FUNDAMENTAL STUDY ON EXTRACTING LEAD FROM CERUSSITE CONCENTRATE IN METHANE SULFONIC ACID BASED SOLUTION

by

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

(Materials Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA

(Vancouver)

December 2012

Abstract

Cerussite ($PbCO_3$) concentrates may be recovered from oxidized lead ores. These concentrates suffers from the intrinsic fuel shortage via traditional smelting route and may lead to widespread contamination in shipment. Therefore, a hydro-electrometallurgical process to treat cerussite concentrate by methane sulfonic acid (MSA) is proposed to solve the above problems.

The leaching of cerussite concentrate by MSA was first studied. The parameters of stirring speed, temperature, acid concentration, particle sizes and solid concentration were considered. It was found that stirring speed, temperature, particle size and proton concentration had a significant influence on the kinetics while solid concentration showed no effect on the final lead extraction under the experimental conditions. The leaching results indicated that MSA is favourable to treat cerussite concentrate and the lead extraction could achieve the theoretical maximum in just 10 min at ambient conditions. The lead content in solution obtained at high solid concentration was sufficiently high, and easily met the concentration requirements for the subsequent electrolysis process.

After leaching, the residue was subjected to a desulfurization treatment to recover the remaining lead in residue. Using desulfurization agent Na_2CO_3, the remaining lead, mainly in anglesite, was transformed to $PbCO_3$ that was followed by a re-leaching treatment with MSA. An overall lead recovery of 98% was finally obtained.

In the electrowinning process from MSA based electrolyte, the individual and synergistic effects of two ligninsulfonate salts and two glycol-type agents on lead deposit quality were first investigated. Compared to the other three additives, the individual use of calcium ligninsulfonate most benefited the morphology of lead deposit. The operating parameters in the lead electrowinning process (i.e. temperature, current density, concentrations of lead ion and protons) had a widely acceptable range. The cathodic current efficiency and specific energy consumption in most tests were around 99% and 0.53Wh/kg, respectively. The SEM micrographs showed that the lead deposits obtained under the optimal conditions were

compact and even. These results for leaching and electrolysis made the MSA system competitive to the comparable fluoborate and fluosilicate systems.

Finally a simplified flowsheet to extract lead from cerussite concentrate in MSA based solution was proposed.

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List of Symbols, Abbreviations or Others

α	the defined ratio of 2 proton over 1 lead ion, as $(H)_2/Pb$
α_2	the fraction of CO_3^{-2} over the total aqueous inorganic carbon anions
C_T	total inorganic carbon anions in the aqueous system
MSA	methane sulfonic acid
Temp. (or T)	temperature
Vol.	volume
CL	calcium ligninsulfonate
SL	sodium ligninsulfonate
PEG	polyethylene glycol
PPG	polypropylene glycol
Mw	the weight average molecular weight
Mn	the number average molecular weight
G	Gibbs energy, in kJ/mol
K_{sp}	solubility product
ΔM_T	theoretical quantity of Pb which could be deposited within τ, in gram
i	current density, in A/m^2
i_0	exchange current density, in A/m^2
i_{lim}	limiting current density, in A/m^2
A	cathodic area, in cm^2
τ	electrowinning duration, in hours
$Q_{Pb/Pb^{+2}}$	the electrochemical equivalent of the reaction equal to 2.867g/Ah.
ΔM	quantity of deposit lead during the run τ, in gram
$\Delta E_{applied}$	applied cell voltage, in volts
$\Delta E_{thermodynamic}$	thermodynamic cell voltage, in volts
ΔE_0	standard equilibrium cell voltage in volts
F	Faraday constant, equal to 96480 C/mol electron
a_j	the activity of reactant or product species

m_j	stoichiometric coefficient of reactant (positive) or product (negative)
η_D	diffusion overpotential, in volts
η_S	charge transfer overpotential, in volts
D	diffusion coefficient, in m^2/s
Λ_m	molar conductivity (or sometimes equivalent conductivity), in Sm^2/mol
Λ_m^0	limiting molar conductivity, in Sm^2/mol
ν_+, ν_-	stoichiometric coefficients for cations and anions in the electrolyte
λ_+, λ_-	limiting ion molar conductivity, in Sm^2/mol

Acknowledgements

1 Chapter: Introduction

Lead is one of the most ancient metals known to mankind. Natural lead enrichment occurs most frequently as minerals galena (PbS), which is widely distributed throughout the world. There are also some other oxidation products of lead ores such as anglesite ($PbSO_4$) and cerussite ($PbCO_3$).

So far, only pyrometallurgical smelting methods have been commercialized for lead extraction from its sulphide ores and some other secondary lead sources. The releases of sulphur dioxide and volatile lead emissions which are usually generated in smelting processes have caused some severe environmental problems[1]. Smelting processes also are best suited to treat high grade concentrates and not generally suitable to treat complex or low grade concentrates. Concern about the environmental impact of the conventional pyrometallurgical smelting route and the rising lead demand has generated significant interest in alternative process for the hydrometallurgical treatment of lead-bearing ores.

Cerussite is the main lead-bearing oxidized mineral from the Magellan Mine in Australia. The shipment of cerussite concentrate is difficult and widespread contamination of the Port of Esperance in Australia through mishandling of Magellan concentrate resulted in the shutdown of the mine for an extended period. Moreover, cerussite lacks the intrinsic fuel characteristics of a sulfide (e.g. PbS) that helps make roasting and smelting economical. An excessive amount of heat and external fuel input would be required during traditional smelting, which will greatly increase the cost of production. This also happens when other lead-bearing oxidized components are treated, like spent lead-acid battery paste[1] and calcinate[2], mainly PbO, PbO_2, $PbCO_3$, or $Pb(OH)_2$.

Given the strict limitations above, the recovery of lead from oxidized resources with hydrometallurgical methods is proposed and has become a worldwide research topic. When employed to treat galena, hydrometallurgical methods could avoid the evolution of sulphur dioxide and lead dust emissions, and could treat complex or low grade flotation concentrates as well. Also when employed to treat lead-bearing oxidized minerals, the requirements for

fuel and energy decrease. So far, a number of lixiviants have been studied for the leaching and dissolution of lead-bearing minerals.

Since both fluosilicic acid and fluoboric acid impart high solubility to lead(II), they have been tested and patented in leaching galena and secondary lead recourses. For example (a) the Fluosilicic Process studied by Alan A. Chen and David Dreisinger[3]; (b) the Fluobor Process developed by Engitic (Italy) and its partner Doe Run (U.S.A.)[4]; (c) the Ginatta Process explored by Marco Ginatta[5]; (d) the RSR Process developed by R.D. Prengaman and H.B. McDonald in the late 1970s and early 1980s[6]; (e) the U.S. Buerau of Mine Process investigated by E.R. Cole, A.Y Lee and D.L. Paulson[7]. However, neither fluosilicic nor fluoboric acid can be kept from decomposing and releasing fluoride ions that could precipitate lead as lead fluoride, which are highly corrosive. Additionally, the high corrosiveness of fluoboric and fluosilicic acid also limits commercialization of processes using these chemicals.

Considering its high solubility for lead and some other heavy metals (i.e. tin, mercury and silver), as well as its "green" chemical and physical properties (non-corrosive, non-toxic, non-volatile, highly conductive and easy-to-handle etc.), methane sulfonic acid (MSA) has received considerable interest as a potential medium to leach lead-bearing concentrates and subsequently electrodeposit metallic lead[8]. However, there are few published results on the use of MSA for lead leaching or dissolution and recovery of lead through electrowinning/electrorefining processes.

In this thesis a fundamental study on extracting and recovering lead using methane sulfonic acid (MSA) based solution was undertaken. The purpose of this exploration was:

(1) To investigate whether lead can be easily recovered from cerussite concentrates via dissolution in an aqueous methane sulfonic acid solution;

(2) To study the effect of leaching duration, stirring speed, temperature, concentration of proton, particle size and solid concentration on the kinetics of dissolution of lead from cerussite concentrate;

(3) To evaluate the desulfurization efficiency of sodium carbonate treatment of the cerussite leach residue;

(4) To explore whether lead could be electrowon from lead methane sulfonate electrolyte with some trace amount of additives;

(5) To study the individual and synergistic effects of selected additives on the lead electrowinning process and the quality of the lead deposit;

(6) To optimize the operating parameters, including current density, temperature, concentrations of lead ions and protons, in the lead electrowinning process based on methane sulfonic acid;

(7) To propose a flowsheet to treat cerussite-containing concentrate in methane sulfonic acid medium.

2 Chapter: Literature Review

2.1 The Applications of Lead

Lead is one of man's most useful commodities, and it has been used for many purposes such as roofing, piping and kitchen/tableware for centuries. This is because[9]:

(1) Lead is relatively abundant and lead concentrates are easily extracted in some 60 countries in the world. The recovery of lead metal from concentrate does not need much energy, reflecting in a fairly low price compared to other non-ferrous metals.

(2) Lead has some important properties, in particular great malleability, low melting point, ease of production and joining, and good corrosion resistance in most environments.

However, compared to other metals, lead has extremely low strength, and thus it is rarely used in its pure form, since small alloying additions considerably increase its strength. Due to its very high density, lead also gets some different applications, such as sound-, vibration- and radiation-proof materials. Nowadays, lead is mainly consumed in the battery industry, which accounts for about 70% of the world lead output[1]. With a boom in the market for electric vehicles, emerging battery and other energy storage applications, there is growing interest in lead, resulting in the rising price for lead[10].

It has been known since ancient times that exposure to lead can lead to serious consequences for health, resulting in harmful effects on many parts of the body. The organs potentially most affected are the brain and nervous system, kidneys, blood, and the reproductive system of both sexes. Thus lead is no longer used for potable water supplies resulting in the decreasing use of lead pipe. However, currently it is still widely used in roofing and other applications.

2.2 The Extractive Metallurgy of Lead

So far the pyrometallurgical route is the principle method to commercially produce lead metal. The production of refined metallic lead from primary lead-bearing minerals in the pyrometallurgical route consists of a number of steps, as shown in **Figure 1**:

(1) Mineral processing: mining, enriching and separating lead-containing minerals from the other minerals to produce a lead concentrate;

(2) Smelting: roasting PbS to form metallic lead;

(3) Refining: removing impurities and recovering pure lead from the crude metal.

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            ┌─────────────────┐
            │  Lead Sulfide   │
            │   Concentrate   │
            └─────────────────┘
                     │
                     ▼
            ┌─────────────────┐
            │   Concentrate   │────────────┐
            │    Smelting     │            │
            └─────────────────┘            ▼
              Bullion │        Sulphur Dioxide and Lead Dust
                     ▼
            ┌─────────────────┐
       ┌────│  Lead Bullion   │────────────┐
       │    │    Refining     │            │
       ▼    └─────────────────┘            ▼
   Residues       │                 By-product Metals
                  ▼
           Refined Lead Metal
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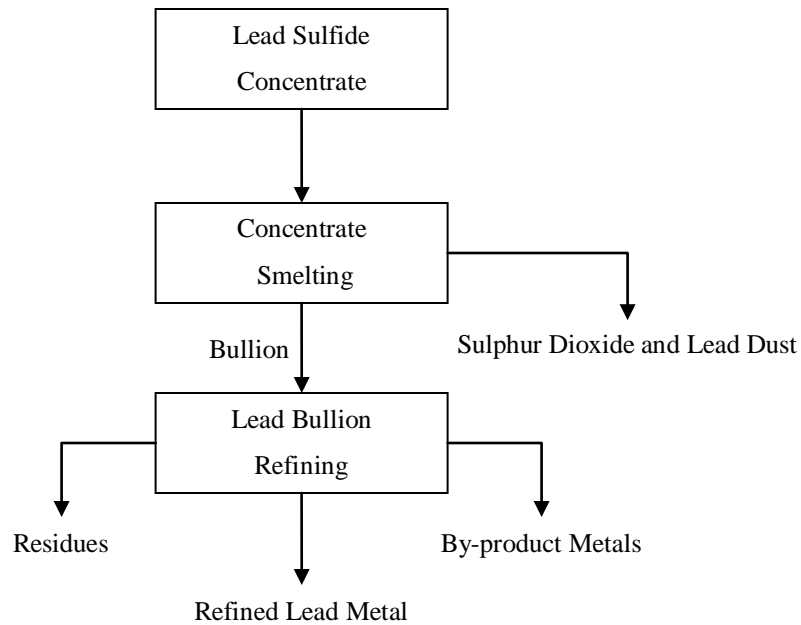
Figure 1   Simplified flowsheet for lead extraction from sulfide concentrates[11]

Lead mine production is mostly commonly a co- or by-product of zinc mining, although it is often associated with silver as well. Therefore, sometimes lead extraction is not the only reason for lead mining. Galena is the principal lead mineral being processed today; it accounts for nearly all primary lead production. Galena is composed predominately of lead and sulphur with minor substitution of iron and zinc. The composition of galena varies from one region to another.

The lead blast furnace has been the standard method of reduction smelting since the 19th century. The sinter machine-blasting furnace process traditionally includes sintering with air to convert lead sulphide to lead oxide and blast smelting with coke to reduce lead oxide to impure lead metal. Technologies, such as Queneau-Schuhmann-Lurgi (QSL)[12],

Isasmelt[13, 14] /Ausmelt[15] and Kivcet[16], introduced into a limited number of Western smelters in the 1990s, has replaced the conventional sinter machine-blast furnace operations. They were intended to improve environmental performance and to widen the range of feed that could be treated. All of these new pyrometallurgical methods are briefly compared in **Table 1** and illustrated in **Figure 2**, **Figure 3**, **Figure 4** and **Figure 5**. The QSL and top submerged lance processes (TSL, including Ausmelt and Isasmelt) smelt raw materials in a liquid bath, which is essentially similar to processes of metallurgical converting and fuming. The Kivcet process uses flash smelting of lead concentrate in a charge-oxygen flame.

Table 1 A brief comparison of various pyrometallurgical processes for primary lead production

Process	Inventor	Features
QSL	Queneau-Schuhmann-Lurgi, Germany	A long and horizontal reactor lined with fused chrome-magnesite bricks. Bottom-blowing tuyere injectors for oxygen and fuel are used.
ISASMELT	Mount Isa Mines Limited, Australia (with CSIRO)	A vertical furnace with a top submerged lance
AUSMELT	Outotec, Australia	A top submerged lance for direct injection of fuel and oxygen enriched air into a molten slag bath. Operation with a well sealed vessel under a negative pressure.
KIVCET	VNIITEVERMET Institute, Kazakhstan	A single oxygen flash smelting step combined with the electrothermic reduction of the metal oxide bearing slag by coke breeze or coal
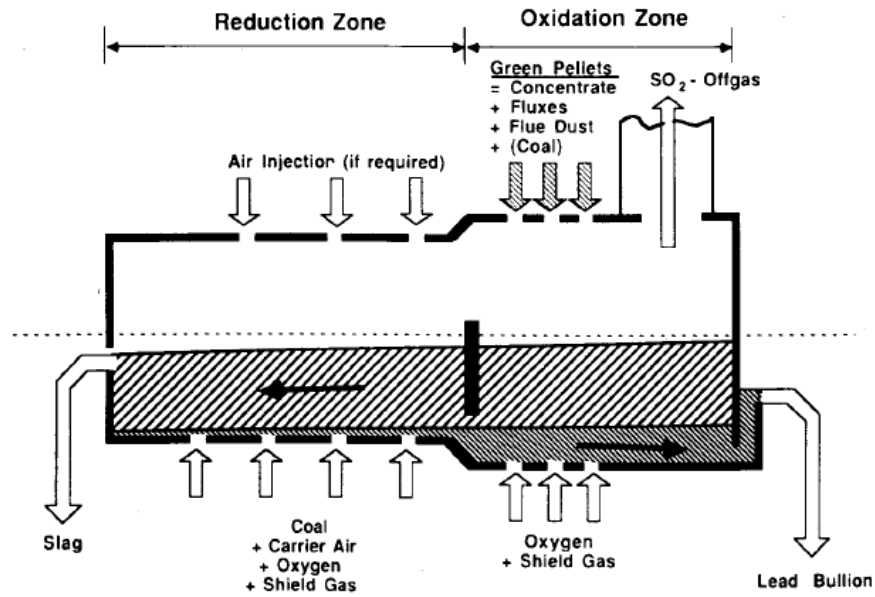
Figure 2   A typical QSL furnace[12]
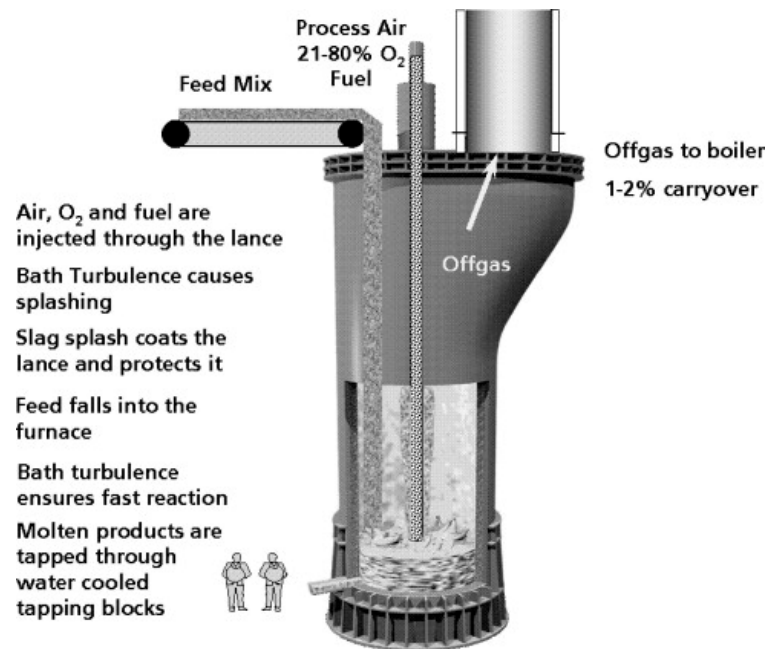
Figure 3   A typical Isasmelt^{TM} furnace[13]
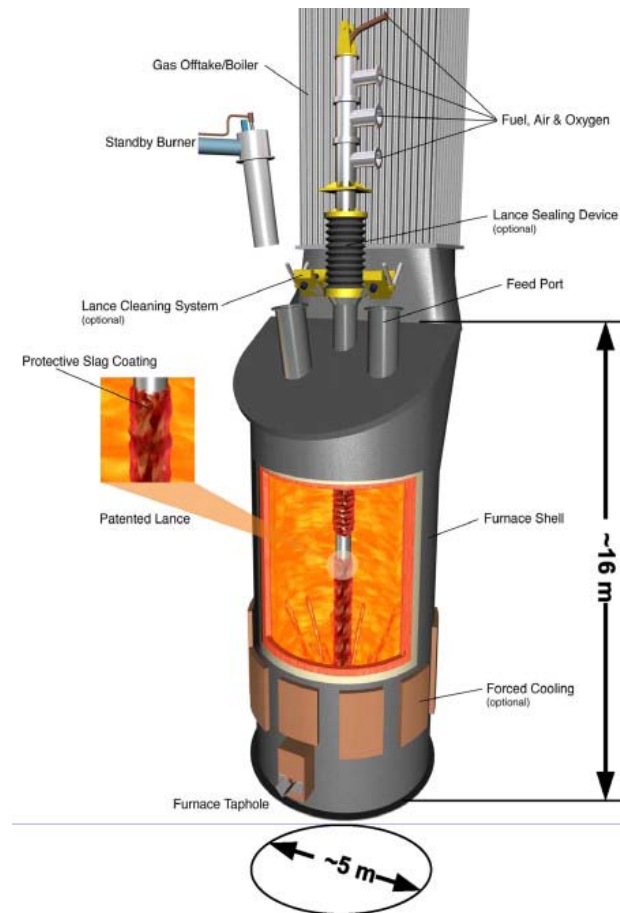
Figure 4   A typical Outotec® Ausmelt furnace [15]
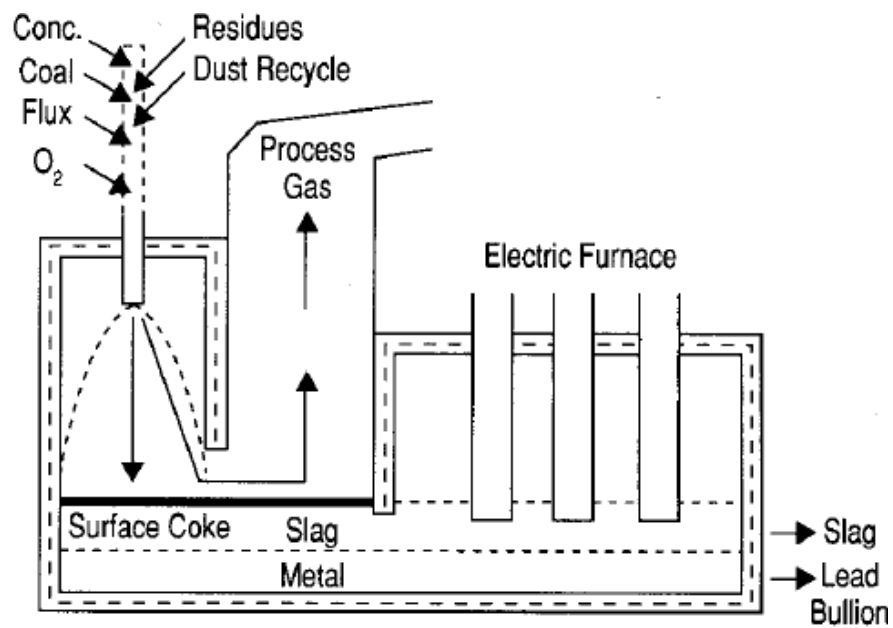
Figure 5   A typical Kicvet furnace [16]

Meanwhile, either pyrometallurgy or hydro-electrometallurgy methods have been used for the treatment of battery pastes[1, 17]. While pyrometallurgical methods still comprised over 90% of the recovery technology, they are under severe environmental criticism. In the most common approach, the battery paste is charged into a smelting furnace. New developments in smelting technology have lead to recycling in processes such as Isasmelt or short rotary furnaces. The SO_2 problems are solved since sulphur in the paste is largely converted to sulphate.

