.65</td>
<td>0.90</td>
<td>2.27</td>
<td>2.05</td>
<td>2.484</td>
<td>8.95</td>
</tr>
</tbody>
</table>

All measurements refer to the geometrical area of the electrode.

Low and high frequency terms refer to the ranges of frequencies used during the deconvolution process.

Low and high frequency arcs were fitted to the whole frequency range (0.063<ω<30000 rad/sec)

Values of statistical parameters related to the quality of the fit:

| Slimes Thickness, mm | $|y_i|^2$, $\Omega^2 cm^4$ | $r^2$ | $|y_i|^2$, $\Omega^2 cm^4$ | $r^2$ | $|y_i|^2$, $\Omega^2 cm^4$ | $r^2$ |
|----------------------|---------------------|---------|---------------------|---------|---------------------|---------|
| 0.80                 | 0.0067              | 0.999   | 0.0661              | 0.777   | -0.0594             | 1.009   |
| 1.61                 | 0.0147              | 0.999   | 0.0185              | 0.978   | -0.0038             | 1.000   |
| 2.23                 | 0.0242              | 0.999   | 0.0136              | 0.991   | 0.0106              | 1.000   |
| 3.10                 | 0.0174              | 1.000   | 0.0107              | 0.997   | 0.0067              | 1.000   |
| 3.72                 | 0.0574              | 0.999   | 0.0143              | 0.997   | 0.0431              | 1.000   |
| 4.72                 | 0.0328              | 1.000   | 0.0095              | 0.999   | 0.0233              | 1.000   |
| 5.33                 | 0.1136              | 1.000   | 0.0449              | 0.997   | 0.0688              | 1.000   |
| 5.95                 | 0.4281              | 0.999   | 0.1344              | 0.993   | 0.2936              | 0.999   |
| 6.56                 | 0.0563              | 1.000   | 0.0083              | 1.000   | 0.0480              | 1.000   |
| 7.18                 | 0.1286              | 1.000   | 0.0054              | 1.000   | 0.1232              | 1.000   |
| 7.79                 | 0.3369              | 1.000   | 0.0045              | 1.000   | 0.3324              | 1.000   |

A total of 6 parameters were curve fitted using between 110 and 113 experimental points.

For the impedance curves obtained at 0.8 and 1.6 mm slimes, $r^2>0.99$ when $1<\omega<30000$ rad/sec
Table 8 Parameters derived from the fitting of the impedance spectra obtained in Exp. CA2 (Circuit B.2, Figs. 6.40, 41)

<table>
<thead>
<tr>
<th>Slimes Thickness (mm)</th>
<th>$r_a$ (Ω cm²)</th>
<th>$r_b$ (Ω cm²)</th>
<th>$C_b$ (F cm²)</th>
<th>$B_a$ (Ω cm² sec⁻¹)</th>
<th>$\Psi_{ZCa}$</th>
<th>$R_{B,total}$ (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.80</td>
<td>0.43</td>
<td>0.23</td>
<td>0.026</td>
<td>11.48</td>
<td>0.58</td>
<td>0.66</td>
</tr>
<tr>
<td>1.61</td>
<td>0.84</td>
<td>0.38</td>
<td>0.068</td>
<td>8.06</td>
<td>0.54</td>
<td>1.22</td>
</tr>
<tr>
<td>2.23</td>
<td>1.15</td>
<td>0.49</td>
<td>0.102</td>
<td>7.46</td>
<td>0.53</td>
<td>1.64</td>
</tr>
<tr>
<td>3.10</td>
<td>1.64</td>
<td>0.66</td>
<td>0.146</td>
<td>8.59</td>
<td>0.56</td>
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</tr>
<tr>
<td>3.72</td>
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<td>0.57</td>
<td>2.76</td>
</tr>
<tr>
<td>4.72</td>
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<td>0.276</td>
<td>9.20</td>
<td>0.59</td>
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<td>0.398</td>
<td>9.51</td>
<td>0.60</td>
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<tr>
<td>5.95</td>
<td>3.87</td>
<td>1.13</td>
<td>0.570</td>
<td>9.88</td>
<td>0.61</td>
<td>5.00</td>
</tr>
<tr>
<td>6.56</td>
<td>4.36</td>
<td>1.60</td>
<td>0.749</td>
<td>10.48</td>
<td>0.61</td>
<td>5.96</td>
</tr>
<tr>
<td>7.18</td>
<td>4.80</td>
<td>2.40</td>
<td>0.975</td>
<td>11.25</td>
<td>0.62</td>
<td>7.20</td>
</tr>
<tr>
<td>7.79</td>
<td>5.29</td>
<td>3.82</td>
<td>1.35</td>
<td>12.61</td>
<td>0.64</td>
<td>9.12</td>
</tr>
</tbody>
</table>

For the AC sweep done at 0.8 mm slimes: $B_a = 1.92 \, \Omega \, \text{cm}^2 \, \text{sec}^{-1}$, and $\Psi_{ZCa} = 0.78$ (this was the only sweep fitted to circuit B.1, all the other sweeps were fitted to circuit B.2)

Values of statistical parameters related to the quality of the fit:

<p>| Slimes Thickness (mm) | $\omega_{min}$ | $\omega_{max}$ | $|y|^2$, $\Omega^2$ cm⁴ | $r^2$ | $|y|^2$, $\Omega^2$ cm⁴ | $r^2$ | $|y|^2$, $\Omega^2$ cm⁴ | $r^2$ |
|-----------------------|----------------|----------------|------------------------|------|------------------------|------|------------------------|------|
| 0.80                  | 0.063          | 28068          | 0.012                  | 0.998| 0.059                  | 0.791| -0.047                 | 1.007|
| 1.61                  | 0.063          | 28068          | 0.031                  | 0.999| 0.013                  | 0.984| 0.018                  | 0.999|
| 2.23                  | 0.063          | 28068          | 0.057                  | 0.998| 0.008                  | 0.995| 0.049                  | 0.999|
| 3.10                  | 0.063          | 28068          | 0.015                  | 1.000| 0.007                  | 0.998| 0.008                  | 1.000|
| 3.72                  | 0.063          | 28068          | 0.028                  | 1.000| 0.009                  | 0.998| 0.019                  | 1.000|
| 4.72                  | 0.063          | 28068          | 0.077                  | 1.000| 0.019                  | 0.998| 0.058                  | 1.000|
| 5.33                  | 0.063          | 28068          | 0.124                  | 0.999| 0.028                  | 0.998| 0.096                  | 1.000|
| 5.95                  | 0.063          | 28068          | 0.181                  | 0.999| 0.038                  | 0.998| 0.143                  | 0.999|
| 6.56                  | 0.063          | 28068          | 0.226                  | 0.999| 0.054                  | 0.998| 0.171                  | 1.000|
| 7.18                  | 0.063          | 28068          | 0.241                  | 1.000| 0.072                  | 0.999| 0.169                  | 1.000|
| 7.79                  | 0.063          | 28068          | 0.253                  | 1.000| 0.086                  | 0.999| 0.167                  | 1.000|</p>
<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>High Frequency Parameters</th>
<th>Low Frequency Parameters</th>
<th>( R_{A,\text{total}} = R_1 + R_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R_1, \Omega \text{cm}^2 )</td>
<td>( \psi_{ZC1}, \Omega \text{cm}^2 \text{sec} )</td>
<td>( D_1, \Omega \text{cm}^2 \text{sec}^{-\infty} )</td>
</tr>
<tr>
<td>0.64</td>
<td>0.101</td>
<td>0.91</td>
<td>0.0013</td>
</tr>
<tr>
<td>1.20</td>
<td>0.017</td>
<td>0.68</td>
<td>0.0115</td>
</tr>
<tr>
<td>1.76</td>
<td>0.069</td>
<td>0.83</td>
<td>0.1972</td>
</tr>
<tr>
<td>1.89</td>
<td>0.817</td>
<td>0.58</td>
<td>0.0599</td>
</tr>
</tbody>
</table>

* All measurements refer to the geometrical area of the electrode.
** Low and high frequency terms refer to the ranges of frequencies used during the deconvolution process.
*** Low and high frequency arcs were fitted to the whole frequency range (6.3<omega<23000 rad/sec)

### Values of statistical parameters related to the quality of the fit:

| Slimes Thickness, mm | \(|y|^2, \Omega^2\text{cm}^4\) | \(r^2\) | \(|y|^2, \Omega^2\text{cm}^4\) | \(r^2\) | \(|y|^2, \Omega^2\text{cm}^4\) | \(r^2\) |
|----------------------|-------------------------------|----------|-------------------------------|----------|-------------------------------|----------|
| 0.64                 | 0.005                         | 0.996    | 0.001                         | 0.990    | 0.005                         | 0.996    |
| 1.20                 | 0.013                         | 0.997    | 0.002                         | 0.994    | 0.012                         | 0.997    |
| 1.76                 | 0.045                         | 0.995    | 0.002                         | 0.998    | 0.043                         | 0.995    |
| 1.89                 | 0.062                         | 0.998    | 0.005                         | 0.997    | 0.057                         | 0.998    |

A total of 6 parameters were curve fitted.
Table 10 Electrical analogue parameters derived from the fitting of the impedance data obtained in Exp. CA5 (Circuit B.2)

<table>
<thead>
<tr>
<th>Slimes Thickness mm</th>
<th>r₀</th>
<th>rₜ</th>
<th>C_b</th>
<th>B_a</th>
<th>ψ_{ZCA}</th>
<th>R_{B,total}</th>
<th>Ωcm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.64</td>
<td>0.38</td>
<td>0.04</td>
<td>0.017</td>
<td>16.10</td>
<td>0.65</td>
<td>0.42</td>
<td>Ωcm²</td>
</tr>
<tr>
<td>1.20</td>
<td>0.72</td>
<td>0.08</td>
<td>0.036</td>
<td>16.10</td>
<td>0.64</td>
<td>0.80</td>
<td>Ωcm²</td>
</tr>
<tr>
<td>1.76</td>
<td>1.44</td>
<td>0.16</td>
<td>0.063</td>
<td>11.39</td>
<td>0.57</td>
<td>1.60</td>
<td>Ωcm²</td>
</tr>
<tr>
<td>1.89</td>
<td>1.50</td>
<td>0.32</td>
<td>0.062</td>
<td>14.71</td>
<td>0.62</td>
<td>1.82</td>
<td>Ωcm²</td>
</tr>
</tbody>
</table>

Values of statistical parameters related to the quality of the fit:

<table>
<thead>
<tr>
<th>Frequency Range</th>
<th>Z_r</th>
<th>-Z_s</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Slimes Thickness, mm</td>
<td>ω_min</td>
<td>ω_max</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.64</td>
<td>6.28</td>
<td>22295</td>
<td>0.002</td>
<td>0.999</td>
<td>0.001</td>
<td>0.978</td>
<td>0.001</td>
</tr>
<tr>
<td>1.20</td>
<td>6.28</td>
<td>22295</td>
<td>0.002</td>
<td>1.000</td>
<td>0.001</td>
<td>0.997</td>
<td>0.001</td>
</tr>
<tr>
<td>1.76</td>
<td>6.28</td>
<td>22295</td>
<td>0.019</td>
<td>0.998</td>
<td>0.001</td>
<td>0.999</td>
<td>0.018</td>
</tr>
<tr>
<td>1.89</td>
<td>0.63</td>
<td>28068</td>
<td>0.056</td>
<td>0.998</td>
<td>0.019</td>
<td>0.991</td>
<td>0.037</td>
</tr>
</tbody>
</table>
Table 11 Parameters derived from the fitting of the impedance data obtained in Exp. CA2 to the Randles analogue circuit (Figs. 6.43, 44)