The role of refining is both to soften the metallic hard lead metal by eliminating impurities content and to recover silver and gold. There are currently two routes to refine the impure metallic lead: pyrorefining and electrorefining. Comparisons between the two routes show that pyrorefining is more suitable to treat ores with low bismuth content and is the dominant method for lead refining. The pyrorefining process consists of a series of steps, as shown in **Figure 6**. The electro-refining process, well known as the Betts Process, is assumed to account for approximately 20% of refined lead (See **Figure 7**). Before anode casting, copper drossing is first performed to remove the bulk of the copper as a combination of matte and arsenide-antimonide. And the levels of arsenic and antimony must be controlled to produce suitable anodes for successful electrorefining practice[11].

Due to the increasingly stringent legislation for the emissions of lead particulates and sulphur dioxide, there has been a large research effort to find a new, more environmentally friendly technology, based on hydrometallurgy and electrometallurgy approaches. Considering the high electrochemical equivalent (the weight in grams of a substance produced or consumed by electrolysis with 100% current efficiency during the flow of a quantity of electricity equal to 1 faraday (96,485.34 coulombs).) of lead, these alternatives technologies make it possible to couple the environmental requirements to the energy savings with substantial reduction of production costs compared to the traditional processes. The recovery of sulphur as elemental sulphur is a significant advantage since elemental sulphur could be more easily stored and shipped, and could be readily converted to sulphur-containing products when needed. The electrowinning process at ambient or slightly higher temperature to produce pure lead has a distinct advantage over the smelting process(1200-1400ºC). Also when compared to the

fused chloride salts process conducted at about 500 ℃, this process also has no need for special cell construction, and the ambient temperature electrowinning is less energy-intensive[18].

Lead Bullion
(Cu, Sb, As, Sn, Ag, Au, Bi)
[Fe,Zn, S, Ni, O]

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        │
        ▼
┌──────────────────┐
│     Drossing     │ ──────────────► Copper Drossing or Matte
└──────────────────┘
        │
   (Sb, As, Sn, Ag, Au, Bi)
        │
        ▼
┌──────────────────┐
│     Softening    │ ──────────────► Antimonial Slag
└──────────────────┘
        │
   (Ag, Au, Bi) [Sb]
        │
        ▼
┌──────────────────┐
│   Desilverising  │ ──────────────► Zinc-Silver Crust
└──────────────────┘
        │
    (Zn, Bi) [Sb]
        │
        ▼
┌──────────────────┐
│    Dezincing     │ ──────────────► Metallic Zinc
└──────────────────┘
        │
    (Bi) [Zn, Sb]
        │
        ▼
┌──────────────────┐
│  Debismuthising  │ ──────────────► Bismuth Dross
└──────────────────┘
        │
   (Ca, Mg) [Zn, Sb]
        │
        ▼
┌──────────────────┐
│  Final Refining  │ ──────────────► Caustic Dross
└──────────────────┘
        │
        ▼
```

Market Lead >99.99% Pb
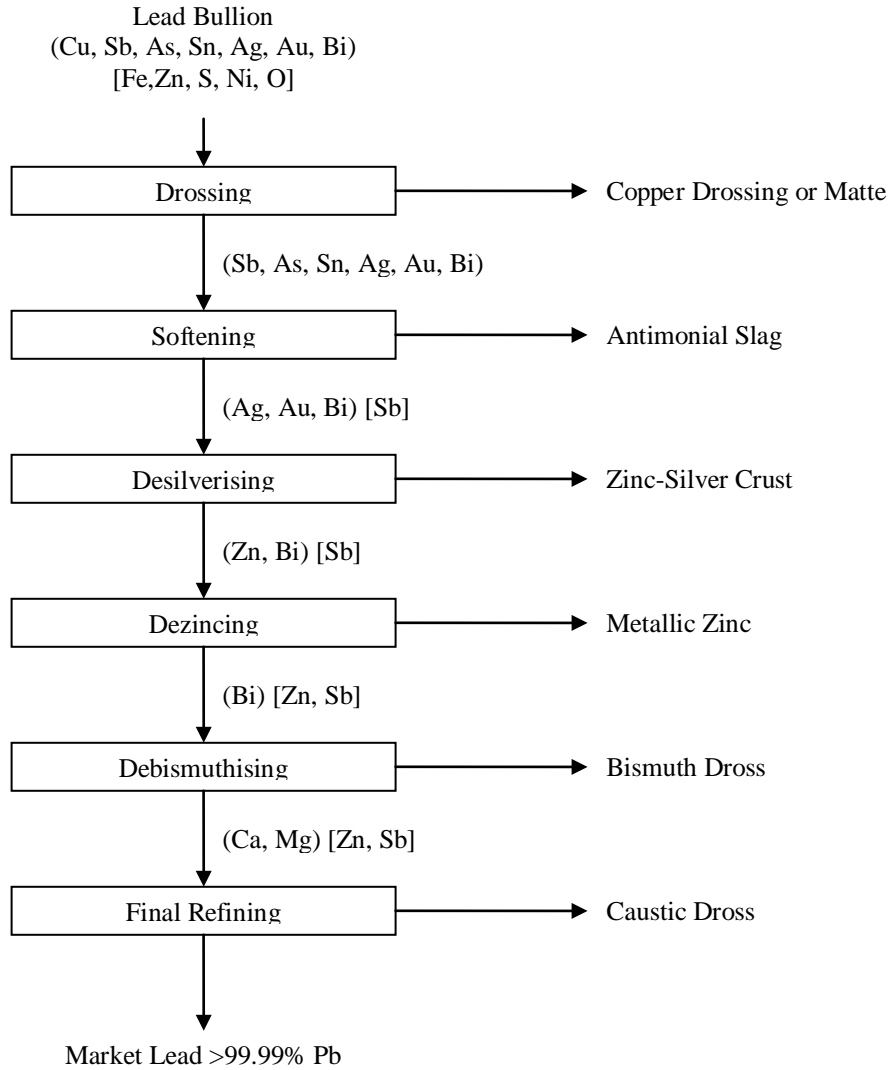
Figure 6   A generalized flowsheet for pyrorefining of lead[11]

Note: Parentheses ( ) indicate a major impurity component; Brackets [ ] indicate a minor impurity component

Molten Crude Lead

Continuous Drossing Furnace

Slag and Matte

Cu Recovery

Casting Kettle

Anode Casting

Anode

Staring Sheet Kettle

Staring Sheet Machine

Staring Sheet

Electrolytic Cell

Electrolyte

Scrap Anode

Mechanical Scrapper

Scrap

Centrifuge

Filtrate

Slime

Precious Metal Recovery

Cathode Deposit

Washing

Pig Casting Kettle

Casting Machine

Pig Lead
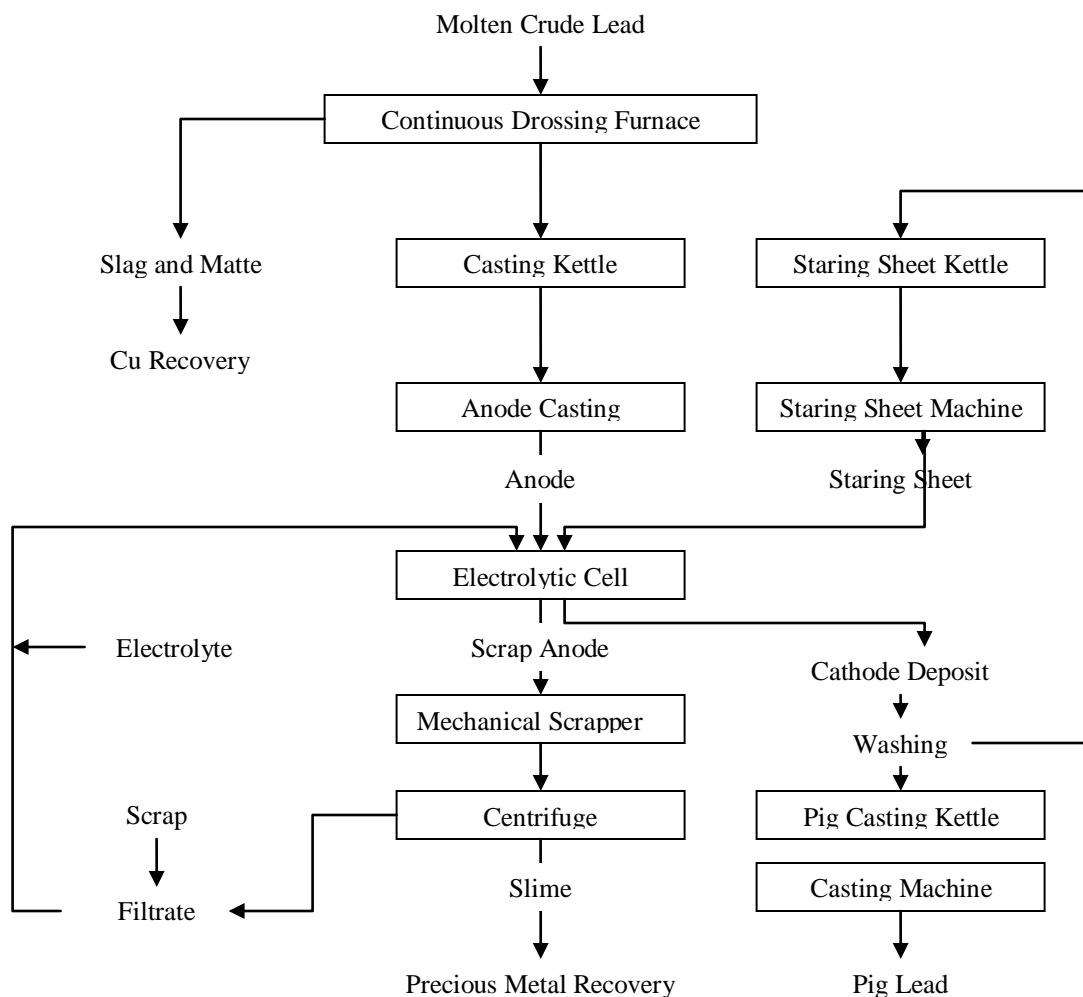
Figure 7   A generalized flowsheet for electrorefining of lead [11]

In particular, the hydro/electro-metallurgical routes, which have been extensively studied and even piloted, include USBM[7], RSR[6], Fluobor[4], Fluosilicic[3], Ginatta[5] and PLACID[19] processes. Integration of these processes with pyrometallurgical processes has been suggested, for example in the case of PLACID process[20].Some of these routes to treat battery paste comprise a preliminary stage in which the exhausted lead-acid batteries are crushed, followed by a separation in sulphuric acid. The plastic portion is submitted to recycling and the metallic portion is re-melted. The non-metallic portion, also called battery sludge, consists of different lead compounds, basically metallic lead, lead dioxide, lead sulphate and also lead oxide[21].

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With the development of technology, the all-inclusive and directly hydro-electrometallurgical route without a pre-treatment to convert lead-bearing minerals to oxidized form would be preferable in the near future. It has been reported that the Fluobor process, developed by Doe Run with its partner Engitec, could successfully and directly treat primary galena containing concentrate in ferric fluoborate medium with a lead recovery up to 99%[4].

2.3   Previous Studies on Lead Leaching

Intensive research on the hydrometallurgy of lead was undertaken in the 1970s and 1980s, without successful development[4]. Many lixiviants have been selected for the extraction of lead minerals and materials. Inorganic acids including mineral acids (i.e. sulphuric acid, hydrochloric acid, and nitric acid) as well as fluosilicic acid and fluoboric acid have attracted public attention (more details given in the later sections). Organic acids, as a probably less expensive leaching agent, have been used for their ability to solubilise iron and other metal oxides, like malic[22], oxalic[22], citric[1, 17, 23], ascorbic[21], acetic[24, 25]and tartaric[26] acids. And in some cases, alkaline solutions like ammonium and sodium hydroxide have been also investigated. However, the low solubility of lead(II) in many aqueous systems becomes the limitation for selecting the right treatment solution (see **Table 2**)[1]. Other aspects (e.g. operating feasibility, environmental impacts, health risk) also should be taken into account. So far none of the proposed processes is in commercial practice.

Table 2   Aqueous saturation solubility of some lead salts and problems of alternative electrolytes [27]

Lead Salts	Saturation Solubility/wt.%	Potential Problems
Methane sulfonate, $Pb(CH_3SO_3)_2$	59 (25 ℃)	--------------------------
Perchlorate $Pb(ClO_4)_2$	69 (25 ℃)	Cathodic decomposition, Corrosive
Chlorate, $Pb(ClO_3)_2$	72 (25 ℃)	Cathodic decomposition, Corrosive
Acetate, $Pb(Ac)_2$	35 (25 ℃)	Low conductivity, Low solubility
Dithionate, $PbS_2O_6.4H_2O$	53 (25 ℃)	Hydrolysis problems, Low conductivity
Fluoborate, $Pb(BF_4)_2$	50 (20 ℃)	Environmental problems
Fluosilicate, $PbSiF_6.4H_2O$	69 (20 ℃)	Environmental problems
Nitrate, $Pb(NO_3)_2$	37 (20 ℃)	Cathodic decomposition

For the electrolysis process, the down stream after leaching and purification to electrowin lead metal, many aqueous systems encounter cathodic decomposition of anion species, which brings about sequential problems, such as the declining current efficiency and the increasing electricity consumption.

2.3.1 The pe-pH Diagram for Pb-C-H₂O System

The thermodynamics of the lead carbonate (or cerussite) and basic lead carbonate (or hydrocerussite) leaching systems can be discussed in terms of the pe-pH diagram for the Pb-C-H₂O system (See **Figure 8**). The calculation is shown in **Appendix A**:.
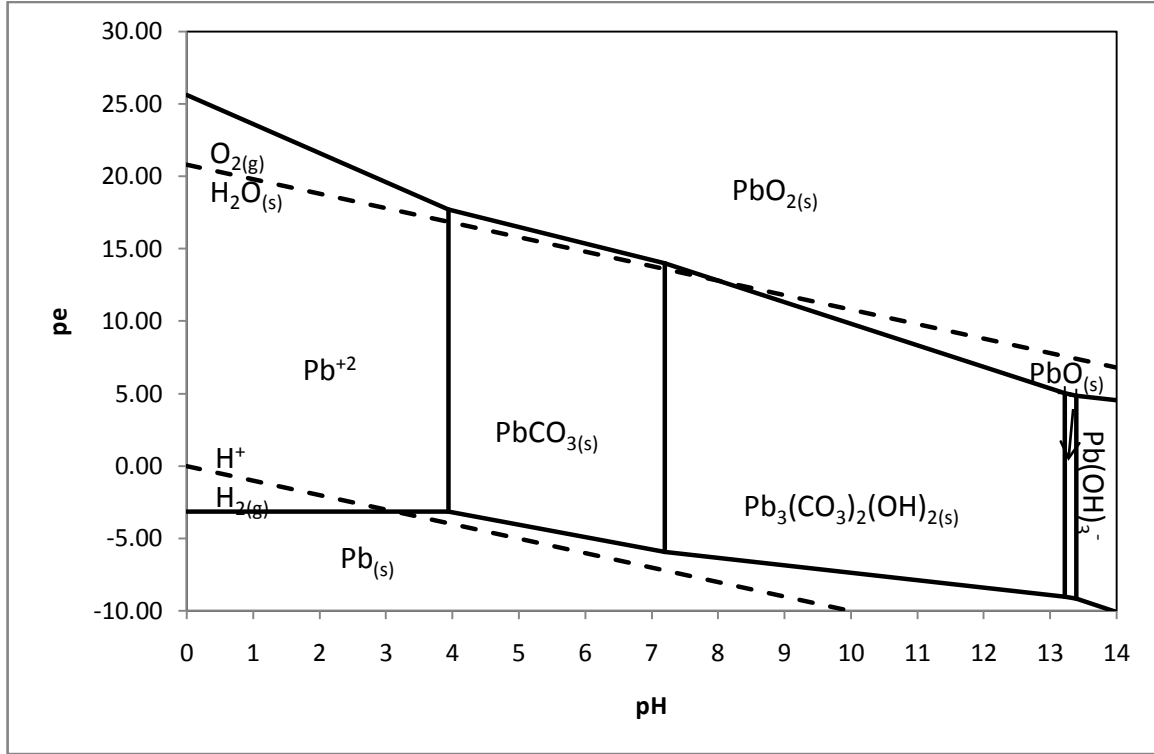
Figure 8   pe-pH diagram of Pb-C-H₂O system

The following conditions are considered for the construction of the figure: total inorganic carbon concentration=0.01M, total soluble Pb concentration =0.01M, ionic strength ~0, T=25ºC. Thermodynamic data were obtained from Pankow[28].

The pe-pH diagram indicates the dissolution opportunities for cerussite and hydrocerussite under the defined conditions. The arrows represent the possible methods for lead extraction from cerussite and hydrocerussite, and corresponding to the dissolution reactions expressed by **Reaction 1**, **Reaction 2**, **Reaction 3** and **Reaction 4**, respectively.

Acidic Leaching:

$$PbCO_{3(s)} + 2H^{+}_{(aq)} \rightarrow Pb^{+2}_{(aq)} + H_2O_{(l)} + CO_{2(g)} \uparrow \qquad \text{Reaction 1}$$

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$$Pb_3(CO_3)_2(OH)_{2(s)} + 6H^+_{(aq)} \rightarrow 3Pb^{+2}_{(aq)} + 4H_2O_{(l)} + 2CO_{2(g)} \uparrow$$ **Reaction 2**

Alkaline Leaching:

$$PbCO_{3(s)} + 3OH^-_{(aq)} \rightarrow Pb(OH)^-_{3(aq)} + CO^{2-}_{3(aq)}$$ **Reaction 3**

$$Pb_3(CO_3)_2(OH)_{2(s)} + 7OH^-_{(aq)} \rightarrow 3Pb(OH)^-_{3(aq)} + 2CO^{2-}_{3(aq)}$$ **Reaction 4**
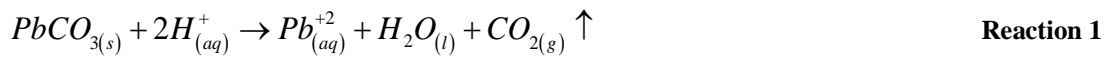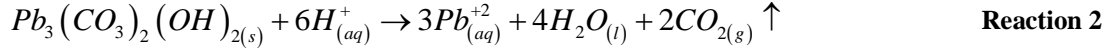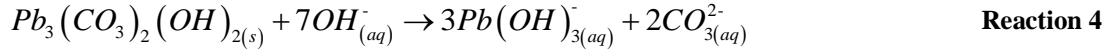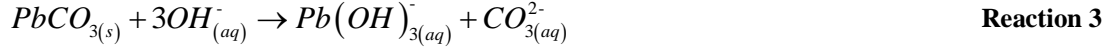
According to the pe-pH thermodynamic diagram of Pb-C-H₂O system[29], it is obvious that lead carbonate and hydrocerussite are rarely soluble in the pH range between 4 and 13.5, but are quite soluble at pH<4 where solution is slightly acidic or at pH>13.5 where solution is highly caustic. The alkaline leaching medium includes: ammoniacal ammonium sulphate, sodium hydroxide and glycerol, sodium potassium tartrate and sodium hydroxide etc.

Compared to alkaline aqueous medium, the acidic medium have been more commonly studied, since low pH is more favourable for dissolution of cerussite and the alkaline processes are usually accompanied with a subsequent acidic treatment, which make the alkaline processes more complicated. These acidic leaching medium can be broadly divided into two categories: inorganic and organic. The inorganic category consists of sulfate, nitrate, chloride, fluosilicate and fluoborate medium etc., while the organic category includes acetate, citrate and methane sulfonate medium etc.

2.3.2   Alkali Leaching of Lead

Morachevskii et al.[30] first reported the feasibility of separating lead from exhausted lead-acid batteries in alkaline glycerol medium. Weiping Chen et al.[31, 32] investigated a new basic method for recovering lead from scrap batteries with NaOH as sulphur-eliminating agent and $KNaC_4H_4O_6$. When the amounts of both NaOH and $KNaC_4H_4O_6$ are sufficient, total lead content in the solution would run to 150g/L or even higher. However, without $KNaC_4H_4O_6$, total lead content in solution can only be around 20g/L. The reactions are shown as follows:

$$PbO_{(s)} + NaOH_{(aq)} \rightarrow NaHPbO_{2(aq)}$$ **Reaction 5**

$$PbO_{(s)} + 2NaOH_{(aq)} \rightarrow Na_2PbO_{2(aq)} + H_2O_{(l)}$$

Reaction 6

$$2PbO_{(s)} + 2KNaC_4H_4O_{6(aq)} + 2H_2O_{(l)} \rightarrow Pb_2\left(C_4H_4O_6\right)_{2(aq)} + 2KOH_{(aq)} + 2NaOH_{(aq)}$$

Reaction 7

$$2PbO_{(s)} + 3KNaC_4H_4O_{6(aq)} + 2H_2O_{(l)} \rightarrow KNaPb_2\left(C_4H_4O_6\right)_{3(aq)} + KOH_{(aq)} + 2NaOH_{(aq)}$$

Reaction 8
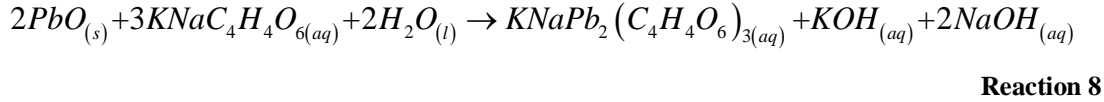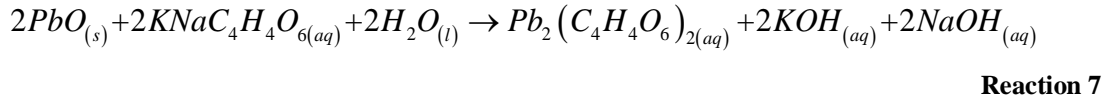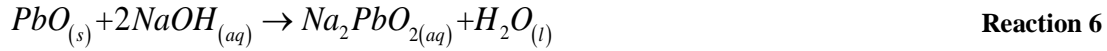
G.C. Bratt et al.[33] explored a novel hydrometallurgical process to recover lead, which was based on the solubility of certain oxidized lead compounds in aqueous ammoniacal ammonium sulphate (AAS) solutions (containing about 140g/L ammonia and 210g/L ammonium sulphate). Soluble lead mainly exists in form of $Pb(OH)SO_4^-$ and under ambient conditions the lead content could reach 100g/L, thus the proposed dissolution reaction is[34]:

$$PbSO_{4(s)} + NH_4OH_{(aq)} \rightarrow NH_4\left[Pb\left(OH\right)SO_4\right]_{(aq)}$$

Reaction 9
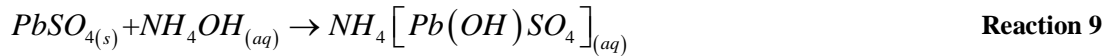
Unlike other metals processed in AAS solution, ammines of the form $Pb\left(NH_3\right)_x^{2+}$ are not created.

However, it was found that the solubility of lead decreased markedly within 24h of leaching, probably due to the ammonia loss via evaporation[35]. And also lead present in jarosite is not soluble in AAS solution and must be treated by acid[33]. The ammonium sulphate is present to buffer the ammonia solution, therefore lead would not precipitate[36]. The previous work has shown that increased ammonia concentration results in higher lead solubility when ammonium sulphate is present. The concentration of ammonium sulphate must be optimized for a given ammonia concentration, or the lead content will decreases. The proposed process for extraction of lead in AAS medium generally consisted of five steps:

(1) Pre-treatment: convert lead-bearing minerals to lead oxidized form;
(2) Leaching: with AAS solution under ambient conditions to produce a pregnant solution containing up to 100g/L lead;
(3) Lead Recovery: via electrolysis, cementation or precipitation;
(4) Treatment of intermediate products: conversion to saleable products;
(5) Recycling the treatment solution.

2.3.3   Acid Leaching of Lead

The commonly used mineral acids include sulphuric acid, nitric acid and hydrochloric acid. The costs of them are much lower compared to other acidic lixiviants. Therefore, their applications to recover lead are first studied. However, due to their limitations in dissolving lead and subsequent processing, some other acidic lixiviants received considerable public attention and got investigation.

2.3.3.1   Sulfate Leaching of Lead

Commercial hydrometallurgical production of zinc began in 1915 and a similar process has been used for copper since 1967. Both zinc and copper processes use sulphuric acid to dissolve or leach the metal oxides into a solution and subsequently the metals are electrowon in a low-voltage electrochemical cell. However, the sulphuric acid hydrometallurgical processes cannot be applied to lead because lead is not soluble in sulphuric acid.

It was reported that lead smelter dust, mainly PbS, could be non-oxidatively reacted in sulphuric acid to produce lead sulphate, which could be carbonated or desulfurized to lead carbonate and be subsequently leached in weak nitric acid. The sulphation of PbS was dramatically increased with the growing concentration of sulphuric acid above 4M and was insignificant at sulphuric acid concentration of 0.1M or lower. However, without the addition of 1M nitric acid in the sulphuric acid, even if the concentration of sulphuric acid was as high as 7M, the 90% leaching efficiency could not be accomplished(See **Reaction 10**)[37].

$$PbS_{(s)} + H_2SO_{4(l)} \rightarrow PbSO_{4(s)} + H_2S_{(g)} \uparrow \qquad\qquad \textbf{Reaction 10}$$

Gabriel da Silva[38] first conducted the ferric sulphate oxidation of galena as an analog to the indirect bio-oxidation mechanism. In most cases, the diffusion-controlled step was the rate determining step, resulting from the formation of a tenacious layer of $PbSO_4$ and S^0 on the surface of the galena. The oxidation product layer was demonstrated to consist solely of lead sulphate and elemental sulphur, in a 1:1 ratio. It was proposed that elemental sulphur and lead ions were formed in a ferric oxidation reaction, while lead sulphate subsequently formed via precipitation of the lead ions (See **Reaction 11**).
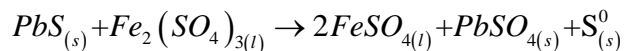
$$PbS_{(s)}+Fe_2\left(SO_4\right)_{3(l)} \rightarrow 2FeSO_{4(l)}+PbSO_{4(s)}+S^0_{(s)} \qquad \textbf{Reaction 11}$$

In contrast to the extensive studies on the dissolution of galena in ferric-chloride solutions, relatively little is known about the leaching of galena in the analogous [$Fe_2(SO_4)_3$-H_2SO_4] system. The surface of galena was rapidly passivated by the formation of $PbSO_4$ or basic lead sulphate, which subsequently would be dissolved for lead recovery. While at higher temperature, much of $PbSO_4$ would dissolve and re-precipitate as lead-bearing jarosite, which is difficult to dissolve[39].

There are some attempts on the hybrid chloride-sulfate system. Significantly, according to the Eh-pH diagram for a system containing galena in the presences of both chloride and sulphate ions, the formation of $PbSO_4$ is found to dominate $PbCl_2$ formation under typical bioleaching or ferric leaching conditions. This observation indicates that even in the presence of relatively high chloride ion concentrations, the oxidation of galena in sulphate medium would still be expected to result in lead sulphate production[38].

An oxygen pressure oxidative leaching process for PbS-Cu_2S mattes operated in sulphate-chloride medium is developed by Borken Hill Associated Smelter (Port Pirie, Australia). A somewhat similar process also has been considered by Naoshima Refinery, in which about 50% of galena converted to lead sulphate in about 20min. Over a period around 100min, the oxidation reaction completed at 100ºC and 1 atm O_2 pressure[39]. Lead sulphate is recovered and recycled to the lead smelter.

2.3.3.2   Chloride Leaching of Lead

Since it permits the direct conversion of lead sulphide into lead chloride, the non-oxidative leaching of galena in acidic chloride solution, releasing hydrogen sulphide has been studied in laboratories and tested in pilot plants as demonstrated by Awakura et al.[40, 41]. The first of these pilot plants is the so-called Chrinstensen process, which utilized HCl-NaCl solution. However, it is a pity that the pilot plant was forced to close due to the lack of corrosion-resistant materials required for the highly concentrated acid-chloride solution[42]. Compared with pyrometallurgy route, another distinct advantage for the chloride process is that the

considerable removal of impurities through crystallizing the concentrated lead chloride solution by cooling is simple and effective.

Even though the non-oxidative leaching studies of galena in hydrochloric acid releasing hydrogen sulphide has been repeated in laboratories, there are insufficient kinetics studies on explaining complete mechanism in literature. Most of the available studies do not address some basic and important kinetics parameters (i.e. reaction order, activation energy, Arrhenius factors and reaction rate constant).

A.A. Baba et al. [43] investigated the non-oxidative dissolution of a Nigerian galena in hydrochloric acid solution. They found that 94.8% of galena was dissolved by 8.06M HCl at 80°C within 120min with a solid concentration of 10g/L. The mechanism of dissolution followed the shrinking core model for the diffusion controlled mechanism with a rate constant with respect to particle diameter around 1. This study presents a very similar results to Olanipekun's work[41], in which about 96% of lead was dissolved within 120min in 8.42M hydrochloric acid solution at 95°C.

Núñez et al.[42, 44] undertook several kinetics studies on the non-oxidative leaching of galena with solutions of hydrobromic, perchloric acid and hydrochloric acid. The leaching rates were described in terms of mean ionic activities of the electrolytes, instead of individual ions. They found that the apparent orders for the mean ionic activities of perchloric acid, hydrochloric acid and hydrobromic acid were 1, 1.5 and 2, respectively. The increasing reaction orders were probably due to the enhanced complex-forming effects of acid anions $(Br^->Cl^->ClO_4^-)$. Perchloric acid has no complex-forming effect.

In the research work of Awakura et al.[40] on non-oxidative dissolution of natural galena in aqueous acid solution with or without sodium chloride, the galena dissolution rate was of the first order with respect to hydrochloric ion activity in hydrochloric acid solutions. They also indicated that the reaction order probably could be greater than one at higher concentration.

The accelerating effect of chlorides in HCl solution used for non-oxidative leaching galena is well known. However, it appears that even when the proton concentration increased from 8.06 to 12M, the effect was still very mild[43]. In summary, to achieve considerable non-oxidative extraction of galena, high reagents concentrations and elevated temperature, as well as moderate salt content sometimes, should necessarily be taken into consideration. Thus a number of studies on oxidative leaching of galena in chloride medium have attracted attention.