<table>
<thead>
<tr>
<th>Time, Hrs</th>
<th>$R_c$, $\Omega$ cm$^2$</th>
<th>$C_{dl}$, $\mu$F cm$^{-2}$</th>
<th>$B_1$, $\Omega$ cm$^2$ sec$^{-\frac{1}{2}}$</th>
<th>$\Psi_{zc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17</td>
<td>0.044</td>
<td>23.75</td>
<td>3.83</td>
<td>0.19</td>
</tr>
<tr>
<td>0.64</td>
<td>0.112</td>
<td>167.42</td>
<td>3.63</td>
<td>0.33</td>
</tr>
<tr>
<td>12.03</td>
<td>0.070</td>
<td>206.32</td>
<td>3.13</td>
<td>0.31</td>
</tr>
<tr>
<td>21.32</td>
<td>0.063</td>
<td>247.86</td>
<td>2.69</td>
<td>0.32</td>
</tr>
<tr>
<td>58.58</td>
<td>0.063</td>
<td>267.78</td>
<td>2.62</td>
<td>0.32</td>
</tr>
<tr>
<td>67.57</td>
<td>0.066</td>
<td>290.23</td>
<td>2.52</td>
<td>0.32</td>
</tr>
<tr>
<td>72.08</td>
<td>0.049</td>
<td>284.79</td>
<td>2.25</td>
<td>0.30</td>
</tr>
<tr>
<td>76.82</td>
<td>0.044</td>
<td>272.15</td>
<td>2.23</td>
<td>0.30</td>
</tr>
<tr>
<td>78.06</td>
<td>0.046</td>
<td>276.70</td>
<td>2.21</td>
<td>0.30</td>
</tr>
<tr>
<td>86.90</td>
<td>0.048</td>
<td>274.37</td>
<td>2.23</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Values of statistical parameters related to the quality of the fit:

| Time, Hrs | $|y_{f}|^2$, $\Omega^2$ cm$^4$ | $r^2$ | $|y_{f}|^2$, $\Omega^2$ cm$^4$ | $r^2$ | $|y_{f}|^2$, $\Omega^2$ cm$^4$ | $r^2$ | $|y_{f}|^2$, $\Omega^2$ cm$^4$ | $r^2$ |
|----------|----------------------------|------|----------------------------|------|----------------------------|------|----------------------------|------|
| 0.17     | 0.28                       | 0.98 | 0.01                       | 0.96 | 0.24                       | 0.98 | 0.24                       | 0.98 |
| 0.64     | 0.11                       | 0.95 | 0.00                       | 0.99 | 0.08                       | 0.97 | 0.08                       | 0.97 |
| 12.03    | 0.06                       | 0.97 | 0.00                       | 0.99 | 0.04                       | 0.98 | 0.04                       | 0.98 |
| 21.32    | 0.04                       | 0.97 | 0.00                       | 0.99 | 0.03                       | 0.98 | 0.03                       | 0.98 |
| 58.58    | 0.07                       | 0.95 | 0.00                       | 0.99 | 0.05                       | 0.96 | 0.05                       | 0.96 |
| 67.57    | 0.07                       | 0.94 | 0.00                       | 0.99 | 0.05                       | 0.96 | 0.05                       | 0.96 |
| 72.08    | 0.07                       | 0.93 | 0.00                       | 0.99 | 0.05                       | 0.95 | 0.05                       | 0.95 |
| 76.82    | 0.05                       | 0.95 | 0.00                       | 0.99 | 0.04                       | 0.97 | 0.04                       | 0.97 |
| 78.06    | 0.05                       | 0.95 | 0.00                       | 0.99 | 0.04                       | 0.97 | 0.04                       | 0.97 |
| 86.90    | 0.05                       | 0.95 | 0.00                       | 0.99 | 0.04                       | 0.97 | 0.04                       | 0.97 |
Table 12 Electrical analogue parameters derived from the Fitting of the impedance data obtained in Exp. CA5 to the Randles analogue circuit (Fig. 6.45)

<table>
<thead>
<tr>
<th>Time, Hrs</th>
<th>R_{ct}, \Omega cm^2</th>
<th>C_{dl}, \mu F cm^{-2}</th>
<th>B_1, \Omega cm^2 sec^{-\omega_c}</th>
<th>\Psi_{zc}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.63</td>
<td>0.010</td>
<td>804.67</td>
<td>1.11</td>
<td>0.21</td>
</tr>
<tr>
<td>2.44</td>
<td>0.018</td>
<td>1350.32</td>
<td>0.85</td>
<td>0.24</td>
</tr>
<tr>
<td>4.26</td>
<td>0.030</td>
<td>1502.48</td>
<td>0.83</td>
<td>0.26</td>
</tr>
<tr>
<td>6.07</td>
<td>0.041</td>
<td>1625.51</td>
<td>0.82</td>
<td>0.27</td>
</tr>
<tr>
<td>7.88</td>
<td>0.046</td>
<td>1707.71</td>
<td>0.82</td>
<td>0.28</td>
</tr>
<tr>
<td>9.70</td>
<td>0.046</td>
<td>1719.34</td>
<td>0.83</td>
<td>0.28</td>
</tr>
<tr>
<td>11.67</td>
<td>0.021</td>
<td>1588.19</td>
<td>0.71</td>
<td>0.25</td>
</tr>
<tr>
<td>17.58</td>
<td>0.024</td>
<td>1579.10</td>
<td>0.71</td>
<td>0.26</td>
</tr>
<tr>
<td>23.45</td>
<td>0.009</td>
<td>1431.30</td>
<td>0.66</td>
<td>0.25</td>
</tr>
<tr>
<td>30.27</td>
<td>0.023</td>
<td>1452.57</td>
<td>0.69</td>
<td>0.26</td>
</tr>
<tr>
<td>34.59</td>
<td>0.023</td>
<td>1308.61</td>
<td>0.70</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Values of statistical parameters related to the quality of the fit:

| Frequency Range | $Z_\omega$ | $\Delta Z_\omega$ | $|Z_\omega|_r^2$ |
|-----------------|-----------|------------------|----------------|
| Time, Hrs       | $\omega_{min}$ | $\omega_{max}$ | $|y_\omega|^2, \Omega^2 cm^4$ | $r^2$ | $|y_\omega|^2, \Omega^2 cm^4$ | $r^2$ | $|y_\omega|^2, \Omega^2 cm^4$ | $r^2$ |
| 0.63            | 177.1     | 44485            | 0.026          | 0.958 | 0.002          | 0.956 | 0.012          | 0.979 |
| 2.44            | 177.1     | 35335            | 0.023          | 0.913 | 0.000          | 0.983 | 0.016          | 0.937 |
| 4.26            | 177.1     | 31492            | 0.014          | 0.936 | 0.000          | 0.987 | 0.009          | 0.955 |
| 6.07            | 177.1     | 31492            | 0.014          | 0.936 | 0.000          | 0.987 | 0.010          | 0.951 |
| 7.88            | 177.1     | 31492            | 0.015          | 0.922 | 0.000          | 0.986 | 0.010          | 0.946 |
| 9.70            | 177.1     | 31492            | 0.013          | 0.979 | 0.001          | 0.990 | 0.010          | 0.985 |
| 11.67           | 17.7      | 31493            | 0.013          | 0.980 | 0.000          | 0.992 | 0.009          | 0.985 |
| 17.58           | 17.7      | 31493            | 0.019          | 0.971 | 0.001          | 0.989 | 0.015          | 0.978 |
| 23.45           | 17.7      | 31493            | 0.012          | 0.978 | 0.001          | 0.990 | 0.010          | 0.983 |
| 30.27           | 17.7      | 39647            | 0.015          | 0.976 | 0.001          | 0.989 | 0.012          | 0.981 |
Table 13 Electrical analogue parameters derived from the fitting of the AC impedance data obtained in Exp. CA4 to the $Z_{ZARC}$-$Z_{ZARC}$ analogue (Circuit A.2, Fig. 6.47)

<table>
<thead>
<tr>
<th>Time, Hrs</th>
<th>$R_1$, $\Omega cm^2$</th>
<th>$\Psi_{ZC1}$</th>
<th>$D_1$, $\Omega cm^2 sec$</th>
<th>$b_1$, $sec$</th>
<th>$\tau_{R_1,sec}$</th>
<th>$R_2$, $\Omega cm^2$</th>
<th>$\Psi_{ZC2}$</th>
<th>$D_2$, $\Omega cm^2 sec$</th>
<th>$b_2$, $sec$</th>
<th>$\tau_{R_2,sec}$</th>
<th>$R_{A, total}$, $\Omega cm^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.08</td>
<td>0.87</td>
<td>0.73</td>
<td>0.0092</td>
<td>94.77</td>
<td>0.00167</td>
<td>1.77</td>
<td>0.43</td>
<td>0.89</td>
<td>1.98</td>
<td>0.77</td>
<td>2.64</td>
</tr>
<tr>
<td>3.89</td>
<td>0.43</td>
<td>0.83</td>
<td>0.0031</td>
<td>139.84</td>
<td>0.00092</td>
<td>1.96</td>
<td>0.35</td>
<td>0.94</td>
<td>2.08</td>
<td>0.85</td>
<td>2.38</td>
</tr>
<tr>
<td>5.70</td>
<td>0.35</td>
<td>0.82</td>
<td>0.0026</td>
<td>137.18</td>
<td>0.00071</td>
<td>1.65</td>
<td>0.39</td>
<td>0.86</td>
<td>1.91</td>
<td>0.69</td>
<td>2.00</td>
</tr>
<tr>
<td>7.52</td>
<td>0.33</td>
<td>0.80</td>
<td>0.0026</td>
<td>126.81</td>
<td>0.00059</td>
<td>1.44</td>
<td>0.43</td>
<td>0.82</td>
<td>1.75</td>
<td>0.63</td>
<td>1.77</td>
</tr>
<tr>
<td>9.33</td>
<td>0.32</td>
<td>0.79</td>
<td>0.0029</td>
<td>108.92</td>
<td>0.00062</td>
<td>1.26</td>
<td>0.47</td>
<td>0.77</td>
<td>1.65</td>
<td>0.56</td>
<td>1.58</td>
</tr>
<tr>
<td>11.18</td>
<td>0.34</td>
<td>0.73</td>
<td>0.0042</td>
<td>79.97</td>
<td>0.00057</td>
<td>0.99</td>
<td>0.55</td>
<td>0.55</td>
<td>1.79</td>
<td>0.34</td>
<td>1.33</td>
</tr>
<tr>
<td>15.37</td>
<td>0.33</td>
<td>0.71</td>
<td>0.0047</td>
<td>71.53</td>
<td>0.00054</td>
<td>0.93</td>
<td>0.59</td>
<td>0.53</td>
<td>1.76</td>
<td>0.34</td>
<td>1.27</td>
</tr>
<tr>
<td>19.55</td>
<td>0.32</td>
<td>0.72</td>
<td>0.0043</td>
<td>75.11</td>
<td>0.00052</td>
<td>0.99</td>
<td>0.59</td>
<td>0.58</td>
<td>1.70</td>
<td>0.40</td>
<td>1.31</td>
</tr>
</tbody>
</table>

The AC sweeps obtained at current interruption times longer than 11 hrs were fitted to the $Z_{ZARC}$-$Z_{ZARC}$-CPE$_0$ analogue (circuit A.1). Thus, 2 additional parameters were obtained:

<table>
<thead>
<tr>
<th>Time, Hrs</th>
<th>$b_0$, $\Omega cm^2 sec$</th>
<th>$\Psi_{ZC0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.18</td>
<td>0.050</td>
<td>0.74</td>
</tr>
<tr>
<td>15.37</td>
<td>0.054</td>
<td>0.73</td>
</tr>
<tr>
<td>19.55</td>
<td>0.046</td>
<td>0.79</td>
</tr>
</tbody>
</table>

* All measurements refer to the geometrical area of the electrode.
** The regression coefficients $r_9^*$ and $r_9^{**}$ were larger than 0.99
Appendix 10 Kramers-Kronig Transformations of NUD Elements

I. Objective:

To obtain the Kramers-Kronig transformation of the non-uniform diffusion element (NUD) used to fit the experimental data presented in Chapter 6.