Oxidative leaching of galena in hydrochloric-chloride medium also has been well studied. Huai-zhong Long et al.[45] investigated the co-extraction of galena and pyrolusite in sodium chloride solution. The pyrolusite (MnO_2) mineral contained in the mixed concentrate acted as the oxidant. It was reported that the main factors were NaCl concentration, reaction time and temperature, and the insoluble $PbCl_2$ film on the galena surface prevented galena from high extraction. However, the addition of sodium chloride could greatly reduce the film resistance, thus improving the dissolution rate.

Ferric chloride leaching in the presence of hydrochloric acid and sodium chloride has been well studied as a possible means of extracting lead via the hydrometallurgical route, since soluble lead-bearing species and elemental sulphur are formed. In the research work of M.C. Fuerstenau et al.[46], the dissolution rate of galena in ferric chloride solution followed the shrinking core model and the mass transportation of ferric chloro-complex through the product layer appeared to be rate determining step under most conditions. There still exists the possibility like in sulphate medium that a passivation film of lead chloride ($PbCl_2$) can be formed on the surface[38]. Now it is commonly thought that diffusion control prevails in the chloride system.

Several lead leaching processes based on ferric chloride medium have been developed at the pilot plant scale: (a) the United States Bureau of Mine ferric chloride leaching process, involving ferric chloride leaching of galena to produce lead chloride and subsequent electrolysis in fused-salts to produce lead; (b) Minemet Recherche ferric leaching process,

including dissolution of lead in a brine of sodium chloride and ferric chloride where lead was electrowon in aqueous electrolyte.

There has been increasing efforts on exploring new methods for recycling lead from scrap batteries and some other oxidized lead materials[47]. A very similar process to Minemet Recherche Process for lead recovery from spent lead acid battery paste in brine medium, the PLACID Process, was developed by G. Diaz and other co-workers in Spain[48]. Lead was leached in warm, slightly acidic hydrochloric acid brine to form soluble lead chloride. Lead was electrowon from lead chloride on the cathode in a novel electrowinning cell. The sponge-form metallic lead was collected by a scraper (more details in **Sub-Section 2.5.2.1**).

In Huang Kai's study[49], the washed fly ash (from Taiheiyo Cement Corp., Japan and mainly contains $Ca(OH)_2$, ZnO and PbO) was subjected to hydrochloric acid dissolution. The optimal metal extraction can be achieved under the following conditions: pH=1.0, Liquid/Solid (L/S) ratio=20, contact time=5min and room temperature. Temperature and L/S ratio showed very slight effect on the lead extraction rate, while the lead extraction rate was strongly dependent on the solution pH value.

It is well known and demonstrated that the reaction rate can be greatly enhanced by the addition of chloride salts in solution. There are two interpretations for the "salt effects": one is the increase of hydrogen ion activity and another one is the enhancement of specific adsorption or surface complexing of chloride ions[40, 50]. While the reaction order is weakly affected by the addition of various metal chloride salts, as demonstrated by C. Núñez[42]. In this study, a reaction order of 3/2 for the mean HCl activity in the solution was constant over a wide range of concentration. At a given hydrochloric acid concentration, various metallic chlorides showed no influence on the reaction order for the mean HCl activity, *vice versa*.

However, none of the processes discussed above have been in commercial use. There are some inherent problems in these processes: (a) relative low solubility of lead in chloride medium; (b) low product purity obtained from molten salt electrolysis; (c) corrosive chlorine gas evolution; (d) corrosiveness that requires expensive materials of construction; (e) the

intermediate product, lead sponge or lead hydroxide is contaminated with chloride which made the subsequent conversion to saleable products difficult; (f) sulphate must be removed from the circuit as gypsum or sodium sulphate[3, 33].

2.3.3.3 Nitrate Leaching of Lead

Although industrial schemes for hydrometallurgy of lead in nitric acid-nitrate salts are sparse, there are some investigations in this field. The nitrate medium is a system in which Pb^{+2} ions are highly soluble. Thus lead nitrate does not exhibit the solubility problems that lead to the poor economics of the lead chloride system[46].

Since currently the majority of lead compounds (oxides, halides and sulphate) are produced from metallic lead through conversion to $Pb(NO_3)_2$ by dissolution in nitric acid, A.G. Kholmogorov and other researchers in Russia have conducted a series of projects on leaching lead concentrate in nitrate based solutions to produce saleable lead compounds instead of metallic lead. The highly purified lead compounds, like $PbSO_4$, PbO, PbO_2 and $PbCO_3$, can be used for the production of accumulators as well as chemicals in organic and inorganic chemistry[51, 52]. The direct production of these compounds by the nitrate based process is economically efficient, which makes [HNO_3-$Fe(NO_3)_3$] solutions very advantageous. They have proposed a hydrometallurgical technology for synthesis of lead salt solution, which is based on the oxidation of lead sulphide.

G.L. Pashkov and A.G. Kholmogorov[53] found that in the low potential range of $-0.4 \sim +0.1V$, the interactions between pure lead sulphide with nitric acid proceeded largely by non-oxid ative mechanism with releasing H_2S. Elevated temperature and increasing HNO_3 addition accelerated the dissolution rate. H_2S slowly reduced nitrate to nitrite (nitrous acid, a much more active oxidant than nitrate). The involvement of nitrite promoted the oxidation of sulphides, including the sulphate formation (See **Reaction 12**, **Reaction 13** and **Reaction 14**). Thus the rising content of HNO_3 increased the yield of sulphate in solid residue.

$$PbS_{(s)} + HNO_{3(aq)} \rightarrow Pb\left(NO3\right)_{2(aq)} + H_2S_{(g)} \uparrow \qquad \text{Reaction 12}$$
$$4HNO_{3(aq)} + H_2S_{(g)} \rightarrow 4HNO_{2(aq)} + H_2SO_{4(aq)} \qquad \text{Reaction 13}$$

$$8HNO_{2(aq)}+PbS_{(s)} \rightarrow 8NO_{(g)} \uparrow +PbSO_{4(s)} \downarrow +4H_2O_{(l)}$$
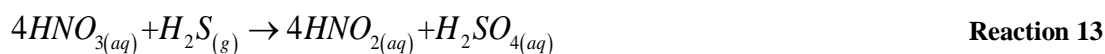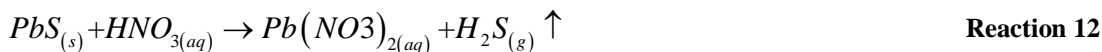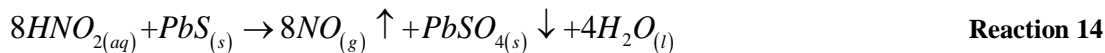
Reaction 14

These reactions also were observed by Lee [37]. Lead dust dissolution (mainly PbS) was considerably enhanced when the concentration of nitric acid was increased up to 8M. When the nitric acid concentration was higher than 10M, non-oxidative dissolution of galena predominated and H_2S gas was released, which subsequently reacts with nitric acid to produce sulphuric acid and NO gas (See **Reaction 15**). The product sulphuric acid would precipitate lead as lead sulphate resulting in the low leaching efficiency at high nitric acid concentration. In this case, an increasing consumption for nitric acid was required and the sulfate production process necessarily needed to be suppressed, compromising the important advantages of nitrate solutions that lead nitrate is highly soluble.

$$PbS_{(s)}+(2x+1)NO_{3(aq)}^{-}+4H_{(aq)}^{+} \rightarrow (1\text{-}x)Pb_{(aq)}^{+2}+(1\text{-}x)S_{(s)}^{0}+xPbSO_{4(s)}+(2x+1)NO_{(g)} \uparrow +2H_2O_{(l)}$$

Reaction 15
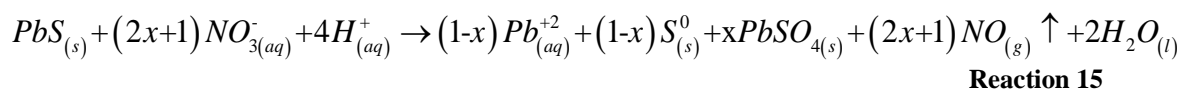
A small amount of ferric nitrate could sharply promote the dissolution kinetics over the whole potential range from -0.4V to 0.8V, along with almost all sulphur from galena converting to elemental sulphur. At higher potential biases, the galena rotating disk electrode (RDE) dissolves for the most part anodically, showing the highest rate at ~0.7V, whereas the rate as a function of acid concentration is maximal in 1M HNO_3. Such behaviour is apparently due to a passivation, although the oxidation remains rapid under the "passive" conditions. Higher ferric concentration could promote lead solubility, and proton concentration could facilitate the lead recovery and also suppress the lead sulphate formation. These facts indicated that nitric acid was a principle oxidant while ferric/ferrous couple acted as catalysts[53]. Lead sulphide could be oxidized by Fe^{+3} and Fe^{+2} ions could be oxidized by HNO_3:

$$3Fe_{(aq)}^{+2}+NO_{3(aq)}^{-}+4H_{(aq)}^{+} \rightarrow 3Fe_{(aq)}^{+3}+NO_{(g)} \uparrow +2H_2O_{(l)}$$
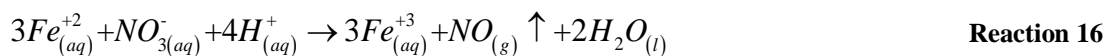
Reaction 16

The kinetics study of the dissolution of galena in nitrate medium performed by M.C. Fuerstenau et al. indicated that the dissolution rate was controlled by surface mixed

electrochemical reaction (See **Reaction 17**)[46]. The mixed electrochemical reaction consisted of anodic and cathodic half-reactions. The anodic half-reaction involved the oxidation of galena to lead ion and elemental sulphur, and the cathodic one included the reduction of ferric to ferrous. In contrast to the addition of chloride salts in chloride system, the addition of nitrate salts (i.e. sodium nitrate) decreased the dissolution rate when the concentration higher than 1M. An analogous situation also happened in the sulphate system, in which the addition of $MgSO_4$ in the ferric sulphate medium decreased the dissolution kinetics.

$$PbS_{(s)} + 2Fe^{+3}_{(aq)} \rightarrow Pb^{+2}_{(aq)} + 2Fe^{+2}_{(aq)} + S^0_{(s)} \qquad\qquad \textbf{Reaction 17}$$

Salih Aydogan et al.[54] conducted the kinetics study of galena leaching in nitric acid solution with another oxidant, hydrogen peroxide. The addition of hydrogen peroxide accelerated the reaction via regenerating the nitric acid compared to nitric acid alone. The standard Gibbs energy of the regeneration reaction (See **Reaction 18**) is negative (-449.62 kJ/mol[55]), showing the reaction is feasible. The dissolution curves were found to fit the shrinking core model over a wide range of parameters with the surface chemical reaction as rate controlling step, and at high proton content the kinetics was diffusion-controlled. The activation energy was 42kJ/mol, which supported the reaction controlled dissolution mechanism. Typically, the Arrhenius activation energy for surface reaction control is higher than 40kJ/mol).

$$3H_2O_{2(aq)} + 2NO_{(g)} \rightarrow 2HNO_{3(aq)} + 2H_2O_{(l)} \qquad\qquad \textbf{Reaction 18}$$
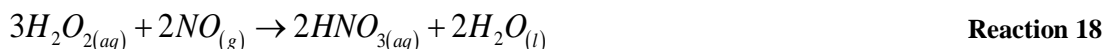
Several nitric acid processes have been patented and developed, including the Arseno, Nitrox and Redox Processes. The first two processes use low temperature and high nitric acid concentration and the last one employs high temperatures. However, none of these has been applied in industry due to unfavourable economic issues. The nitric-sulfuric acid pressure oxidation NSC Process at Sunshine Mine in Idaho has been reported to recover silver and copper from refractory ores, however, this is process would not be applicable to lead

concentrates due to the high sulphuric acid content in the leach which precipitates lead sulphate[56].

2.3.3.4   Fluosilicate Leaching of Lead

Fluosilicic acid imparts a high solubility to lead(II), which has been widely used for refining anode lead, well known as the Betts Process. Another advantage for fluosilicic acid medium is that the electrolyte is an inexpensive waste product readily available from phosphoric acid plants[18].

The direct leaching of galena in fluosilicic acid medium was first reported by Pinaev and Novinskii [57]. They found that ferric fluosilicate leaching of galena followed by aqueous electrolysis was much more feasible and cheaper than the ferric chloride process. E.R. Cole et al. [18] proposed a hydrometallurgical method to recover lead and sulphur from sulphide ores in fluosilicic acid medium. The patent demonstrated that a two-step procedure could be carried out using moderate reaction conditions. The two steps included a first leaching step with fluosilicic acid in the presence of an oxidant, followed by an electrowinning step to produce the pure lead and recycle fluosilicic acid from lead fluosilicate solution. Chen and Dresinger[3] also conducted a similar study on leaching galena by fluosilicic acid and proposed to recover lead metal through electrowinning process.

Alexander Krstev et al. [58] studied the recovery of lead from galena ores through a hydrometallurgical method including two steps. The first step was to leach galena synthetic mixtures in waste fluosilicic acid with hydrogen peroxide and lead dioxide as oxidants at 95ºC (See **Reaction 19**, **Reaction 20** and **Reaction 21**). And the second step was to produce 99.99% lead from lead fluosilicate solution at 35 ºC via electrolysis and recover Sulfur by solvent extraction. The leaching results showed that the combined use of H_2O_2 and PbO_2 was unnecessary and H_2O_2 was more effective and cheaper than PbO_2. Probably it is beneficial to adopt H_2O_2 at the beginning and PbO_2 at the end of leaching process to avoid over-oxidizing PbS to $PbSO_4$. The leaching rate showed strong dependence on temperature but was independent of free acid concentration, which was consistent with the results of Chen and Dreisinger's study[3].

$$PbS_{(s)}+H_2O_{2(aq)}+2H^+_{(aq)} \rightarrow Pb^{+2}_{(aq)}+2H_2O_{(l)}+S^0_{(s)}$$ **Reaction 19**

$$PbS_{(s)}+PbO_{2(s)}+2H^+_{(aq)} \rightarrow Pb^{+2}_{(aq)}+PbO_{(s)}+H_2O_{(l)}+S^0_{(s)}$$ **Reaction 20**

$$PbO_{(s)}+2H^+_{(aq)} \rightarrow Pb^{+2}_{(aq)}+H_2O_{(l)}$$ **Reaction 21**
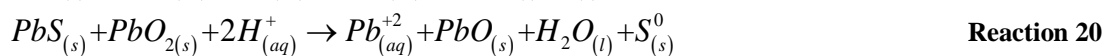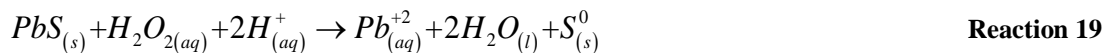
P.R. Taylor [59, 60] has conducted a series of kinetics studies on oxidative leaching of galena in fluosilicic acid medium. Various oxidants were investigated, among which hydrogen peroxide was also proven to be the most effective. Decreasing the particle size and increasing the leaching temperature increased the extraction rate. The initial apparent activation energy was calculated to be 11.72kJ/mol, indicating that galena leaching in fluosilicic acid solution with hydrogen peroxide as an oxidant was proposed to be fluid film mass transfer controlled initially. In contrary, another study on galena leaching in ferric fluosilicate medium[3] found the oxidation process to be surface chemical reaction controlled, with an apparent activation energy of 62kJ/mol. Temperature had a significant effect on the dissolution compared to concentrations of Pb^{+2}, H^+ and Fe^{+3}. The acidic fluosilicate medium was selective for metal extraction, since the kinetics of zinc extraction is much lower than those of lead extraction, which made the fluosilicic-based medium very desirable and feasible for treatment of complex lead-zinc sulphide concentrates.

The U.S. Bureau of Mines process was developed by Lee et al. to recover lead from spent batteries and galena concentrate in fluosilcic acid medium[6, 61, 62]. The oxidative leaching process was usually performed at 95ºC. The oxidants used consisted of high pressure oxygen, hydrogen peroxide, lead dioxide and ferric ions. Compared with H_2O_2 and PbO_2, high pressure oxygen was cheaper. A lead extraction of 93% was achieved when galena was leached in H_2SiF_6 at 95ºC with 200psig O_2 pressure for 40min, using ferric nitrate as catalyst. The element sulphur could be recovered from the leach residue through solvent extraction.

Stauter et al. [63-65] proposed a production route for metallic lead from lead-bearing sources through a series of steps including halogenations, brine leaching, recrystalization, carbonation, dissolution and electrowinning. The last two steps were to dissolve the intermediate lead carbonate in fluosilicic acid and to electrowin metallic lead sheet on the

cathode. The indirect treatment for lead-bearing materials using fluosilicic acid made these processes rather complicated when compared to the direct leaching.

However, both fluosilicic acid and fluoboric acid undergo hydrolysis to form free fluoride species and silicates. The free fluoride species are potentially hazardous and strongly corrosive (as HF of air-borne fluorides) and may result in the undesirable precipitation of lead as lead fluoride or lead oxy-fluoride. For these reasons, the fluo-containing acid medium are not used.

2.3.3.5   Fluoborate Leaching of Lead

Like fluosilicate medium, fluoborate electrolyte also possesses a high solubility for lead and also has use in electrodeposition of tin-lead solder. Luiz C. Ferracin et al.[21] conducted a study on lead recovery from lead acid batteries using a hydro-electrochemical process. A total of 13 aqueous solutions were investigated, among which the fluoboric acid (200g/L) showed an attractive performance as a leaching electrolyte due to its low cost and reasonable leaching strength. Besides, other oxidized lead materials, like insoluble sludge or filter cake from hydrometallurgical desulfurization process, also could be dissolved in fluroboric acid (HBF_4) [2]. The solution was then purified by cementation followed by electrowinning.

In the U.S. Patent of Olper and Francchia[66], a process was proposed in which galena concentrate was leached with an aqueous solution of ferric fluoborate and fluoboric acid with ferrous fluoborate, lead fluoborate and elemental sulphur being formed according to **Reaction 22**:

$$2Fe\left(BF_4\right)_{3(aq)} + PbS_{(s)} \rightarrow 2Fe\left(BF_4\right)_{2(aq)} + Pb\left(BF_4\right)_{2(aq)} + S^0_{(s)}$$ **Reaction 22**
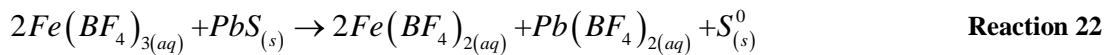
The above ferric fluoborate process may also be used to leach crude lead to be refined according to **Reaction 23** [67]:

$$2Fe\left(BF_4\right)_{3(aq)} + Pb_{(s)} \rightarrow Pb\left(BF_4\right)_{2(aq)} + Fe\left(BF_4\right)_{2(aq)}$$ **Reaction 23**
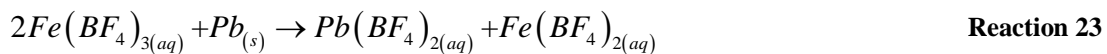
Compared to the redox couple of Fe^{+3}/Fe^{+2}, the redox couple of Ti^{+4}/Ti^{+3} ($E^0 = 100mV$ vs. NHE, between the potential of Pb^{+2}/Pb and PbO_2/Pb^{+2}) was proposed for a more efficient and quick dissolution of lead (See **Reaction 24** and **Reaction 25**)[68]. For industrial application, a concentration of Ti ions (around 0.05M) and the use of a counter-current electrolyte flow in the electrolysis cell can feasibly accomplish the leaching process of pastes and slimes in a batteries recycling plant.

$$Pb_{(s)} + 2HBF_{4(aq)} + 2Ti_{(aq)}^{+4} \rightarrow Pb(BF_4)_{2(aq)} + 2Ti_{(aq)}^{+3} + 2H_{(aq)}^{+} \qquad \textbf{Reaction 24}$$

$$PbO_{2(s)} + 2HBF_{4(aq)} + 2Ti_{(aq)}^{+3} + 2H_{(aq)}^{+} \rightarrow Pb(BF_4)_{2(aq)} + 2Ti_{(aq)}^{+4} + H_2O_{(l)} \qquad \textbf{Reaction 25}$$
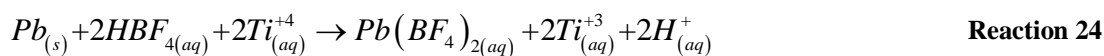
Another U.S. patent proposed by King also gave a description of fluoroboric acid control in its application in hydrometallurgical process to recover metals from metal sources containing more than one metal such as antimony, lead, copper, zinc, bismuth, tin, cadmium and other metals by leaching the metal containing source with a ferric fluoborate/fluoboric acid so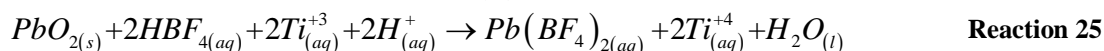lution. The leached solution is extracted with organic extractants, ion exchange resins and the like to provide a loaded extract and a raffinate which contains fluoboric acid produced in the extraction step, then followed by an electrowinning process[69].

In the USA, Doe Run Company, in partnership with Engitec, has developed a proprietary new technology as a breakthrough in traditional lead industry since the early 1990s. The breakthrough technology improved lead processing efficiency and dramatically reduced air, land and water releases. The all-inclusive hydrometallurgical route, so-called Fluobor® Process, for the recovery of refined lead was fed by lead sulphide concentrates without a high-temperature pre-treatment to create an oxide[4]. The recovery of lead directly to a finished product is approximately 99%, compared to 95% with traditional smelting. The Fluobor® Process shown in **Figure 9** uses four primary steps, of which the first step was "Multi-Stage Leaching/Purification Process". In this step, lead-bearing concentrate was placed in contact with ferric fluoborate; iron was consumed and other impurities were precipitated; lead sulphide was converted into soluble lead fluoborate and insoluble elemental sulphur.
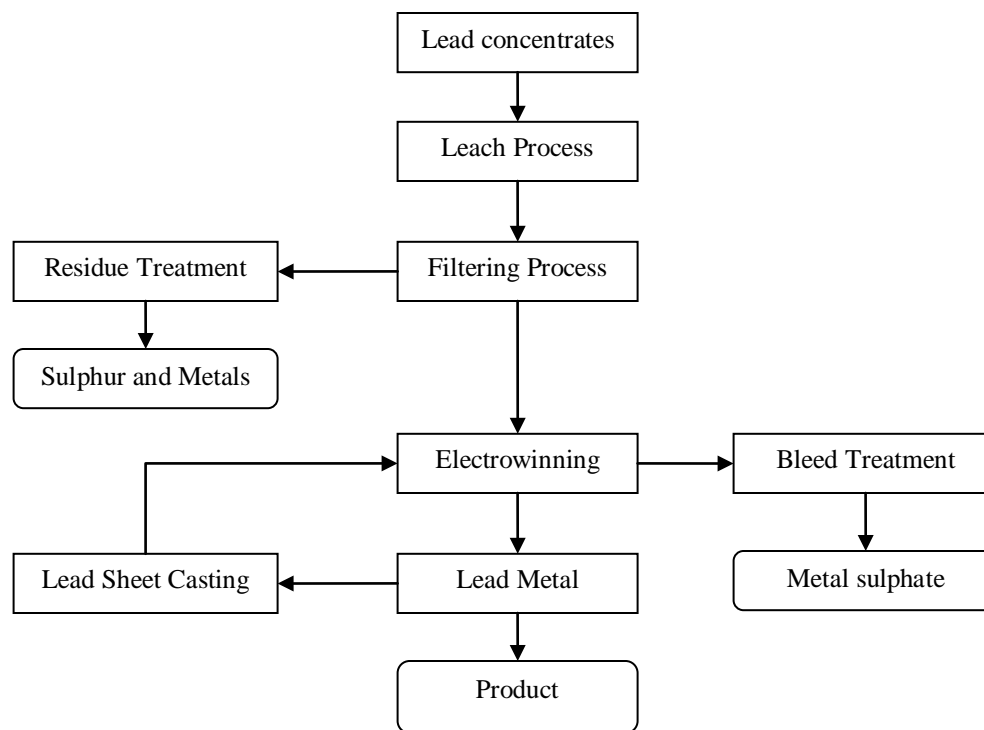
Figure 9 Schematic diagram of Doe Run technology for producing primary lead from ore [4]

2.3.3.6   Methane Sulfonic Acid (MSA) Leaching of Lead

As discussed before in **Table 2**, Methane Sulfonic Acid (MSA) provides a moderate solubility of lead but it avoids the potential problems occurring in other medium (See **Table 2**). MSA is also non-oxidizing and highly conductive acid [27]. As a result it has largely replaced the fluoboric acid, the previous industrial standard for electroplating tin/lead solder over the past 20 years. Besides, MSA has the potential application for other metal production, such as an emerging electrolyte choice for electroplating pure tin and for copper deposition.

MSA has a "green" character in two different ways[8]:

(1) It is odorless and does not generate toxic gas fumes, which make it very safe to handle compared to fluosilicic acid and fluoboric acid;

(2) It is readily bio-degradable and recyclable, ultimately forming sulphate and carbon dioxide.

It was reported that methane sulfonic acid (200g/L) was used to dissolve spent lead-acid sludge/paste. Even if the solubility of sludge in methane sulfonic acid was lower than

fluoboric acid, there was no doubt that both fluoboric acid and methane sulfonic acid could easily dissolve PbO. However, pure lead metal as well as lead dioxide and lead sulphate was insoluble in both fluoboric and methane sulfonic acids[21].

A U.S. Patent was proposed to employ methane sulfonic acid as a leaching agent to remove lead from the surface of brass component waterway[70]. Then over a predetermined time period the lead content in the potable water supply was directly measured. The novel method for determining the lead content on the surface of a brass component was simpler and cheaper than the conventional standard NSF-61 method.

Another U.S. Patent described an electrolysis process to produce a low alpha lead methane sulfonate through dissolving lead in methane sulfonic acid[71]. This process is currently utilized in the electronics fabrication industry such as in the flip chip packaging technology which uses controlled collapse chip connection (C4 process) to connect electronic components. The chemical reactions involved in the process are shown below:

Anode reactions:

$$Pb_{(s)} \rightarrow Pb_{(aq)}^{+2} + 2e^-$$ **Reaction 26**

$$Pb_{(aq)}^{+2} + 2CH_3SO_{3(aq)}^- \rightarrow Pb\left(CH_3SO_3\right)_{2(aq)}$$ **Reaction 27**

Cathode reaction:

$$2CH_3SO_3H_{(aq)} + 2e^- \rightarrow 2CH_3SO_{3(aq)}^- + H_{2(g)} \uparrow$$ **Reaction 28**
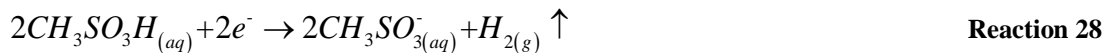
The formation of lead methane sulfonate in the anodic compartment became possible when an anion exchange membrane was employed. The Pb^{+2} ions that form at the anode would be prevented by the membrane from migrating to the cathode electrode surface. Hydrogen gas evolved at the cathode surface. And methane sulfonate ions in the catholyte migrated through the membrane to the anolyte and then reacted with the Pb^{+2} ions to form the desired lead methane sulfonate solution.

2.4   Previous Studies on Desulfurization Treatment

The desulfurization process is most widely studied in the field of lead recovery from waste lead-acid battery paste[1, 25], and some other applications for Pb-cake from Zn hydrometallurgical cycle[72], fly ash and oxidized residue[1, 25].

Due to the low solubility of lead sulphate in acidic medium, lead sulphate was usually treated in soluble carbonate or hydroxide solutions (i.e. sodium or ammonium) to transform it into lead carbonate or hydroxide (desulfurization or carbonation process)[21]. The desulfurization process is based on the solubility products K_{sp} of $PbSO_4$, $Pb(OH)_2$, and $PbCO_3$. For example, the K_{sp} of $PbSO_4$ is defined as $K_{sp}=[SO_4^{2-}][Pb^{+2}]/PbSO_4=[SO_4^{2-}][Pb^{+2}]$, since the activity of pure solid is regarded as 1. The K_{sp} value is a constant at a given temperature and varies slightly with temperature. At 25ºC, the solubility product K_{sp} of $PbSO_4$ is $10^{-7.8}$ at 25ºC, which is much lower than those of $Pb(OH)_2$ and $PbCO_3$ are, respectively $10^{-15.3}$ (20 ºC) and $10^{-13.1}$ (25 ºC) (See **Reaction 29**)[73]. Sulphate salts are then crystallized from the solution and sold off as by-products[1]. For **Reaction 29** the Gibbs' energy is $G_{298}^0 = -41.91 \text{kJ/mol}$ and the equilibrium constant at T=298K and T=343K are respectively, $K_{298} = 2.314 \times 10^7$ and $K_{343} = 2.174 \times 10^6$ [72].

$$PbSO_{4(s)} + Na_2CO_{3(aq)} \rightarrow Na_2SO_{4(aq)} + PbCO_{3(s)} \qquad \textbf{Reaction 29}$$
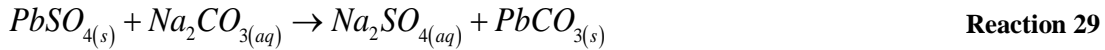
The conversion of $PbSO_4$ to carbonate is fast and proceeds through the formation of $Pb_3(CO_3)_2(OH)_2$ and $NaPb_2(CO_3)_2(OH)$; the conversion of $PbSO_4$ to $Pb_3(CO_3)_2(OH)_2$ (hydrocerussite or basic cerussite) occurs within 5 min under mild conditions; the formation of sodium-bearing compounds ($NaPb_2(CO_3)_2(OH)$) are favoured by long reaction time, high sodium carbonate content and high temperature[74]. On the other hand, the reaction of $Pb_2O(SO_4)$ is kinetically much slower and lead oxides are practically inert in carbonate medium[75].

In the late 1970s and early 1980s, Prengaman and McDonald of RSR developed several processes to convert spent batteries to metallic lead via electrowinning[76]. In one of these

processes, $PbSO_4$ reacted with ammonium carbonate to produce $PbCO_3$ and ammonium sulphate. Other alkali carbonate such as lithium, sodium, or potassium may also be used to desulfurize the paste. Compared with $NaHCO_3$, $(NH_4)_2CO_3$ and NH_4HCO_3, Na_2CO_3 is the most powerful for desulfurization of lead sulphate. But when the CO_3^{-2}/Pb^{+2} mole ratio (based on the stoichiometric relationship between carbonate and lead sulfate) exceeds about 2, the difference in desulfurization power among 4 carbonates is almost negligible[37]. The conversion of carbonation reached more than 90% at the CO_3^{-2}/Pb^{+2} mole ratio above 2, while the carbonation efficiency obviously decreased at ratios lower than 2. However, the excess of sodium carbonate (higher than 20%) induces the formation of compounds containing Na^+ or SO_4^{-2} ions, like $NaPb_2(CO_3)_2OH$ and $Pb_4(SO_4)(CO_3)_2(OH)_2$. These compounds increase the reagent consumption and create difficulties in the subsequent processing and use of the final product[77]. Apart from the impacts of carbonation agents and CO_3^{-2}/Pb^{+2} mole ratio, temperature also plays a very important role in the desulfurization of lead sulphate. Desulfurization efficiency increased with increasing temperature ranging from 10 to 50°C[37].

Gone, Dutrizac and Chen[74] performed an extensive study on the reaction of sized $PbSO_4$ powder with Na_2CO_3 under various conditions. They found that the reaction followed the shrinking core model with rate controlled by diffusion through the $PbCO_3$ product layer formed on the particle. The reaction rate decreased with the increasing concentration of sodium sulphate reaction product and increased as the first power of the sodium carbonate. It was found that the pH value can change the reaction products/product morphologies and change the occurrence of carbonate ions (i.e. from CO_3^{2-} to HCO_3^-), thus decreasing the dissolution rate.

In the work of Lyakov et al.[77], the optimal conditions for desulfurization by Na_2CO_3 were: excess of Na_2CO_3 up to 10%, liquid/solid ratio = 2~2.5, T = 35~55°C and leaching time t = 15~30 min. The desulfurization degree under such conditions was 92.4~94.4% and $S_{SO_4^{2-}}$ (sulphur content from sulphate in the desulfurized residue) was 0.49~0.36%.

In the carbonation process of burnt lead dust, 95% desulfurization efficiency can be approached when desulfurization process was performed under following conditions: T=30ºC, solid density = 100 g/L, $CO_3^{-2}/Pb^{+2} \geq 2$, reaction time = 1hr[37].

Desulfurization by K_2CO_3 can be optimized under conditions: T = 50ºC, liquid/solid ratio = 5, process duration = 2h. The desulfurization degree was in the range of 95~99%. It should be noted that in contrast to desulfurization with Na_2CO_3, no double salt was formed in desulfurization with K_2CO_3 [73].

2.5 Previous Studies on Lead Electrolysis

To recover lead in a hydro-electrometallurgical route, lead electrowinning accounts for an important part. So far, there have been various electrolyte tested or operated in pilot plants for lead electrowinning. **Table 3** shows the advantages and disadvantages in some existing or proposed electrowinning processes to recover lead from lead-acid batteries[21].

Table 3   Comparisons between various processes of lead electrowinning [21]

Classification	Electrolyte	Advantages				Disadvantages
		Current Efficiency/%	Energy Conspt./ kWh/tPb	Purity/%	Others	
Acidic Media	HBF$_4$	99	800	99.98	low cost	PbO$_2$ formation on the anodes and anodes (graphite) deterioration
	HBF$_4$ with Fe^{+3}/Fe^{+2}	High	500	99.99	desulfurization not needed	Diaphragm cell with membranes
Basic Media	NaOH-glycerol	85~90	400~500	99.98	anodes of stainless steel, desulfurization not needed	PbO$_2$ formation on the anodes and cost of chemicals
	NaOH-NaKC$_4$H$_4$O$_6$	≥98	400~500	99.99	anodes of stainless steel, desulfurization not needed	PbO$_2$ formation on the anodes and cost of chemicals

In a comparative study on alkaline and acidic electrowinning operated by Ferracin[21], three electrolytes were chosen, including fluoboric acid, mixture of glycerol and sodium hydroxide,

and mixture of sodium potassium tartrate and sodium hydroxide. Each electrolyte contained three electrodes: for acidic fluoborate electrolyte, two graphite anodes and one AISI-304 stainless steel foil cathode; for alkaline electrolyte, two cathodes and one anode were made of the same stainless steel foil. Boric acid as fluoride ions inhibitor and phosphoric acid as PbO_2 inhibitor were added into the acidic solution while animal gelatine or glue (2g/L) as grain refiner was added in both acidic and alkaline electrolytes. Although the lead deposits were compact for the three electrolytes, high values of cathodic current efficiency (99%) were only obtained for tartrate and fluoboric acid. Despite the lower specific energy consumption obtained for the tartrate electrolyte, the fluoborate electrolyte was better for the electrowinning process due to its low costs.

A major difficulty with all the electrolytic processes, however, is the life of the anodes. Sophisticated anodes are required to evolve O_2 from highly corrosive fluoride-containing medium. A number of anode materials have been identified to perform satisfactorily in short term pilot plant campaigns. None of the anodes, however, seems capable of providing industrially acceptable anode longevity (i.e.~2y)[78]. The main problem is the poisoning of anodes by deposition of lead dioxide, which not only decreases the amount of lead recovered but also diminishes the lifetime of the anode. Fortunately, the addition of ~1g/L As [79] as AsO_4^{3-} or P [80, 81] as PO_4^{3-} or cobalt [5] can either enhance the oxygen evolution or suppress the anodic deposition of PbO_2 at the whole study potential range. The employment of divided cell or a special anode (Dimensionally Stable Anode (DSA) and Hydrogen Diffusion Electrode (HDE) anode[82]) also could prevent the formation of lead dioxide. The anodic reaction taking place at the HDE is the oxidation of H_2 (See **Reaction 30**) instead of the evolution of oxygen:
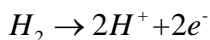
$$H_2 \rightarrow 2H^+ + 2e^- \hspace{4cm} \textbf{Reaction 30}$$

Thus the change of DSA-O_2 to HDE decreases the thermodynamic cell voltage by 1.23V at standard temperature and pressure. Considering the fact that the oxygen evolution reaction is more sluggish than hydrogen oxidation, the real voltage saving should be higher practically.

However, the price of hydrogen and safety issues in the handling of hydrogen gas should also be taken into consideration.

However, the problem is not as critical in concentrated chloride medium since lead electrowinning from concentrated chloride medium does not result in the formation of PbO_2[75] and titanium mesh-DSA anodes may be suitable for chloride-based electrowinning cells.

2.5.1   Lead Electrolysis in Alkaline Medium

Alkaline electrolytes have also been proposed for lead electrowinning, giving a stable electrolysis process. However, only a few reports have been published in this field. Compared with some acidic systems, alkaline solution electrolysis is a good alternative because of low corrosion, less toxicity, and less volatility[83, 84]. Publications on alkaline electrolysis of lead have not been focused on electrorefining, but on electrowinning from secondary sources of lead, such as spent lead-acid batteries.

Since Morachevskii et al.[30]first reported the feasibility of separating lead from exhausted lead-acid batteries in alkaline glycerol medium, there have been some reports on lead electrowinning from alkaline glycerol medium. The addition of glycerol could benefit the morphology of the lead film via avoiding the dendritic growth but could not favour the adherence of deposit lead. Also it could hinder the passivation of the anode and dissolve the oxide fraction of the scrap. Other additives, like oxylitol (1,2,3,4,5-pentahydroxypentane)[83] and sorbitol[85, 86], also were studied in alkaline medium for lead electrowinning or electrodeposition. Sorbitol was demonstrated to reduce the dendritic growth of lead more significantly than glycerol and to avoid spontaneous growth of tin crystals in the alkaline solution. The reduction of lead occurring at the cathode was considered through the complex species $[Pb(OH)_4]^{2-}$, not Pb^{+2}[87, 88].

Weiping Chen et al.[31, 32] investigated the electrochemical process of lead electrodeposition from alkaline tartrate solutions and demonstrated that under proper

conditions, lead was recovered in powder form with a current efficiency $\geq 98\%$. The electrolysis half-reactions at anode and cathode are shown below:

Cathodic reactions:

$$Pb^{+2}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$$ **Reaction 31**

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$$ **Reaction 32**

Anodic reactions:

$$4OH^-_{(aq)} \rightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-$$ **Reaction 33**

$$Pb^{+2}_{(aq)} + 4OH^-_{(aq)} \rightarrow PbO_{2(s)} + 2H_2O_{(l)} + 2e^-$$ **Reaction 34**
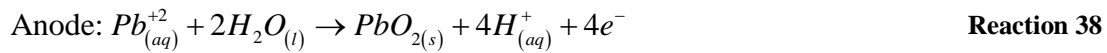