II. Fundamental Equations

The Kramers-Kronig transformations (KKT) have been proposed as a way of validating experimental data obtained from AC impedance measurements [1]. They imply that causality, linearity, and stability were observed during the experimental measurement. Basically, KKT indicate that there is a unique relationship between the real ($Z_\Re$) and the imaginary ($-Z_\Im$) parts of the impedance. Thus, for a sufficiently wide impedance spectrum, the real part of the impedance can be obtained from the imaginary part and vice versa.

One of the mathematical forms of the KKT is as follows [2,3]:

$$Z_\Im(\omega) = \left(\frac{2\omega}{\pi}\right) \int_0^\infty \left[ \frac{Z_\Re(x) - Z_\Re(\omega)}{x^2 - \omega^2} \right] dx \quad \ldots 1$$

where the total impedance as a function of the frequency, $Z(\omega)$, is given by the following relationship:

$$Z(\omega) = Z_\Re(\omega) - jZ_\Im(\omega) \quad \ldots 2$$

Eq. 1 indicates that if $Z_\Re$ is known in the whole frequency range, $-Z_\Im$ can be obtained. Thus, if the derived $-Z_\Im$ values match those experimentally measured, the data follows the KKT.

To evaluate Eq. 1 at least two problems (one experimental and another mathematical) have to be overcome:

1) Impedance data are not usually available in the whole frequency range ($0<\omega<\infty$).

2) Eq. 1 has singular points at $x=\omega$.

Several experimental procedures and mathematical arrangements have been used to evaluate the KKT [2,3]. The approach followed here is to evaluate Eq. 1 by assuming that the NUD element fits the experimental data in the whole frequency range:

[360]
The second assumption, is that when Eq. 1 is solved numerically, at the singularity point (i.e. at $x=\infty$) the bracketed term in Eq. 1 is equal to one.

Thus, with these two assumptions the problem consists in evaluating numerically Eq. 1 for the NUD element represented by Eq. 3. Thus, the KKT to be solved is as follows:

$$Z_{\text{NUD}}(\omega) = B_1(j \omega)^{-\Psi_{xc}} \tanh B_2(j \omega)^{-\Psi_{xc}} \quad \ldots 3$$

$$Z_3(\omega) = -\left( \frac{2 \omega}{\pi} \right) \int_0^\infty \text{Re} \left[ \frac{B_1(j \omega)^{-\Psi_{xc}} \tanh B_2(j \omega)^{-\Psi_{xc}} - B_1(j \omega)^{-\Psi_{xc}} \tanh B_2(j \omega)^{-\Psi_{xc}}}{x^2 - \omega^2} \right] dx \quad \ldots 4$$

The steps followed to obtain the KKT of the NUD element were as follows:

1) From the experimental data obtained in Exp. CC1 obtain the $B_1$, $B_2$, and $\Psi_{zc}$ values (e.g. for the sweep taken at 1.79 mm, $B_1 = 1.03 \ \Omega \ cm^2 \ sec^{-\Psi_{xc}}$, $B_2 = 0.91 \ \sec^{-\Psi_{xc}}$, and $\Psi_{zc} = 0.33$, Table 14, Chapter 6).

2) Assume the impedance was measured in the frequency range between 0.0001 and 10000 rad/sec at 2500 equidistant discrete intervals.

3) Evaluate numerically Eq. 4 for each of the 2500 discrete frequency points assuming that at $x=\infty$, the bracketed term in Eq. 4 is equal to one.

By following these steps the data presented in Fig. 1 were obtained. The theoretical (obtained directly from the imaginary component of Eq. 3) and the computed (obtained from Eq. 4) $-Z_3$ values are shown to be very similar. This appears to indicate that the NUD follows the KKT. Furthermore, the fulfillment of the KKT implies that the data fitted to such a function adhere to experimental stability, causality, and linearity which are the foundations of impedance spectroscopy.

---

1 i.e.:

$$\left. \frac{Z_3(x) - Z_3(\omega)}{x^2 - \omega^2} \right|_{x=\infty} = 0 \quad \left. \frac{0}{0} \right|_{x=\infty} = 1$$
Fig. 1 Kramers-Kronig Transforms of the impedance data fitted to the NUD element.
From the experimental data presented in Table 6.14 (sweep taken at 1.79 mm, $B_z = 1.03 \, \text{cm}^2 \, \text{sec}^{-1}, B_z = 0.91 \, \text{sec}^{-1},$
and $E_z = 0.33$).
(A) Comparison of the theoretical imaginary impedance component, $-Z_3(\omega)$, with $-Z_3(\omega)$ obtained by KKT of the real component. (B) Detail of Fig. A at low frequencies.
The Eh-pH diagrams presented in Chapter 7 were generated using the THERMODATA computer program. In this appendix, the input files required to draw these diagrams are presented alongside the output files.

(F)-Si-H$_2$O System

Input File:

<table>
<thead>
<tr>
<th>TITLE</th>
<th>Eh vs pH diagram for the (F)-Si-H$_2$O system</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACTIVITIES of all components = 1</td>
<td></td>
</tr>
</tbody>
</table>

DIAGRAM

<table>
<thead>
<tr>
<th>AXES</th>
<th>&lt;&lt; (AQ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H &lt;-&gt; (AQ)</td>
<td></td>
</tr>
<tr>
<td>H$_2$ O</td>
<td></td>
</tr>
<tr>
<td>LIGANDS</td>
<td></td>
</tr>
<tr>
<td>H$_2$ Si O3</td>
<td></td>
</tr>
<tr>
<td>H Si O3 &lt;1&gt; (AQ)</td>
<td></td>
</tr>
<tr>
<td>Si O3 &lt;2&gt; (AQ)</td>
<td></td>
</tr>
<tr>
<td>Si H$_4$ (G)</td>
<td></td>
</tr>
</tbody>
</table>

AREAS

| F Si F6 <2> (AQ) |
| F Si F4 (H$_2$O)$_2$ (AQ) |
| F Si F5 (H$_2$O) <1> (AQ) |
| F < (AQ) |
| H F (G) |
| H F (AQ) |
| H$_2$ F2 <1> (AQ) |
| F$_2$ O (G) |

UNITS

| JOU |

FILE

| cpdalber |
| gbalber |
| cpdjandat |
| cpdnpdat |
| cpdpsdpat |
| cpdpsgtat |

ACTIVITY

1.

ALL

<table>
<thead>
<tr>
<th>COMPONENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,1</td>
</tr>
</tbody>
</table>

AXES

| ABCISSA PH |
| H < (AQ) |
| ORDINATE EH |
| => (AQ) |
| LIMITS |

| abcissa = 4.9 |
| ORDINATE = -1.0 2.5 |

TEMPERATURE

298.15

PRESSURE

1.

AREAS

| gibbs |

ORDINATE EH MULTIPLIER 1.0

| SPECIES < (AQ) |
| ABCISSA PH MULTIPLIER 1.0 |
| SPECIES H < (AQ) |
| CURRENT PRESSURES IN ATM |
| 1.0000 |
| TEMPERATURE OF SYSTEM 298.15 K |

G VS T COEFFICIENTS FOR SPECIES JOU

| SPECIES |
| GA |
| GB |
| CB |

| F Si F6 <2> (AQ) |
| F Si F4 (H$_2$O)$_2$ (AQ) |
| F Si F5 (H$_2$O) <1> (AQ) |
| F < (AQ) |
| H F (G) |
| H F (AQ) |
| H$_2$ F2 <1> (AQ) |
| F$_2$ O (G) |
| O$_2$ (G) |
| H$_2$ O (G) |

TOTAL LIGAND AREAS 2

TOTAL MAIN AREAS 7

A | B | C | D | E | F | G |

| SI F6 <2> (AQ) |
| SI F4 (H$_2$O)$_2$ (AQ) |
| SI F5 (H$_2$O) <1> (AQ) |
| F < (AQ) |
| H F (AQ) |
| H$_2$ F2 <1> (AQ) |
| G历程 |

| input will be taken from F:PB07_0.INP |
| output will be written to F:PB07_0.OUT |
| SPECIES 17 ELEMENTS 5 E H O Si F |
| UNITS CHANGED TO JOU |
| MAIN SPECIES PER AREA 1 |
| LIGAND SPECIES PER AREA 1 |

[363]
(Pb-F)-Si-H$_2$O System

**Input File**

**Title**

Eh vs pH diagram for the (Pb-F)-Si-H$_2$O system

**Activities of all components = 1**

**Diagram**

**Axes**

- $H^+ \leftrightarrow$ (AQ)
- $H_2O$

**Ligands**

- $H_2SiO_3$
- $SiO_3^{2-} \leftrightarrow$ (AQ)
- $SiH_4$ (G)

**Areas**

- $SiF_6^{2-} \leftrightarrow$ (AQ)
- $SiF_4[H_2O]_2$ (AQ)
- $SiF_5[H_2O] <1->$ (AQ)
- $F^- \leftrightarrow$ (AQ)
- $HF(G)$
- $HF(AQ)$
- $HF_2<1->(AQ)$
- $F_2O(G)$
- $Pb$
- $Pb<2+>(AQ)$
- $PbO$
- $Pb_2O_3$
- $Pb_3O_4$
- $PbO_2$
- $PbO_2H_2$
- $PbO_2H<1->(AQ)$
- $PbF_2(S)$
- $PbSiO_3$

**Lines**

- $O_2(G)$
- $H_2(G)$

**Units**

**Jou**

**File**

cpdalber
gibalber
cpjjandat
cpmdpldat
cpndsdat
cpdsdat

**Activity**

1.

**All Components**

2,1

**Axes**

$H^+ \leftrightarrow$ (AQ)

**Ordinate Eh**

$H^+ \leftrightarrow$ (AQ)

**Limits**

$abscissa$ -4.9

$ordinate$ -1.0 2.5

**Temperature**

298.15

**Pressure**

1.