2.5.2 Lead Electrolysis in Acidic Medium

In **Reaction 35** and **Reaction 36**, the standard potential for lead in aqueous solution is -0.12V that is lower than the potential for H^+/H_2 couple. But this metal has a high hydrogen overpotential, which means it can be easily deposited from strongly acid solutions with a cathodic efficiency approaching 100%. So several acidic medium have been investigated for electrolytic deposition of lead, in chloride, fluosilicate or fluoborate electrolytes[89].

Desired half cell reactions in acidic electrowinning process are:

Cathode: $Pb^{+2}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$ $\qquad E^0 = -0.12V\,(SHE)$ **Reaction 35**

Anode: $2H_2O_{(l)} \rightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^-$ $\qquad E^0 = 1.23V\,(SHE)$ **Reaction 36**

Potential side half cell reactions in acidic electrowinning process are:

Cathode: $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ **Reaction 37**

Anode: $Pb^{+2}_{(aq)} + 2H_2O_{(l)} \rightarrow PbO_{2(s)} + 4H^+_{(aq)} + 4e^-$ **Reaction 38**

In acidic solution, lead is predominately electro-oxidized to tetragonal β-PbO$_2$ at the anode, although a small amount of the orthorhombic α-PbO$_2$ may also form depending on the operating conditions. The β-PbO$_2$ is an open, porous structure and its conductivity is higher than that of α-PbO$_2$, due to its higher electron mobility[90]. PbO$_2$ possesses high overpotential for the oxygen evolution reaction (OER), which merely raises the overpotential

and lowers the yield of lead metal[91]. In contrast, lead electro-winning from concentrated chloride medium does not result in the formation of PbO_2[75].

2.5.2.1 Lead Electrolysis in Chloride Medium

There have been several pilot plants or proposed processes developed in chloride medium. The concept of Lead Recovery From Lead Oxide Secondaries (LEREFLEOS) Process is developed within the CEU Brite Euram II Programme[19]. In the electrowinning step, electrowinning is operated in a tank reactor with compartments separated by a cationic membrane in order to avoid lead dioxide formation and chlorine evolution at the anode. The anolyte is sulphuric acid solution and a dimensionally stable anode for oxygen evolution ($DSA-O_2$) anode was adopted. The LEREFLEOR process uses a scraper to remove the lead deposit from the cathode. The deposit must have negative buoyancy (not in a spongy form) because it is collected at the bottom of the tank by a mechanical system. Therefore, the hydrogen evolution must be kept low to avoid positive buoyancy[92].

Exposito et al.[47, 92] optimized the conducting parameters of lead electrowinning in chloride medium in a divided cell. The catholyte composition was 4.3M NaCl+ xM HCl + 0.048M Pb^{+2} (x value from 0.05 to 0.2) while the anolyte was 1M NaOH solution. The operating temperature was around 60ºC. At a working current density of 10 A/m^2, the current efficiency, specific energy consumption and production were 90%, 1.32kWh/kg Pb and 83.4kg Pb/m^2 per day, respectively. Ti metal is selected for the cathode since the lead deposit is not strongly adhered on the surface and can be easily removed by mechanical scraping and meanwhile hydrogen evolution at the at the beginning of deposition is not high at this Ti metal cathode.

A very similar process, the PLACID Process, was also developed to recover lead in acidic chloride electrolyte from exhausted lead acid batteries for reuse in the manufacture of new battery pastes. The difference between the LEREFLEOR process and the PLACID Process is the composition of anolyte. The anolyte adopted in the LEREFLEOS process is sulphuric acid, while in the PLACID Process both anolyte and catholyte are brine solutions.

The PLACID Process was developed by the technical team in the R&D Center of Tecnicas Reunidas (Spain) during the 1980s and the early 1990s [19, 48]. The PLACID Process features the leaching of lead in warm and slightly acidic hydrochloric acid brine to form soluble lead chloride. In the cathode compartment, lead is deposited on the cathodes as small non-adherent flakes that fall to the bottom of the cell and must be recovered as sponge lead (See **Figure 10**). Chloride anions are released simultaneously, and then react immediately with protons that have been liberated stoichiometrically from water electrolysis in the anolyte and passed into the catholyte through a membrane. The electrochemical half-reactions show as following:

Cathodic half-reaction: $PbCl_{2(aq)} + 2e^- \rightarrow Pb_{(s)} + 2Cl^-_{(aq)}$ **Reaction 39**
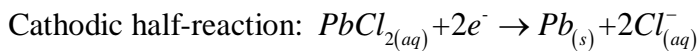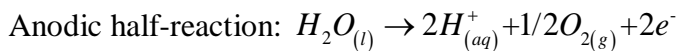
Anodic half-reaction: $H_2O_{(l)} \rightarrow 2H^+_{(aq)} + 1/2O_{2(g)} + 2e^-$ **Reaction 40**
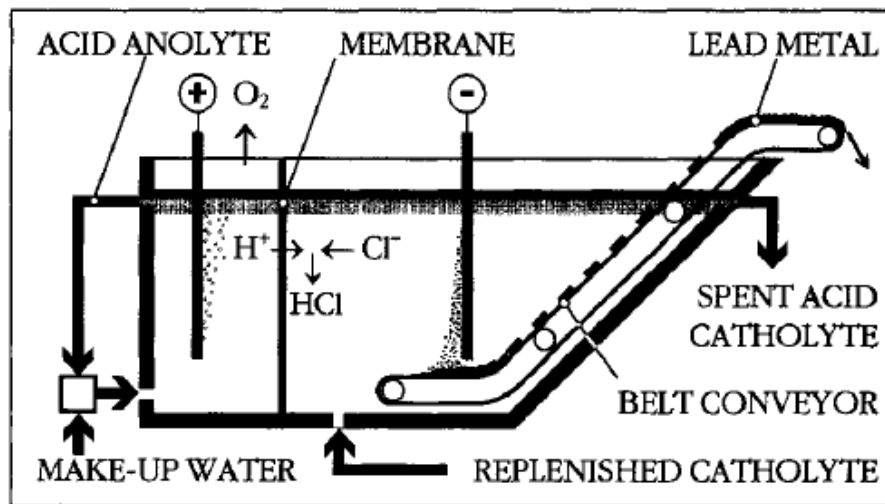
Figure 10   A diagram of the PLACID Process eletrowinning cell [19]

Electrolysis is typically carried out at a current density of 150-400A/m^2 and with specific energy consumption less than1kWh/kg Pb. The lead deposit typically contains 99.99% Pb. No significant emission of lead fumes is observed since the maximum operating temperature in the PLACID Process is around 80°C.

Although the purity of the electrodeposit is high, it is often inadequate for some other industrial use (i.e. battery bar) and must be further refined by the smelting route (See **Figure**

11). The combination of the PLACID Process and a smelting step (just a melter) shows more industrial and economical benefits: increases the purity of lead to above 99.99%; extends the furnace life though reducing the temperature in furnace (from 850~1000ºC to just above melting point ~370ºC); eliminates the hazardous wastes and reduces the total amount of wastes and the fume emission.
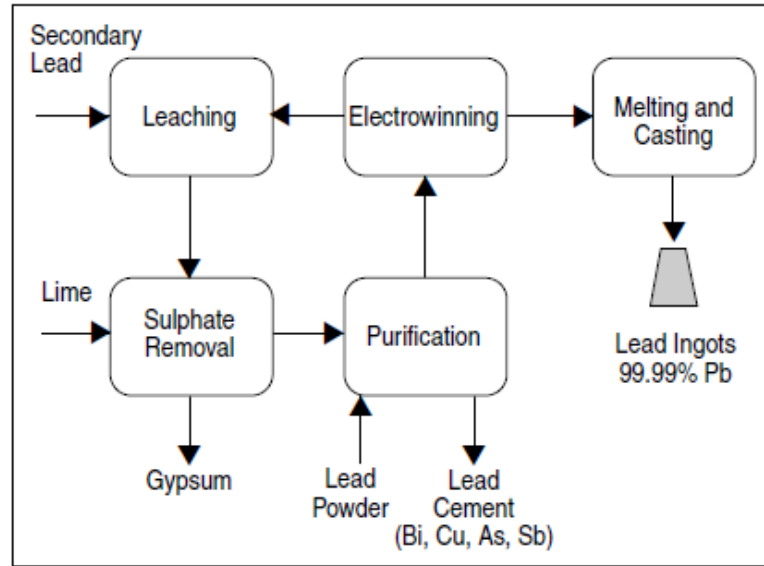
Figure 11   The PLACID process conceptual diagram [48]

However, the PLACID Process and other chloride-based processes have not found favour because the lead must be recovered as in a sponge form as well as some other inevitable problems like high chloride corrosiveness and the evolution of Cl_2 gas[93].

2.5.2.2   Lead Electrolysis in Fluosilicate Medium

The electrolysis based on fluorosilicate medium is well developed for lead refining by a process known as the Betts process[11, 80]. A commercial lead cathode (>99.99%) and an anode with an adhering slime are produced. In the conventional Betts process, the electrolysis operation parameters have a wide acceptation range, showing no strong influence on the final quality of refined lead. For example, the lead concentration in the electrolyte can be varied between 30 and 270g/L Pb^{+2} as $PbSiF_6$ without seriously affecting the refined lead quality.

Dobrev et al.[80] undertook an extensive study on lead electrorefining and electrowinning in fluosilicate based solution. The initial electrolyte contained 100g/L Pb as $PbSiF_6$ and 80~90g/L H_2SiF_6 with or without additives. Graphite anodes and lead foil cathode substrates were used. They concluded that with the use of H_3PO_4, the formation of β-PbO_2 would not happen at the inert graphite anodes at any values of the anodic potential. Under the optimal conditions of current density = 200A/m^2 and temperature within 39~42ºC, the current efficiency was within 96.5~98% and the specific energy consumption was 0.57 kWh/kg Pb.

The RSR process developed by R.D. Prengaman and H.B. McDonald in the late 1970s and early 1980s involved an acidic leaching and electrowinning process by fluosilicic or fluoboric acid. The solution contained 70~200g/L lead and at least 50g/L free acid[6]. Some boric acid and arsenic acid were present in the electrolyte. Boric acid was used to eliminate the hydrolysis products of fluoride and subsequent evolution of HF (See **Reaction 41**). Arsenic was added in a concentration above 500ppm to prevent the deposition of PbO_2 at the anode. The anode used in the RSR process was designed to be graphite substrate covered with a tight-fitting sheet of a non-conductive and PbO_2-coated inert mesh material. The anode with such design was highly conductive and stable, and thus was protected from damage and erosion during the electrolysis.

In the early 1980s, Cole, Lee and Paulson[7, 61, 62] developed the U.S. Bureau of Mines Process, which was very similar to the RSR process but with some inherent differences. In many cases, the process utilized waste fluosilicic acid to dissolve the spent battery paste. Apart from phosphate compounds, the electrolyte also contained as high as 150g/L lead with 0.05g/L animal bone glue and 4g/L lignin sulfonate as levelling agent and grain refiners. The levelling agent (also often called inhibitor) aims to thicken the small recesses and to thin the protrusions on the deposit surface while the grain refiner (also often called brightening agent or accelerator) can facilitate the fine deposits that consist of smaller crystallites smaller than the wavelength of visible light and having oriented structure. The current densities of 150-250A/m^2 were employed and the operating temperature was around 35ºC. The U.S Bureau of Mines process adopted PbO_2-coated titanium anode and lead cathodes. Under the above
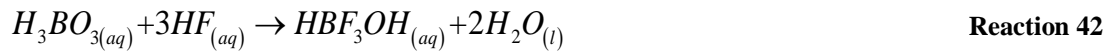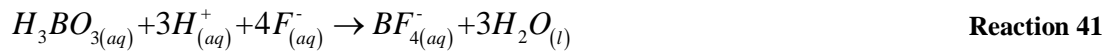
operating conditions, the current efficiency and specific energy consumption of the lead deposit were 95~97% and 0.8 kWh/kg Pb, respectively.

Since fluosilicic acid is produced as a by-product during the dissolution of apatite with sulfuric acid, the production cost is relatively cheap. However, the hydrolysis products of fluosilicic acid, SiF_4 and HF, are both corrosive and toxic, and also could cause precipitation of lead as lead fluoride in electrolyte.

2.5.2.3   Lead Electrolysis in Fluoborate Medium

Fluoborate electrolyte possesses several inherent advantages over other electrolytes, including high deposition rate, stability, high anode and cathode efficiencies and fine grained deposits. As a result, fluoborate based solutions have been frequently used to commercially plate tin, lead and tin-lead alloys for many years [82, 94]. Tin-lead fluoborate bath with peptone as an additive is a commonly used solution for tin-lead plating in the printed circuit board industry[95].

The hydrolysis products of fluoboric acid, free fluoride and boric acid, are highly toxic and aggressive and could possibly cause the precipitation of lead fluoride[11]. Thus, a quantitative amount of boric acid is required in the electrolyte to eliminate the hydrolysis of fluoboric acid and the subsequent evolution of HF according to **Reaction 41** and **Reaction 42** [95]:

$$H_3BO_{3(aq)}+3H^+_{(aq)}+4F^-_{(aq)} \rightarrow BF^-_{4(aq)}+3H_2O_{(l)}$$ **Reaction 41**
$$H_3BO_{3(aq)}+3HF_{(aq)} \rightarrow HBF_3OH_{(aq)}+2H_2O_{(l)}$$ **Reaction 42**

In this solution, the principle fluoro-complex is BF_4^- and a relatively small amount of HBF_3OH.

An extensive study on leaching lead-acid battery sludge was undertaken through comparing the leaching performance of 13 different aqueous solutions and the electrolysis performance of selected three electrolytes[21]. In this study, fluoboric acid showed attractive performance due to its low cost and moderate leaching strength. At a current density of $250A/m^2$, a compact deposit of lead was obtained from the electrolyte containing 200g/L fluoboric acid,

1g/L phosphoric acid, 10g/L boric acid and 2g/L animal gelatine. The current efficiency and energy consumption were 99% and 0.59 kWh/kg Pb, respectively. The cell voltage varied between 2.25 and 2.30.

A series of U.S. Patents were developed by M. Olper et al. to dissolve galena or raw lead to be refined by ferric fluoborate solution[66, 67]. The leachate lead fluoborate was sent to a divided electrolytic cell where pure lead was electrodepoited at the cathode. The lead-depleted catholyte was then sent to the anodic compartment as anolyte, where ferrous ions were oxidized to ferric ions and could be regenerated to the leaching step.

After intensive research conducted by Engitec in cooperation with Doe Run Company, a new hydrometallurgical route Fluobor® Process based on fluoborate technology was developed to a pilot-plant scale for primary recovery from galena concentrates. The pilot plant in Missouri was designed to process 8 tons of concentrate (80% Pb) per day, which equates to approximately 6.4 tons/day of lead. Doe Run has announced that it has scheduled to construct a commercial plant at an estimated cost of $150 million by 2013[96]. In the last step of this process, the purified solution from the leaching step is fed to a diaphragm-divided electrowinning cell with special anodes and stainless steel cathodes. The configuration is simple, easily handled and very efficient in electrochemical performance. The specially designed composite anode could operate at a very high anode current density, which facilitates the oxygen evolution and thus suppress the deposition of PbO_2 at the anode. Metallic lead can be electrowon in acidic fluoborate electrolyte at current density of $320A/m^2$. Glue was added as levelling agent.

Based on Engitec Fluobor Technology, a novel route to refine primary lead by "Granulation-Leaching-Electrowinning" was reported by F. Ojebuoboh et al.(See **Reaction 43**)[97]. Even though Betts Electrorefining Process (BEP) also operates the refining treatment in electrochemical route, however, BEP only accounts for approximately 20% of the total lead-refining capacity. Also BEP requires certain impurities in anodes to be controlled under specified levels. While through the "Granulation-Leaching-Electrowinning" process, it is

robust enough that it does not restrict impurity load in the bullion and could decouple the smelting furnace from the refining operations.
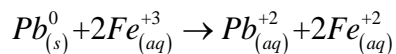
$$Pb^0_{(s)} + 2Fe^{+3}_{(aq)} \rightarrow Pb^{+2}_{(aq)} + 2Fe^{+2}_{(aq)}$$ **Reaction 43**

The Ginatta Process[5] to recover lead from used lead-acid batteries was divided into four stages. The last stage was the lead electrowinning from fluoborate bath in an electrolysis cell with graphite anodes. There was no desulfurization treatment required while an activation treatment that converted lead sulphate to lead and lead dioxide was designed. A cobalt additive was utilized in the electrolyte in an amount of 200ppm, which could enhance the evolution of oxygen at the anode and eliminate the need for PbO_2-coated or special alloy anodes for lead electrowinning. The anode was made of graphite while the cathode was a thin strip of lead instead of large sheet of lead or stainless steel. The electrolyte contained 35g/L Pb as $PbBF_4$ and 180g/L free acid as H_2BF_4, as well as Triton x-100 and phenolphthalein (up to 1g/L) as grain refiners and levelling agents instead of animal glue and lignin sulfonate salts. The operating cell voltage and temperature were around 3.5V and 40ºC, respectively. When the electrolysis was operated at a current density of 400 A/m^2, the current efficiency was around 99%.
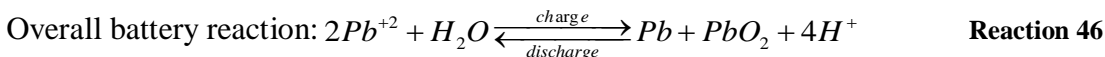
2.5.2.4   Lead Electrolysis in Methane Sulfonate Medium

Methane sulfonic acid (MSA) is a strong electrolyte and its conductivity in water is similar to other strong acids such as sulphuric or hydrochloric acid and higher than that of other organic acids[8]. Due to its inherent advantages, such as being non-oxidizing, MSA has largely replaced the fluoboric acid, the previous industrial standard for the electroplating of tin/lead solder, over the past 20 years[27]. Some research papers and patents concerning MSA electrolyte place more emphasis on the high solubility and a subsequent high plating current which is regarded as "high speed plating". There have been numerous studies on metals and alloys electrodepostion based on methane sulfonate electrolyte, such as nickel[98], copper[8], zinc[99], tin[100] and its alloys[101].

However, there are limited reports devoted to the studies of electrowinning of metallic lead from methane sulfonate electrolyte. The use of MSA for deposition of lead was first mentioned in a patent by Proell and co-workers in 1950. However, MSA did not receive commercial interest until the 1980s and now it is becoming a preferred system.

It was also reported for lead electrowinning processes in alkanesulfonic acids (especially MSA) based electrolytes in the absence of a redox couple in a US patent [102]. Another US patent proposed a method for selective deposition tin/lead solder bumps and other structures at a high deposition rate pursuant to manufacturing a microelectronic device from a workpiece, such as a semiconductor wafer[103].

In recent years, Pletcher and co-workers have reported the employment of MSA in undivided, highly soluble lead-acid flow battery includes the lead deposition (when charging) and dissolution (when discharging) at negative electrode, as shown in **Reaction 44**, **Reaction 45** and **Reaction 46** [104-107]. Soluble lead ions (as $Pb(CH_3SO_3)_2$) are the only reactant in the electrolyte. The presence of MSA in the electrolyte does not cause the mechanism to change but only brings about a quantitative difference in the PbO_2 electrodeposition process, resulting in a higher deposition rate and thicker coatings compared to classical acidic medium.

Negative electrode: $Pb^{+2}+2e^- \underset{discharge}{\overset{charge}{\rightleftarrows}} Pb$ **Reaction 44**

Positive electrode: $Pb^{+2}+2H_2O \underset{discharge}{\overset{charge}{\rightleftarrows}} PbO_2 + 4H^+ + 2e^-$ **Reaction 45**

Overall battery reaction: $2Pb^{+2}+H_2O \underset{discharge}{\overset{charge}{\rightleftarrows}} Pb + PbO_2 + 4H^+$ **Reaction 46**