**Current Pressures in ATM**

1.0000

**Temperature of System**

298.15 K

**G vs T Coefficients for Species**

**S**

$GA$ $GB$

$H^+ \leftrightarrow$ (AQ) $0.901164E-12$ $0.000000$

$H_2O$ $-18.9665$ $0.000000$

$H_2SiO_3$ $-237190.0$ $0.000000$

$SiO_3^{2-} \leftrightarrow$ (AQ) $-1.02300E+07$ $0.000000$

$SiF_6^{2-} \leftrightarrow$ (AQ) $-955460.0$ $0.000000$

$SiF_4[H_2O]_2$ (AQ) $-878000.0$ $0.000000$

$SiF_5[H_2O] <1->$ (AQ) $-39310.0$ $0.000000$

$F^- \leftrightarrow$ (AQ) $-278820.0$ $0.000000$

$HF(G)$ $-273220.0$ $0.000000$

$HF(AQ)$ $-296850.0$ $0.000000$

$HF_2<1->(AQ)$ $-578150.0$ $0.000000$

$F_2O(G)$ $46000.0$ $0.000000$

$Pb$ $0.168155E-11$ $0.000000$

$Pb<2+>(AQ)$ $-24310.0$ $0.000000$

$PbO$ $-188500.0$ $0.000000$

$Pb_2O_3$ $411780.0$ $0.000000$

$Pb_3O_4$ $-616200.0$ $0.000000$

$PbO_2$ $-218900.0$ $0.000000$

$PbO_2H_2$ $-420900.0$ $0.000000$

$PbO_2H<1->(AQ)$ $-339000.0$ $0.000000$

$PbF_2(S)$ $302500.0$ $0.000000$

$PbF_2(S)$ $-619000.0$ $0.000000$

$PbSiO_3$ $-1.00000E+07$ $0.000000$

$O_2(G)$ $0.183206E-11$ $0.000000$

$H_2(G)$ $0.180604E-11$ $0.000000$

**Total Ligand Areas**

2

**Total Main Areas**

23

A $SiF_6 <2->(AO) + Pb$

B $SiF_6 <2->(AO) + Pb <2+>(AO)$

C $SiF_6 <2->(AO) + PbO_2$

D $SiF_6 <2->(AO) + PbF_2(S)$

E $SiF_4[H_2O]_2$ (AQ) + Pb

F $SiF_4[H_2O]_2$ (AO) + Pb $<2+>(AO)$

G $SiF_4[H_2O]_2$ (AQ) + Pb $O_2$

H $SiF_4[H_2O]_2$ (AQ) + Pb $<4->$

I $SiF_5[H_2O] <1->$ (AO) + Pb

J $SiF_5[H_2O] <1->$ (AO) + Pb $<2+>(AO)$

K $SiF_5[H_2O] <1->$ (AQ) + Pb $O_2$

L $F^- \leftrightarrow$ (AO) + Pb

M $F^- \leftrightarrow$ (AQ) + Pb $O_2$

N $F^- \leftrightarrow$ (AO) + Pb $F_2(S)$

O $F^- \leftrightarrow$ (AQ) + Pb $SiO_3$

P $F_2O(G) + PbO_2$

Q $F_2O(G) + Pb<4->$

R $Pb + PbF_2(S)$

S $Pb <2->(AO) + PbF_2(S)$

T $PbO_2 + PbF_2(S)$

U $PbF_2(S) + PbSiO_3$

V $H_2F(AQ) + Pb$

W $HF_2<1->(AO) + Pb$

**Output File**

**Input Will Be Taken From**

F:\PB013_0.INP

**Output Will Be Written To**

F:\PB0103_0.OUT

**Species**

28 Elements 6 H O Si F Pb

**Units Changed To**

Jou

**Species Per Area**

2

**Ligand Species Per Area**

1

**Ordinate Eh Multiplier**

1.0

**Species Multiplier**

1.0

**Abscisca Limits**

4.000 TO 9.000

**Ordinate Limits**

1.000 TO 2.500

[364]
(Sb-F)-Si-H₂O System

Input File:

TITLE
Eh vs pH diagram for the (Sb-F)-Si-H₂O system
Activities of all Sb soluble components = 1e-6

OUTPUT FILE:

INPUT WILL BE TAKEN FROM F:\SB017_2.INP
OUTPUT WILL BE WRITTEN TO F:\SB017_2.OUT

Eh vs pH diagram for the (Sb-F)-Si-H₂O system
Activities of all Sb soluble components = 1e-6

ACTIVITIES OF SPECIES

Sb O F (aq)
-0.75
Sb O2 H₂ F (aq)
-0.75
Sb O6 H₆ <1-> (aq)
-0.75
Sb O6 H₆ <1-> (aq)
-0.75
Sb O6 H₆ <1-> (aq)
-0.75
Sb O6 H₆ <1-> (aq)
-0.75
Sb O6 H₆ <1-> (aq)
-0.75
Sb O6 H₆ <1-> (aq)
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Sb O6 H₆ <1-> (aq)
-0.75
Sb O6 H₆ <1-> (aq)
-0.75
Sb O6 H₆ <1-> (aq)
-0.75
Sb O6 H₆ <1-> (aq)
(Bi-F)-Si-H$_2$O System

Input File:
TITLE
Eh vs pH diagram for the (Bi-F)-Si-H$_2$O system
Activities of Bi soluble components = 1e-4
DIAGRAM
AXES
<< (AQ)
H+>> (AQ)
H$_2$O
LIGANDS
H$_2$SiO$_3$
HSiO$_3$$^-$ (AQ)
SiO$_3$$^{2-}$ (AQ)
SiH$_4$ (G)
AREAS
Bi
Bi$^{+3}$ (aq)
BiOH$^{+2}$
Bi$_6$O$_{12}$H$_{12}$$^{+6}$ (aq)
Bi$_9$O$_{21}$H$_{21}$$^{+6}$
Bi$_9$O$_{22}$H$_{22}$$^{+5}$ (aq)
Bi$_2$O$_3$
Bi$_2$O$_5$
Bi$_2$O$_4$
Bi$_4$O$_7$
BiO$^-$
Bi$_3$H$_3$ (g)
SiF$_6$$^{2-}$ (aq)
SiF$_4$ [H$_2$O]$_2$ (AQ)
SiF$_5$ [H$_2$O]$_2$ (AQ)
SiO$_2$ (G)
SiO$_2$ (AQ)
SiO (G)
Si (G)
H$_2$ (G)

AREAS
check all

LIMITS
abscissa 0.4
ORDINATE -0.51

TEMPERATURE
298.15
PRESSURE
1.
AREAS
check all

OVERLAY
H$_2$ (G) = 2 << (AQ) + 2 H+>> (AQ)
1.,1.,1.
OVERLAY
2 H$_2$O = O$_2$ (G) + 4 << (AQ) + 4 H+>> (AQ)
1.,1.,1.,1.