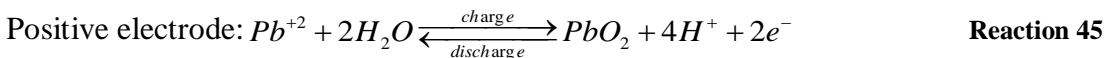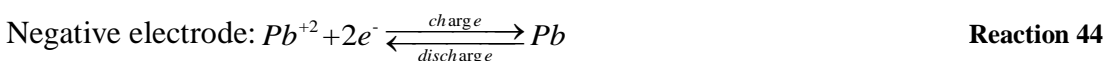
2.5.3 Additives in Lead Electrolysis

No matter what electrolyte is employed, organic additives are the key ingredients in the bath that influence the quality of the deposit. In additive-free electrolyte, the slopes of the cathode polarization against current density curves are very low. Therefore, lead will be deposited in a dendritic form[108]. Deposition of a dense pore-free coating is possible only when the electrolyte contains sufficient quantity of special inhibitors. Inhibitors are required to increase the cathode deposition over-potential to produce a smooth and dense deposit.

Most of the organic additives are extracted from natural compounds and are commonly categorized as: (1) carriers or suppressors, (2) brighteners or accelerators, and (3) levellers. Usually, the suppressors are poly-ethers (e.g. polyethylene glycol (PEG)), the accelerators are organic sulphur compounds and the levellers are molecules with amine functionally or aromatic rings[109]. The selection of the additive(s) often depends on the nature of the metal of interest as well as the pH and temperature of the electrolyte[110]. However, it is very hard to build up a relationship between the nature and the structure of additives and the nature of deposit metal. Different metals and different electrolysis bath compositions may require different additives. They are specific for each formulation. There are few chances to use one and the same agent in different baths[108].

Table 4 gives some examples of organic additives in lead electrorefining and electrodeposition. Obviously animal glue and lignin sulfonate salts are commonly used in lead electrolysis processes. Some other extracts of plants are also reported, such as extracts of aloes, mimosa and horse chestnut[111]. It also can be assumed that there are several other chemicals not mentioned in publications that are used as proprietary additives.

Table 4   Organic compounds used as leveling agents in lead electrorefining and electrodeposition [108]

Electrolyte	Additives
$H_2SiF_6 + PbSiF_6$	Ligninsulphonate + animal glue
	Ligninsulphonate + aloes extract
	Ligninsulphonate + flavones or flavanones
	Ligninsulphonate + quinones
	Ligninsulphonate + chestnut extract
	Ligninsulphonate + block-copolymer of ethylene oxide with propylene oxide
	Ligninsulphonate + red cedar extract
	Goulac + mimosa extract
$HBF_4 + Pb(BF_4)_2$	Dibenzenesulphonamide + aloin
Acid solution	Ligninsulphonate + antraquinonesulphonate
$PbCl_2 + CH_3COONH_4 + CH_3COOH$	Phenol + ethanol + gelatin

As a commonly used additive in fluosislicate and fluoborate system, lignin sulfonate salts have been well studied. The levelling mechanisms are well understood, especially by Cominco researchers[112]. As grain refiners, lignin sulfonate salts are supposed to block the

growth of individual crystals, thus resulting in an increased nucleation rate for lead crystallites. However, the solubility of lignin sulfonate salts is low and not stable, varying with time and pH[94]. In addition, lignin sulfonates evenly dispersed in the deposit as small inclusions accounted for up to a volume fraction of 1.1-1.2%. The usage of lignin sulfonic acid sodium salt in MSA based electrolyte has been investigated in Pb-MSA flow battery and 1g/L lignin sulfonic acid sodium salt leads to uniform deposits without the tendency to form dendritic crystals[104].

However, the presence of lignin sulfonate salts alone in lead electrolyte does not give good levelling benefits for lead cathodic deposit with heavy edges[108]. Higher amounts of lignin sulfonate salts (i.e. calcium lignin sulfonate >200 g/L) could result in brittle lead deposits[113]. Thus, both lignin sulfonate salts and other additives (i.e. animal glue, aloin, horse chestnut) must be present to maintain good deposit and ductility[111]. The combination of lignin sulfonate salts with other additives results in a larger polarization resistance with a stronger levelling power suppressing totally any dendritic growth and ensuring a uniform distribution of the lead deposit on the entire surface[80].

As a part of this study an attempt has been made to consider other additives. The glycol-type additives are considered, since they have been studied in many different MSA based electrolytes. Polyethylene glycol (PEG) is reported as an additive employed in Sn-MSA, Cu-MSA and Pb-MSA electrolytes[8, 104, 109, 110]. PEG can absorb on electrodes and then form a passivation film thereby suppressing the deposition without chloride ions in the electrolyte, since chloride ions would destroy PEG adsorption to the electrode surface[109]. PEG also was capable of suppressing hydrogen gas evolution at low overpotential and refining the grain structure across a wide current density range[110]. The smaller molecular weight PEG has less adsorption ability on the electrode surface, and thus the inhibiting effect decreases gradually. Also polypropylene glycol (PPG) enhances the reduction process and produces a smoother surface in Sn-MSA electrolyte.

There also appeared to be a synergy between the compositions and concentrations of the additives used in Sn-MSA electrolytes. However, the synergistic use of glycol-type additives

with other non-glycol type additives (e.g. lignin sulfonate salts) in MSA based bath for lead electrowinning process has not been investigated.

In summary, a survey study in this thesis was undertaken to explore the leaching performance of MSA for lead-bearing oxide (cerussite) concentrate and the electrolysis performance to recover lead metal as electrolydeposit, including the additives selection and the working condition optimization.

3 Chapter: Leaching and Desulfurization Tests

3.1 Introduction

There is no report in the literature about cerussite or hydrocerussite leaching in methane sulfonic acid (MSA) solution. Therefore, this is the first study on extracting lead from cerussite concentrate sourced from the Magellan Mine in Australia in MSA solution. However, there is a vast literature on recovering lead from spent lead-acid battery paste. The main components in the pastes are oxidized lead-bearing materials: PbO, PbO_2 and $PbSO_4$. The dissolution of PbO in acidic solution and treatment for $PbSO_4$ using desulfurization agents can provide valuable references for studies on the acidic leaching and residue recovery. In this study, the repeatability of a baseline experiment under pre-determined conditions was first tested (See **Section 3.3**); in addition, the effects of several variables on the leaching system were investigated (See **Section 3.4**); the recovery of lead from leached residue was then undertaken (See **Section 3.5**); finally, some conclusions in this part of study were given (See **Section 3.6**).

3.2 Experimental

3.2.1 Materials

All the cerussite concentrate samples used in this study were provided by Magellan Mine (located in Australia), Ivernia Inc (Canada). All the experiments were performed with sieved concentrate. Sieved material was prepared by wet screening into various mesh fractions. The sieved particles were washed repeatedly to remove finer particles and then air-dried at room temperature to eliminate the moisture in the powder and to minimize mineral decomposition. The chemical and phase composition are shown in **Table 5**, **Table 6**, **Table 7** and **Table 8**. Lead content in samples of different particle size ranges varied a little. The potentially extractable lead accounted for 85.8%, including galena by non-oxidative dissolution releasing hydrogen sulfide gas. Methane sulfonic acid (Lutropur® MSA 100) was provided by BASF, Germany. Deionized water was used in the preparation of all lixiviants.

Table 5 X-ray diffraction results for cerussite concentrate in baseline experiment

Mineral	Ideal Formula	Concentrate wt/%
Cerussite	$PbCO_3$	67.8
Galena	PbS	1.0
Anglesite	$PbSO_4$	10.3
Susannite	$Pb_4(CO_3)_2(SO_4)(OH)_2$	7.1
Leadhillite	$Pb_4(CO_3)_2(SO_4)(OH)_2$	3.3
Quartz	SiO_2	8.0
Kaolinite	$Al_2Si_2O_5(OH)_4$	2.6
Total	---	100.0

Table 6 Variety of lead content in different particle size ranges for cerussite concentrate

Particle size/um	-109+75	-75+53	-53+45	-45+38	-150+75	-75+45
Lead Content/%	67	67.71	68.34	68.48	67.12	67.96

Table 7 Chemical composition of cerussite (-150+75um) by ICP-ES

Element	Pb	Zn	Fe	Al	CO_2	S_{total}	SO_4
Concentrate Wt/%	67.12	0.03	1.52	1.57	11.81	1.53	4.42

Table 8 Lead content distribution in various lead-bearing minerals (-150+75um)

Speices	$Pb_{(S)}$	$Pb_{(SO4)}$	$Pb_{(CO3)}$	$Pb_{(OH)}$	$Pb_{(Total)}$
Wt%	0.53	14.20	82.86	2.41	100.00

Note: the calculation for lead content distribution in various lead-bearing minerals is in the Appendix.

3.2.2   Apparatus and Procedure

The leaching apparatus used in this research provided controlled conditions for studies of cerussite dissolution. The leaching apparatus is shown in **Figure 12**. The 1L three-baffled glass reactor was manufactured by CanSci Glass Products Ltd. There were six openings incorporated in the polypropylene cover for insertion of a 316 stainless steel stirring rod connected with an impeller, a thermometer, a pH probe and three sampling ports (one port for adding sieved cerussite samples and two ports for withdrawing solution samples through glass tubing). The glass tubing connected with a syringe was immersed into the lixiviant. Stirring was provided by a variable speed motor. The concentrate sampling opening was covered by a rubber stopper while the two syringe openings were sealed by small plastic plugs. The surface of the water tank was covered by plastic balls and plastic film to prevent heat and water vapour loss. The water bath was heated by two immersion heaters. A temperature controller was used to measure and control the temperature of water bath. To

maintain a uniform temperature (±1°C), the water bath was stirred continuously by a constant speed motor.
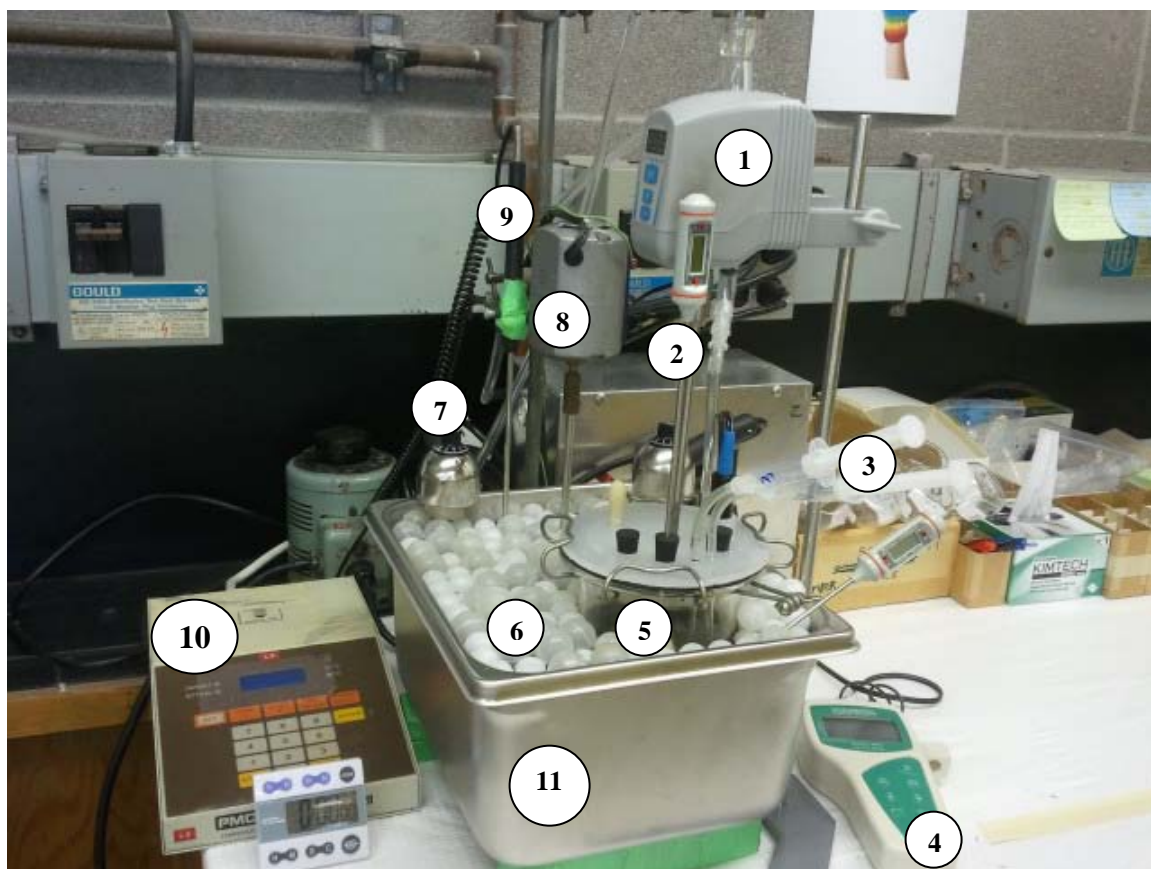

Figure 12   Experimental apparatus for leaching tests

(1-speed monitor; 2-thermometer; 3-syringe; 4-pH meter; 5-glass reactor; 6- hollow balls; 7-heater; 8-motor; 9-J type thermocouple probe; 10-temperature controller; 11-water tank)

The experimental procedure consisted of the following steps:

(1) The thermostated water bath was filled with water and covered with plastic balls and films to avoid loss of heat and water vapour, the immersed heater turned on and the temperature set at a desired value;

(2) 500ml MSA solution of pre-determined concentration was prepared in volumetric flask, and was added into1L glass reactor with three baffles;

(3) The reactor was covered and then placed into the water bath, with incorporations of a stirring rod connected with impeller, a pH meter, a thermometer and glass tubing;

(4) When the desired temperature reached, 2 gram sieved cerussite sample was quickly added into the lixiviant through the sampling port; the leaching reaction was started at this time; the leaching process was recorded by means of a digital LED-screen timer;

(5) Samples of about 2mL solution were withdrawn by syringe at predetermined intervals and then were filtered by PVDF syringe filters (pore size 0.45 um);

(6) Filtered solution samples were accurately diluted by 1mL pipet 100-fold and then analyzed for dissolved lead content using an Atomic Absorption Spectrometer (AAS).

3.2.3   Analytical Methods

The diluted solution samples were assayed for lead content using a Varian 240 Atomic Absorption Spectrometer (AAS) instrument with air-acetylene flame. AAS is a widely used method for accurate determination of metal concentrations in solution.

The morphology of solid particle samples before and after leaching was observed by Scanning Electronic Microscope (SEM, Hitachi S3000N).

The X-ray diffraction (XRD) tests for cerussite concentrate and leached residue were obtained using a Bruker D8 Focus Bragg-Brentano diffractometer (CoKα, 35kV, 40mA).

Multiple elements in solution and solid samples were analyzed by ICP-ES, operated by ACME, Vancouver.

3.3   Baseline Experiment Repeatability

To investigate whether the applied apparatus and procedure were reliable and effective, the baseline experiments were first repeated three times under the same conditions as described in **Table 9**.

Table 9 Operating conditions for most experiments (or baseline experiment)

Temperature/ºC	25	Sample Weight/g	2
Sample Particle Size/um	-150~+75	Lixiviant/mL	500
Stirring Speed/rpm	400	Proton concentration/M (or α ratio)	0.039 (or α=1.5)

*According to the stoichiometric relationship between lead and proton content in the **Reaction 1** and **Reaction 2**, α is defined as $α=(H)_2/Pb$*

Good repeatability was achieved under the experimental conditions (See **Figure 13**). The maximum lead extraction was as high as around 85% and could be reached within 600s. The residue was sent for XRD analysis and the results are shown in **Table 10**. The main phase in the concentrate sample after leaching was anglesite. As expected from the distribution of lead in various lead-bearing minerals (See **Table 8**), the remaining lead in anglesite accounts for 15% of the original lead content. This part of the lead was proposed to be recovered by desulfurization treatment followed by MSA re-leaching process. More details will be given in **Section 3.5**.
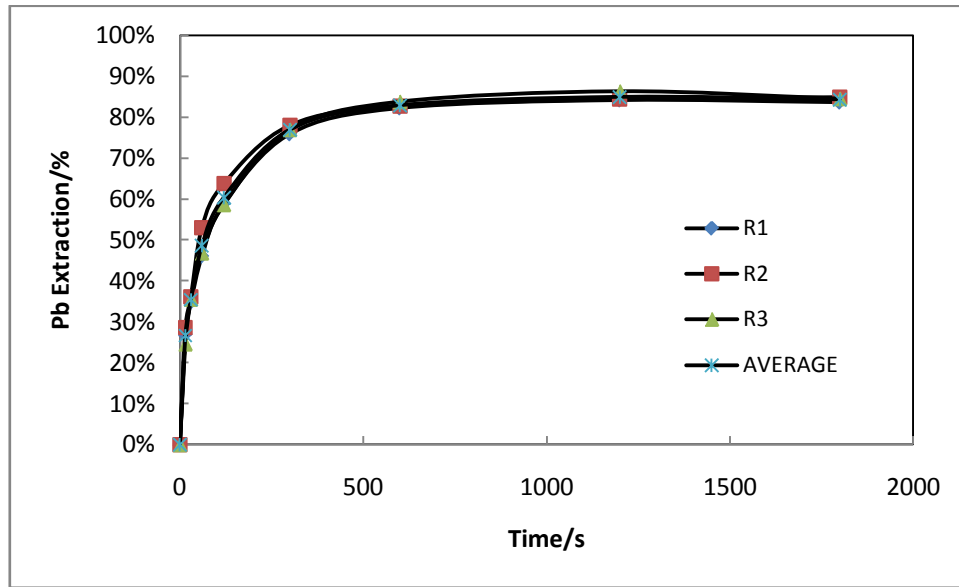

Figure 13 Repeatability checking for baseline experiment

(Temp. =25ºC, Stirring speed=400rpm, lixiviant Vol. =500mL, particle size=-150~+75um,α=1.5)

Table 10   X-ray diffraction results for cerussite leach residue in baseline experiment

Mineral	Ideal Formula	Residue wt/%
Cerussite	$PbCO_3$	0.5
Galena	PbS	1.5
Anglesite	$PbSO_4$	62.4
Susannite	$Pb_4(CO_3)_2(SO_4)(OH)_2$	---
Leadhillite	$Pb_4(CO_3)_2(SO_4)(OH)_2$	---
Quartz	SiO_2	24.5
Kaolinite	$Al_2Si_2O_5(OH)_4$	11.1
Total	---	100

Finally the solid samples were sent for SEM analysis to investigate the surface morphology before and after leaching (See **Figure 14** and **Figure 15**).
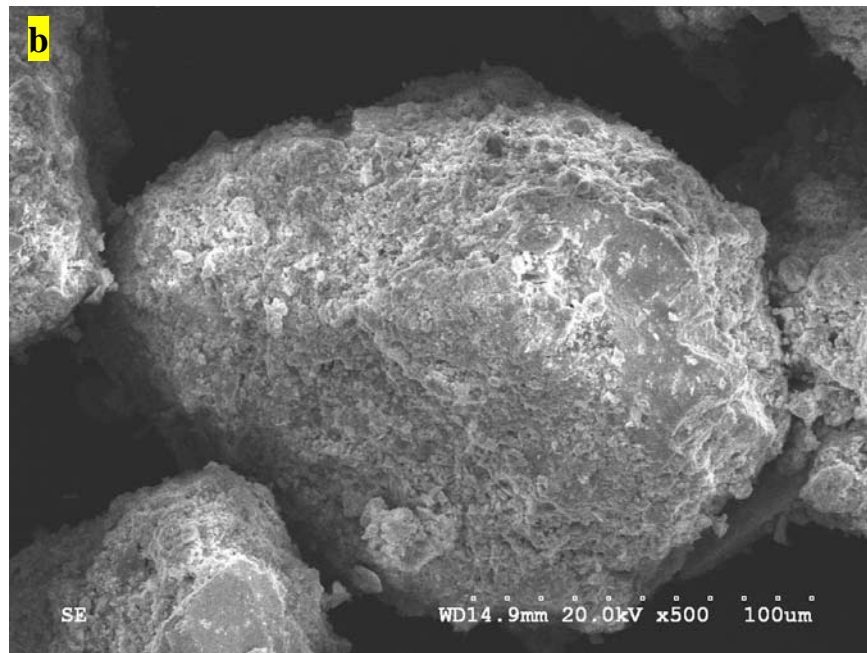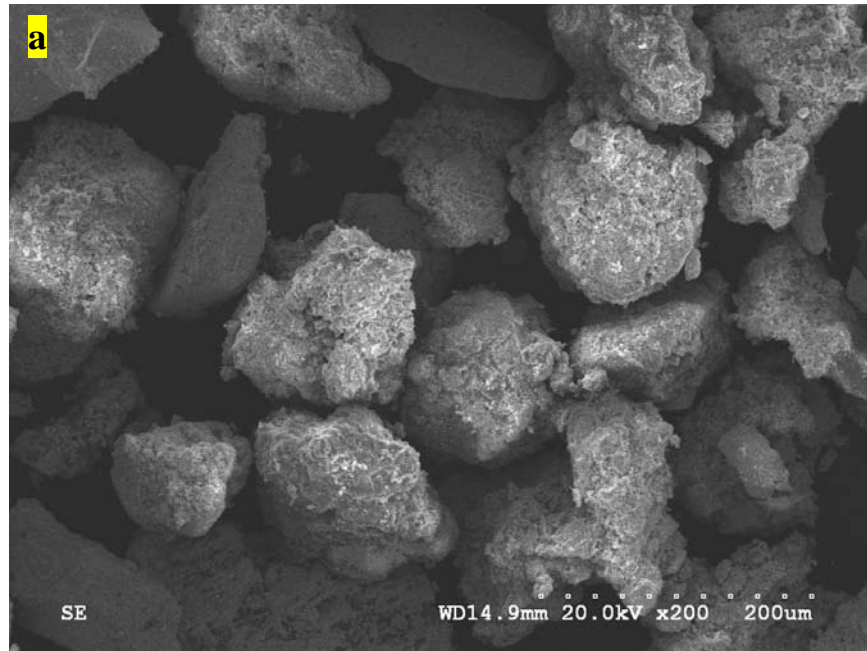
Figure 14　SEM images for cerussite concentrate before leaching treatment

(a – magnification ×200; b –magnification ×500)

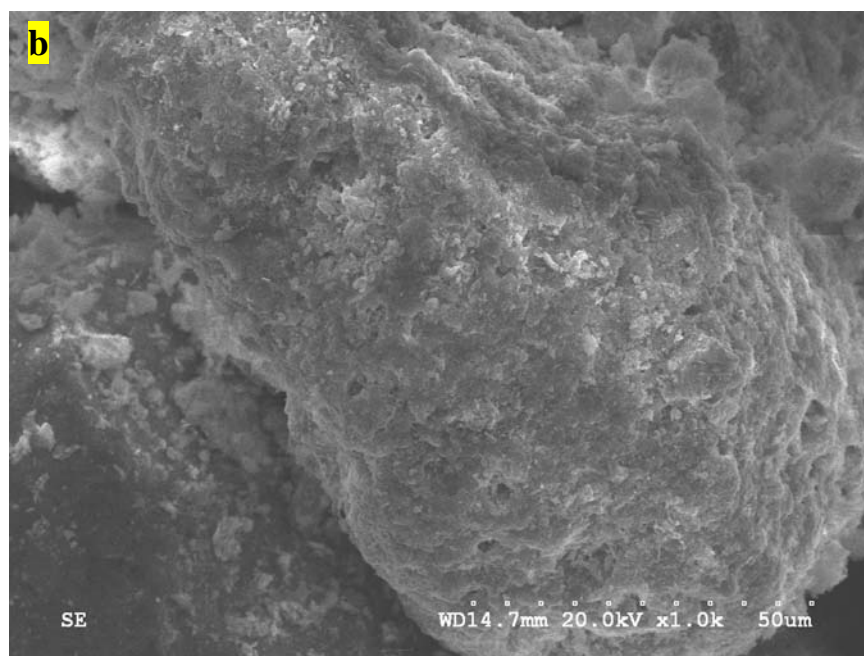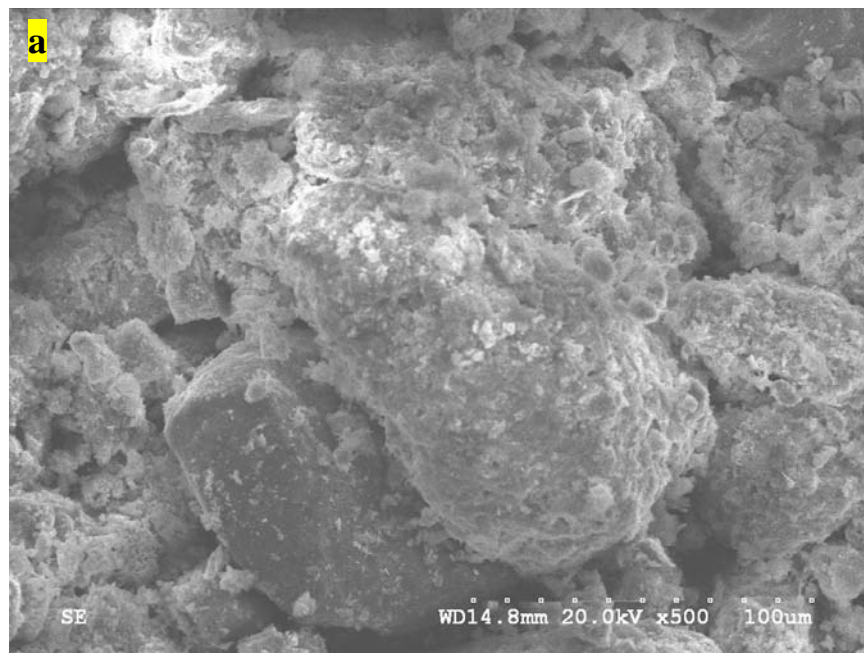**Figure 15 SEM images for residue after leaching treatment**

(a – magnification ×500; b –magnification ×1000)

3.4   Effects of Leaching Variables

A number of experimental variables including stirring speed, temperature, proton concentration, particle size fractions and solid concentration were studied. A series of comparable tests is a standard researching method for a new hydrometallurgical process to increase fundamental knowledge of the leaching system. Unless otherwise noted, most experiments were undertaken under conditions shown in **Table 9**. The results and discussion have been organized in the following manner.

3.4.1   Effect of Stirring Speed

The effect of stirring speed on the leaching rate was determined at 25ºC in 500mL solution with α ratio equal to 1.5. The stirring speed varied in the range from 200 to 600rpm. The experimental results in terms of lead extraction *vs.* time are shown in **Figure 16**.
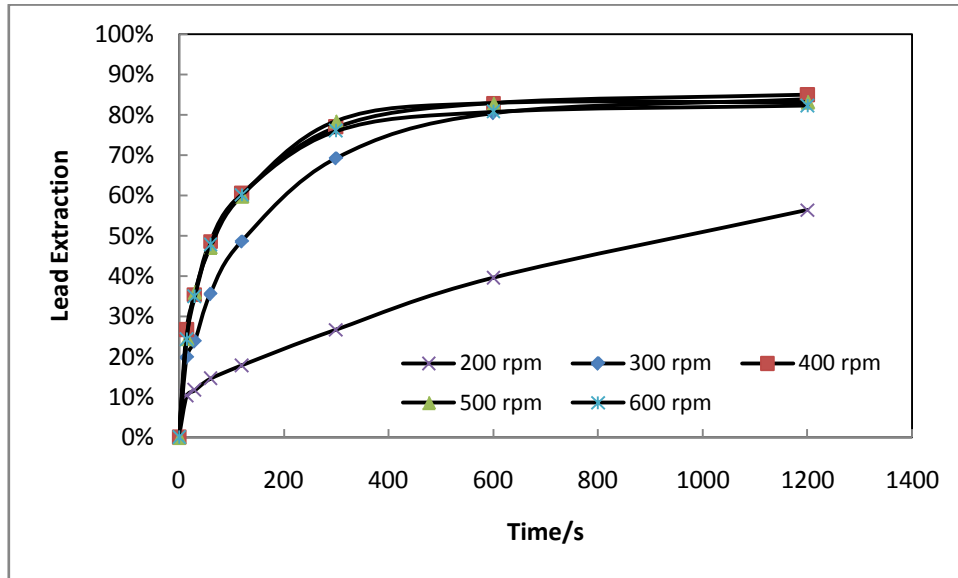

Figure 16 Effect of stirring speed on lead extraction

(Temp. =25ºC, lixiviant Vol. =500mL, particle size=-150~+75um, α ratio=1.5)

In the higher stirring speed range between 400 and 600rpm, there is no significant effect on the reaction rate, while in the lower range (200~400rpm) stirring speed greatly affected the reaction rate. Particularly at the stirring speed of 200rpm, the slow kinetics probably resulted from the poor off-bottom suspension. Based on these results, a stirring speed of 400 rpm was sufficient and thus was chosen for all the subsequent experiments.

3.4.2 Effect of Temperature

The effect of temperature on dissolution rate was carried out in the temperature range between 25 and 65 ℃ (See **Figure 17**). At 25 ℃ the maximum lead extraction was obtained within around 600s, while at 65 ℃ 300s was sufficient to achieve the same final extraction. The leaching rate increased moderately with temperature. To investigate the details of the whole leaching process, relatively slow kinetics process at 25℃ was preferable. Meanwhile the ambient temperature (~25℃) was beneficial to save energy and heat in practically industrial production.
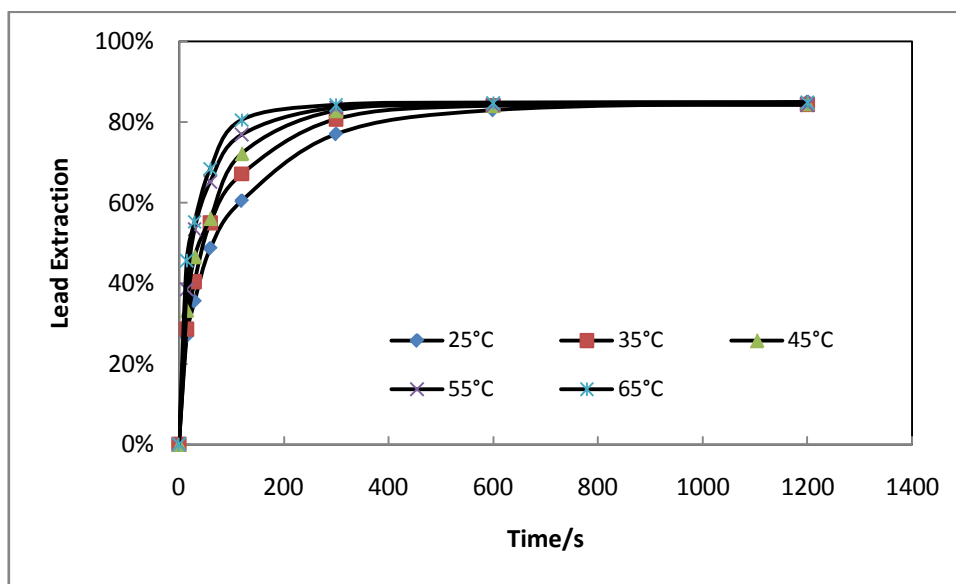

Figure 17   Effect of temperature on the lead extraction

(Lixiviant Vol. =500mL, stirring speed=400rpm, particle size=-150~+75um, α ratio=1.5)

3.4.3 Effect of Particle Size

The effect of particle size on lead extraction was examined by measuring the kinetics of dissolution processes for four size fractions (See **Figure 18**). Smaller particle size fractions resulted in faster dissolution rate. But the difference was not so great that fine grinding would not necessarily be required.
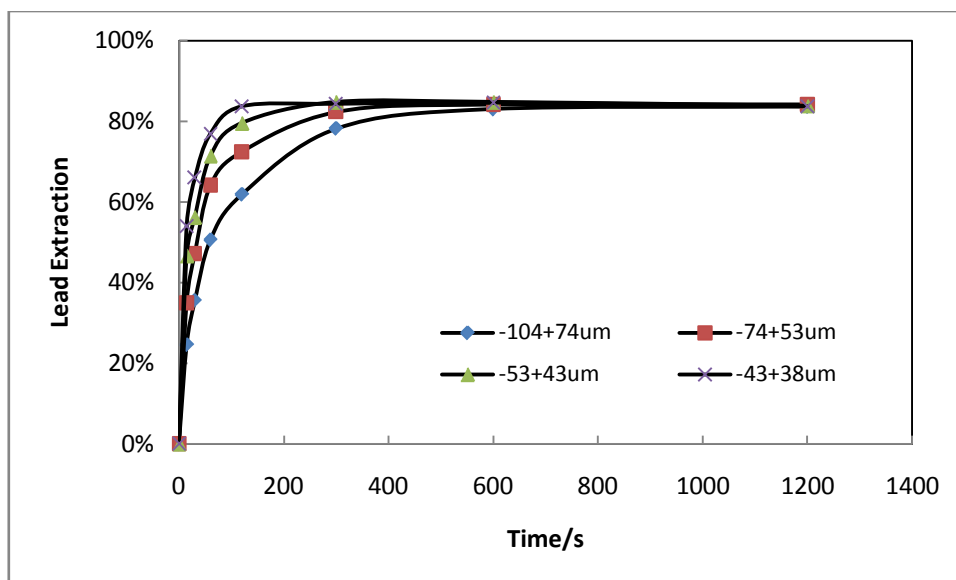
Figure 18 Effect of particle size on the lead extraction

(Temp. =25ºC, lixiviant Vol. =500mL, stirring speed=400rpm, α ratio=1.5)

3.4.4   Effect of MSA Concentration

The effect of MSA concentration was inspected by conducting dissolution tests with α ratio (concentration) range from 1 to 5 (0.026M~0.130M MSA) (See **Figure 19**). The MSA concentration had a significant influence on the dissolution rate. When α = 5 (MSA conc. = 0.130M), lead extraction reached a maximum in about 120 s. Even when α = 1, the lead extraction almost approached 100%, which proved the effectiveness of MSA to treat cerussite concentrate.