PLOT
VISUAL 16.5,16.5,2.1,
mark lower abscissa 7
0.51,1.5,2.5,3.5,3.5
MARK LOWER ORDINATE 5
-0.25,0.25,0.5,0.75
label lower abscissa 9
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.0
LABEL LOWER ORDINATE 7
0.5 -0.5
-0.25 -0.25
0.0
0.25
0.5
0.75
1.0

Joule

Output File:
TITLE
Eh vs pH diagram for the (Bi-F)-Si-H$_2$O system
Activities of all Bi soluble components = 1e-4
ACTIVITIES OF SPECIES
<< (AQ)
1.00000
H+>> (AQ)
1.00000
H$_2$O
1.00000
H$_2$SiO$_3$
1.00000
HSiO$_3$$^-$ (AQ)
1.00000
SiO$_3$$^{2-}$ (AQ)
1.00000
SiH$_4$ (G)
1.00000
Bi
1.00000
Bi$^{+3}$ (aq)
0.100000E-03
BiOH$^{+2}$
0.100000E-03
Bi$_6$O$_{12}$H$_{12}$$^{+6}$ (aq)
0.100000E-03
Bi$_9$O$_{21}$H$_{21}$$^{+6}$
0.100000E-03
Bi$_9$O$_{22}$H$_{22}$$^{+5}$ (aq)
0.100000E-03
Bi$_2$O$_3$
1.00000
Bi$_2$O$_5$
1.00000
Bi$_2$O$_4$
1.00000
Bi$_4$O$_7$
1.00000
BiO$^-$
0.100000E-03
Bi$_3$H$_3$ (g)
1.00000
SiF$_6$$^{2-}$ (aq)
1.00000
SiF$_4$ [H$_2$O]$_2$ (AQ)
1.00000
SiF$_5$ [H$_2$O]$_2$ (AQ)
1.00000
F$^-$ (AQ)
1.00000
H$_2$ (G)
1.00000
H$_2$ (AQ)
1.00000
H$_2$O
1.00000
MAIN SPECIES PER AREA 2
LIGAND SPECIES PER AREA 1

TEMPERATURE OF SYSTEM 298.15 K

[366]
(As-F)-Si-H$_2$O System

**Input File:**

TITLE
Eh vs pH diagram for the (AS-F)-Si-H$_2$O system
Activities of all As soluble components = 1e-4

DIAGRAM
AXES
<= (AQ)
H <= (AQ)
H$_2$ O
LIGANDS
H$_2$ Si O$_3$
H Si O$_3$ <-1 (AQ)
Si O$_3$ <-2 (AQ)
Si H$_4$ (G)
AREAS
As
As$_4$ O$_6$
As O <= (aq)
H As O$_2$
H As O$_4$ <-2
H As O$_4$ <-3
H As O$_4$ <-4
H$_3$ As O$_3$ <-2
As$_2$ O$_5$
As H$_3$ (g)
Si F$_6$ <-2 (AQ)
Si F$_4$ [H$_2$O]$_2$ (AQ)
Si F$_5$ [H$_2$O] <-1 (AQ)
F <= (AQ)
H F (G)
H F (AQ)
H F$_2$ <-1 (AQ)
F$_2$ O (G)
LINES
O$_2$ (G)
H$_2$ (G)

UNITs
Jou.

Gibbs
As$_4$ O$_6$
-1151000.
As O <= (aq)
-163800.
H As O$_2$
-402700.
H As O$_4$ <-2
-707100.
H$_2$ As O$_3$ <-2
-587200.
H$_2$ As O$_4$ <-3
-753000.
H$_3$ As O$_3$ <-4
-639900.
As H$_3$ (g)
-68900.
As O$_4$
-781400.
As O$_5$

FILE
cpdalber
gbalber
cpdjandat
cpdpntdat
cpntsbdat
cpdsigdat

**Output File:**

INPUT WILL BE TAKEN FROM F:AS014_2.INP
OUTPUT WILL BE WRITTEN TO F:AS014_2.OUT

Eh vs pH diagram for the (AS-F)-Si-H$_2$O system
Activities of all As soluble components = 1e-4

ACTIVITIES OF SPECIES
<= (AQ) 1.00000
H <= (AQ) 1.00000
H$_2$ O 1.00000
H$_2$ Si O$_3$ 1.00000
H Si O$_3$ <-1 (AQ) 1.00000
Si O$_3$ <-2 (AQ) 1.00000
Si H$_4$ (G) 1.00000
As 1.00000
As$_4$ O$_6$ 1.00000
As O <= (aq) 0.100000E-03
H As O$_2$ 0.100000E-03
H As O$_4$ <-2 0.100000E-03
H$_2$ As O$_3$ <= 0.100000E-03
H$_2$ As O$_4$ <= 0.100000E-03
H$_3$ As O$_3$ <= 0.100000E-03
As$_2$ O$_5$ 1.00000
As H$_3$ (g) 1.00000
Si F$_6$ <-2 (AQ) 1.00000
Si F$_4$ [H$_2$O]$_2$ (AQ) 1.00000
Si F$_5$ [H$_2$O] <-1 (AQ) 1.00000
F <= (AQ) 1.00000
H F (G) 1.00000
H F (AQ) 1.00000
H F$_2$ <-1 (AQ) 1.00000
F$_2$ O (G) 1.00000
O$_2$ (G) 1.00000
H$_2$ (G) 1.00000
CURREnT TEMPERATURES IN K 298.15
CURREnT PRESSURES IN ATM 1.0000
TOTAl LIGAND AREAS 2

TOTAl MAIN AREAS 11
A As + Si F$_6$ <-2 (AQ)
B As + Si F$_5$ [H$_2$O] <-1 (AQ)
C As$_4$ O$_6$ + Si F$_6$ <-2 (AQ)
D As O <= (aq) + Si F$_6$ <-2 (AQ)
E As O <= (aq) + Si F$_5$ [H$_2$O] <-1 (AQ)
F H$_2$ As O$_4$ <= + Si F$_6$ <-2 (AQ)
G H$_2$ As O$_4$ <= + Si F$_5$ [H$_2$O] <-1 (AQ)
H H$_3$ As O$_3$ <= + Si F$_6$ <-2 (AQ)
I As H$_3$ (g) + Si F$_6$ <-2 (AQ)
J As H$_3$ (g) + Si F$_5$ [H$_2$O] <-1 (AQ)
K As H$_3$ (g) + H F (AQ)