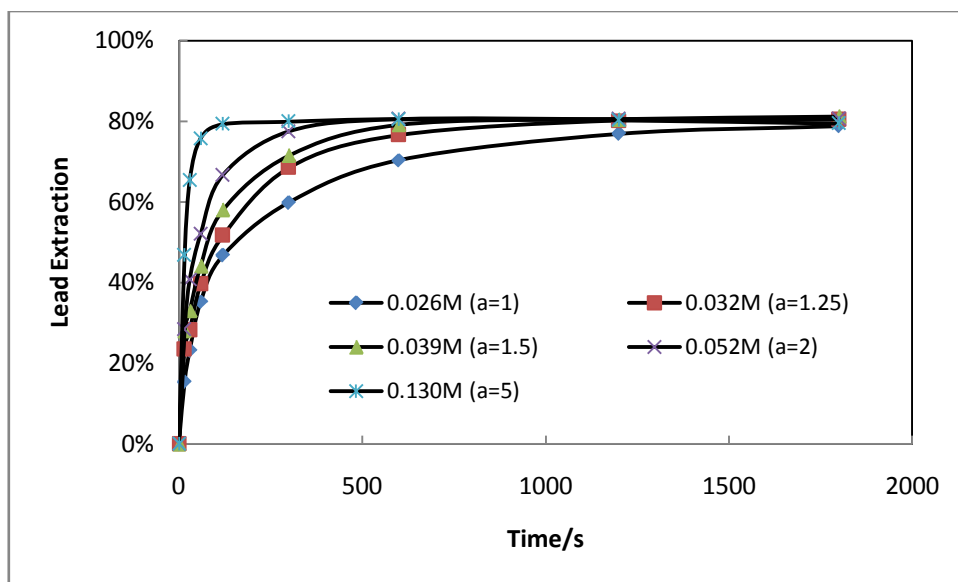
Figure 19　Effect of MSA concentration on the lead extraction.

(Temp. =25ºC, lixiviant Vol. =500mL, stirring speed=400rpm, particle size=-150~+75um)

3.4.5　Effect of Solid Concentration

Finally the effect of solid concentration was explored. But when the study of solid concentration ($\geq$20g/L) was operated, the immediate addition of the large amount of cerussite concentrate into the reactor generated a great deal of carbon dioxide gas, which caused leachate to overflow. Therefore, experiments with high pulp densities could not be accurately studied for the kinetics, but only the final concentrations or extractions of Pb^{+2} could be obtained. Therefore, in this study, the solid samples were slowly added into the leaching tank to prevent the overflow. The final lead extractions for different pulp densities of 20, 50, 100 and 200g/L (L/S ratio decreased from 50 to 5) were very close to each other (See **Figure 20**). High solid concentration was still suitable in MSA medium while the optimal slurry density in nitric acid medium is just 50g/L[37]. Lead concentrations of around 100g/L could be reached at the solid concentration of 200g/L, which was comparable to that obtained in the conventional Betts Electrorefining Process, and also to the reported electrowinning process in fluosilicate electrolyte[80]. It can be estimated that higher lead concentration can be achieved to reach the industrial requirement since MSA has such a high solubility for lead (146g $Pb(SO_3CH_3)_2$/100g H_2O at 25°C, as indicated in **Table 2**).
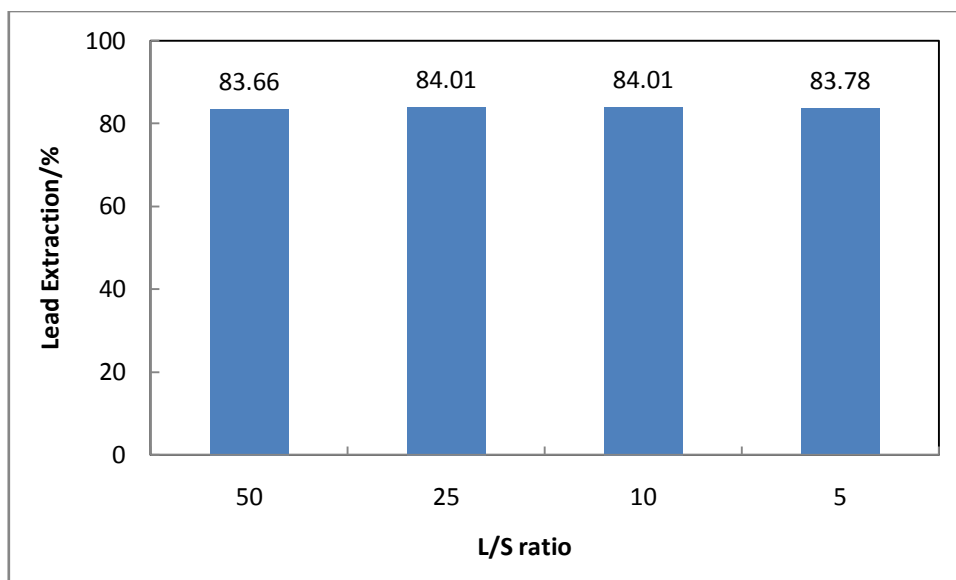
57

Figure 20   Effect of solid concentration on the final lead extraction

(Temp. =25ºC, lixiviant Vol. =500mL, stirring speed=400rpm, α ratio=1.5, duration=1hr)

3.5   Desulfurization Treatment for Leached Residue

After the leaching process, the residue mainly contained anglesite, clay and quartz. To recover the portion of lead from anglesite, a desulfurization treatment was proposed and the experiments in Step B were carried out under the following conditions: temperature T = 50ºC, liquid/solid (L/S) ratio ≈ 10 (25 mL Na_2CO_3 solution), the excess of sodium carbonate ≈ 20% and the process duration = 1h (See **Table 11**). In the leaching Step A, 10 gram sieved cerussite sample (-200+325 mesh or -75+45um) was adopted. In both Step A and Step C, 500mL MSA solution was heated at set temperature (25ºC) with α ratio equal to1.5; the stirring speed was 400rpm and the leaching duration was 1hr. The overall lead recovery through a "Leaching-Desulfurization-Releaching" route was approximately 98%. Also, the mass balance of the whole process displayed the satisfactory results, around 100%.

Table 11 Experimental data for desulfurization process

Procedure	Content	#1	#2	#3
Concentrate Sample Step A (Leaching)	Sample Weight/g		10	
	Pb% in concentrate		67.96	
	Pb% in #A Leachate	85.38	84.42	84.65
	#A Residue weight/g	2.63	2.65	2.63
	Pb% in #A Residue	41.39	---	---
Step B (Desulfurization)	#B Residue weight/g	---	2.34	2.39
	Pb% in #B Residue	---	43.10	---
Step C (Re-leaching)	Pb% in #C Leachate	---	---	13.39
	#C Residue weight/g	---	---	1.20
	Pb% in #C Residue	---	---	11.31
Total Pb Recovery	Pb%	---	---	98.04
Mass Balance	Pb%	101.42	99.28	100.04

3.6   Summary

The following points can be summarized from this work:

(1) Cerussite concentrate was easily leached by methane sulfonic acid (MSA). The kinetics were fast and the equilibrium could be achieved in a short time of 600s for most experiments in this study.

(2) Sufficient stirring speed, elevated temperature, finer particle size and greater MSA concentration could speed up the kinetics of the process. There was an upper-limit to the benefits of the measured stirring speed: when the stirring speed was higher than 400rpm, there was no further influence on the leaching kinetics. Solid concentration in the range from 20g/L to 200g/L also did not affect the final lead extraction.

(3) The leached residue mainly consisted of anglesite, which ultimately accounted for the remaining 15% lead extraction. This part of lead could be recovered by a desulfurization process via transforming $PbSO_4$ to $PbCO_3$, then followed by the MSA re-leaching treatment. The total lead extraction approached 98%.

4 Chapter: Electrowinning of Lead

4.1 Introduction

There is scarce literature in the field of fundamental study on lead electrowinning from Methane Sulfonic Acid (MSA) electrolyte, while there is vast literature on fluosilisic, fluoboric and chloride medium. These well-studied medium can offer invaluable references for this study, particularly fluosilicic and fluoboric medium that possess high solubility for lead. In this study, the concentrations of selected additives including two lignin sulfonate salts and two glycol-type agents in the electrolyte were first determined (See **Section 4.3**). In addition, the operating factors including temperature, concentrations of acid and lead ions, and current density were optimized for the MSA-based system (See **Section 4.4**); finally, some conclusions are given (See **Section 4.5**).

4.2 Experimental

4.2.1 Materials

The lead electrolyte was prepared from analytical grade chemicals and deionized water. Lead (II) oxide was from Acros Organics and methane sulfonic acid (Lutropur® MSA 100) was provided by BASF, Germany. The Pb-MSA Stock Electrolyte was 1M Pb (207g/L) as $Pb(SO_3CH_3)_2$ and 0.25M free MSA. O-phosphoric acid (Fisher Scientific) was added in electrolyte as inhibitor for β-PbO_2 at anode[80]. Both lignin sulfonic acid sodium salt (SL) and lignin sulfonic acid calcium salt (CL) were from Sigma-Aldrich. Polyethylene glycol (PEG, Mw 600) was from Fisher Scientific and polypropylene glycol (PPG, Mn 425) was from Sigma-Aldrich.

4.2.2 Apparatus and Procedure

The electrowinning apparatus used during this study provided controlled conditions for lead electrowinning. The apparatus is shown in **Figure 21**:
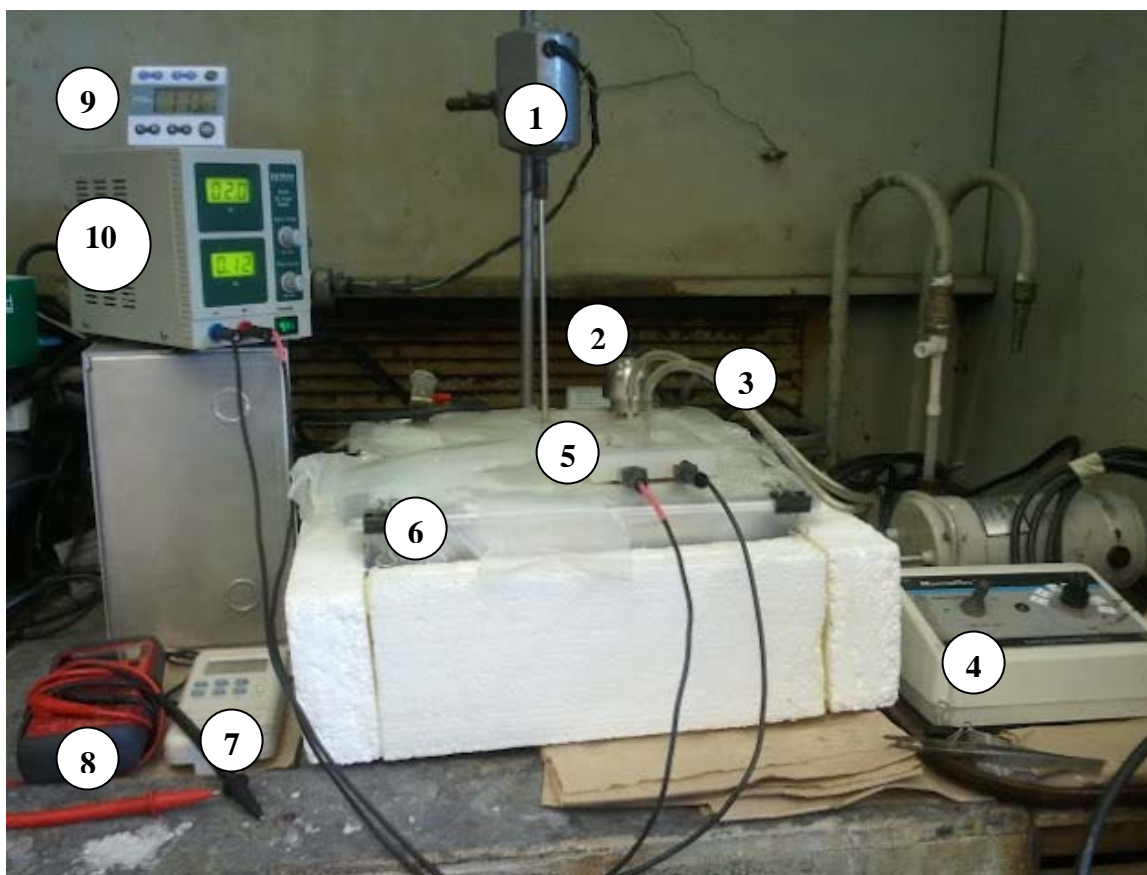
Figure 21 Experimental apparatus for electrowinning tests

(1-motor; 2-heater; 3-circulation tubing; 4-flow rate controller; 5-electrode holder; 6-water tank; 7-temperature regulator; 8-multimeter; 9-timer; 10-DC supplier)

A suitable electrochemical cell was assembled using a 250mL beaker and an electrode holder made of polypropylene. The distance between the cathode and anode was kept constant (40 ± 1 mm) through fixing the electrode position with the polypropylene holder. In another study by Dobrev[80], the distance was kept around 32mm. The anode was made of graphite with dimensions of 3.81cm×7.62cm×0.25cm (1.5" ×3" ×0.1") and the cathode was made of 316 stainless steel with the same dimensions. However, the real deposit area on the cathode was kept 6 cm^2 by framing the edges of cathode using electroplaters marking tape. A thermostated water bath was filled with water and covered with plastic balls and film to avoid loss of heat and water vapour. Two heaters were immersed into the water tank and a motor connected with an impeller was inserted to the water tank to continuously maintain a uniform temperature. A temperature controller was used to measure and control the water

temperature in the water bath. The temperature and composition of the electrolyte were kept uniform using a pump with a flow rate of 80mL/min.

The experimental procedure consisted of the following steps:

(1) Before each experiment, the cathode was first washed with 1M nitric acid solution, 1M MSA solution, deionized water, and then was dried at room temperature.

(2) The dried cathode was first framed by electroplating tape and then weighed. The depositing area was $6cm^2$ ($2 \times 3cm$).

(3) The current through the electrowinning cell was pre-determined by calculation based on the deposit area and desired current density, and then measured with a multimeter.

(4) Electrolyte of about 200mL was freshly prepared in a beaker before each experiment: lead methane sulfonate stock solution (containing around 200g/L Pb and 0.5M H^+), methane sulfonic acid and additives were added according to the test compositions.

(5) The beaker containing electrolyte was placed in the water bath to equilibrate.

(6) When the desired temperature in the electrolyte was reached, the electrowinning process was started. The process time was recorded with a timer.

(7) During the 3-hour duration, voltage measurements were once per hour using multimeter and the mean value was used to calculate the specific energy consumption.

(8) When each electrowinning test was done, the cathode was taken out of the electrolyte and washed using deionized water. Soft tissues were used to absorb the water remaining on the cathode surface. The cathode with deposited lead was weighed and recorded until the value did not change any more.

4.2.3   Evaluation Factors and Analytical Methods

There are some key factors to evaluate the electrowinning process, in particular Cathodic Current Efficiency (CCE) and Specific Energy Consumption (SEC). To determine the cathodic current efficiency related to the lead deposit, **Equation 1** was used, and **Equation 2** for the specific energy consumption (unit lead quantity on the cathode) calculation was also necessary[80].

$$CCE = \frac{\Delta M}{\Delta M_T} \times 100\% = \frac{\Delta M}{I \cdot \tau \cdot Q_{Pb/Pb^{+2}}} \times 100\% = \frac{\Delta M}{i \cdot A \cdot \tau \cdot Q_{Pb/Pb^{+2}} \times 10^{-4}} \times 100\%$$ **Equation 1**

$$SEC = \frac{\Delta E_{applied} \cdot I \cdot \tau}{\Delta M} = \frac{\Delta E_{applied} \cdot i \cdot A \cdot \tau}{10 \cdot \Delta M} \left[Wh/kg\right]$$ **Equation 2**

Deposit morphology also is a key factor to evaluate the quality of deposited lead. The micro-morphology was observed by Scanning Electronic (SEM) and Back-scattered Electrons (BSE) (Hitachi S3000N).

4.3 Optimization for Additives Use

The individual and synergistic uses of additives in MSA based electrolyte were organized as shown in **Table 12**. All the experiments in this section contained 100 g/L Pb^{+2} as $Pb(CH_3SO_3)_2$, 0.5 M free acid and 2 g/L O-phosphoric acid , and were carried out under following conditions: current density = 215.8 A/m^2, temperature = 40 ± 1°C, circulation flow rate = 80 mL/min. The variables in this section were the concentrations of four additives in the electrolyte, which were 0.2~2.5 g/L (for sodium lignin sulfonate, SL), 0.2~2.5 g/L (for calcium lignin sulfonate, CL), 0.5~2.5 g/L (for polyethylene glycol, PEG) and 0.25~2.5 g/L (for polypropylene, PPG), respectively.

Table 12 Test design for optimizing additives use

Variables	Sample NO.		
	#1	#2	#3
SL	0.2g/L	1g/L	2.5g/L
CL	0.2g/L	1g/L	2.5g/L
PEG	0.5g/L	1g/L	2.5g/L
PPG	0.25g/L	0.5g/L	2.5g/L
SL+PEG	SL=1g/L PEG=0.5g/L	SL=1g/L PEG=1g/L	SL=1g/L PEG=2.5g/L
CL+PEG	CL=2.5g/L PEG=0.5g/L	CL=2.5g/L PEG=1g/L	CL=2.5g/L PEG=2.5g/L
SL+PPG	SL=1g/L PPG=0.25g/L	SL=1g/L PPG=0.5g/L	SL=1g/L PPG=2.5g/L
CL+PPG	CL=2.5g/L PPG=0.25g/L	CL=2.5g/L PPG=0.5g/L	CL=2.5g/L PPG=2.5g/L
CL+PEG+PPG	CL=2.5g/L, PEG=1g/L, PPG=0.25g/L		
Additives -free	---		

The cathodic current efficiency and specific energy consumption for each lead electrowinning test were first evaluated. The results are shown in **Table 13**. As can been seen from the results, the individual addition of either PEG or PPG in the electrolyte did not change the voltage much compared to the additives-free test. However, both of the addition of SL and CL caused a considerable increase in voltage with or without the presence of PEG or PPG. It can be estimated that lignin sulfonate salts have an obvious polarization effect on the electrolysis process, resulting in an increase of electrode overpotential and thus a higher cell voltage. The cathodic current efficiency (CCE) for each electrowinning test in MSA-based electrolyte was over 90% and even could be as high as 99% when lignin sulfonate salts were adopted.

Table 13   Experimental data for optimizing additives use

Sample #	CCE (%)	SEC (kWh/kg)	Cell Voltage (V)	Sample #	CCE (%)	SEC (kWh/kg)	Cell Voltage (V)
SL1	96.53	0.55	2.05	SL+PEG1	93.20	0.58	2.08
SL2	99.19	0.53	2.04	SL+PEG2	99.86	0.53	2.05
SL3	100.53*	0.53	2.06	SL+PEG3	91.21	0.58	2.06
CL1	99.19	0.53	2.03	CL+PEG1	98.53	0.53	2.01
CL2	99.19	0.53	2.04	CL+PEG2	99.19	0.53	2.03
CL3	98.53	0.53	2.04	CL+PEG3	99.19	0.52	2.01
PEG1	91.87	0.56	1.98	SL+PPG1	99.86	0.52	2.01
PEG2	N/A	N/A	1.98	SL+PPG2	97.86	0.58	2.17
PEG3	N/A	N/A	2.00	SL+PPG3	98.53	0.55	2.09
PPG1	N/A	N/A	1.97	CL+PPG1	99.19	0.54	2.09
PPG2	93.87	0.55	2.00	CL+PPG2	100.53*	0.53	2.07
PPG3	N/A	N/A	1.97	CL+PPG3	99.86	0.54	2.07
Additive-free	104.52*	0.49	1.97	CL+PEG+PPG	98.73	0.54	2.07

(Note:*probably due to the contamination of impurities in the deposit)

However, from some high CCE values (>100%), it could be estimated that the deposit was impure and probably contaminated by the electrolyte. For example, the CCE obtained from the additives-free electrolyte was 104.52%. In this case, 104.52 g deposited lead would be necessarily required when the theoretical deposition mass is 100 g. Since the lead deposit

was air-dried until the weight did not change any more, the over 100% CCE issue could mot be caused by the moisture. Also if the overweight (4.52 g) is assumed totally due to the oxidation by oxygen, around 58.3 g lead would be involved in the oxidation reaction, accounting for 55.8% of the whole deposit mass. Therefore, the only explanation for the overweight issue is the contamination in the lead deposit. However, with the presence of calcium lignin sulfonate salt, the lead deposit became dense with small amount of impurity (See **Table 14**, **Figure 23(b) ~ Figure 26(b)**).

Table 14   EDX analysis for the surface of some lead deposits

Sample Name	Area	Pb wt%	O wt%	C wt%
CL#3	1	95.92	4.08	---
	2	97.21	2.79	---
	3	100	---	---
CL+PEG#1	1	100	---	---
	2	97.83	2.17	---
	3	97.53	2.47	---
CL+PPG#1	1	93.61	6.39	---
	2	94.55	5.45	---
	3	95.76	4.24	---
CL+PEG+PPG	1	96.11	3.89	---
	2	79.49	10.95	9.56
	3	95.38	4.62	---

The specific energy consumption (SEC) was around 0.53Wh/kg. This value was considerably lower than the reported values obtained from fluosilicate-based electrowinning process, varying between 0.57kWh/kg and 0.8Wh/kg[80].

The macro-morphologies of lead deposits plated at various concentrations of additives were observed, as shown in **Figure 22**. In additives-free electrolyte, the dendritic and powdered deposits were weakly adherent to the substrate. Large isolated lead crystals were formed especially on the edges of depositing area. Hence, it is reasonable and necessary to add additives to the electrolyte.

With the concentration increase of lignin sulfonic acid sodium salt (SL) from 0.2g/L to 2.5g/L, the deposit became smoother and the grains grew finer. On the edges of deposit nodular crystals, instead of dendritic crystals, were generated. But the adherence of the deposit to the cathode substrate did not increase significantly, and the deposited lead still

shed off during the electrowinning process. The optimal concentration of SL was around 1~2.5g/L.

By individually using PEG or PPG as electrolyte additives, dendrite crystals of lead inevitably presented on the edges. The surface was still rough and uneven. It could be concluded that PEG and PPG individually used in this study had no obvious impact on improving the quality of deposit lead. With the increase of PEG concentration in electrolyte, the adherence of deposit lead got much worse, especially when PEG concentration was 2.5g/L or higher.

Synergistic effects of those additives on the morphologies of lead deposit also have been tested. In the electrolyte containing both SL and PEG, deposit adherence improved somewhat while bulge formation could not be inhibited. With the presence of SL (1g/L), the optimal concentration of PEG is 0.5g/L. The synergistic influence of PPG with 1g/L SL was obviously weaker compared to that of PEG with same amount of SL. But PPG had a positive influence on inhibiting bulge formation on the surface.

In contrast, lignin sulfonic acid calcium salt (CL) was tested in the same concentration range as lignin sulfonic acid sodium salt. Compared to SL, CL could better benefit the morphologies of deposits, and the adherence of deposit also improved and made it easier to peel off the deposit as a whole. When 2.5g/L CL was utilized, fewer voids appeared on the deposit surface and the edges became trim with few nodular crystals around. Therefore, the optimal CL concentration was 2.5g/L. When PEG (or PPG) was synergistically adopted with 2.5g/L CL, better morphologies could be achieved than those from electrolyte with PEG (or PPG) and SL. Synergistic effects of PEG with CL were rather better than those of PPG with CL. The optimal concentrations of PEG and PPG with the presence of CL were 1g/L and 0.25g/L, respectively.

Finally, synergistic effect of three agents including CL, PEG and PPG were tested. The optimal concentration for each additive was adopted. However, the morphology became worse as many fine cavities presented on the edges.

Some lead deposits with good morphology were sent for SEM tests for more detailed analysis of the micro-structure (See **Figure 23~ Figure 26**). Compared to CL#3, the addition of glycol-type additives (CL+PEG#1 and CL+PPG#1) resulted in very fine grains dispersed between lead crystals. When PEG and PPG both existed in the electrolyte with CL (CL+PEG+PPG), microscopic interlaced structure was induced. Therefore, individual use of CL effectively improved the morphology of lead deposit, making it smoother with few fine grains on the surface.
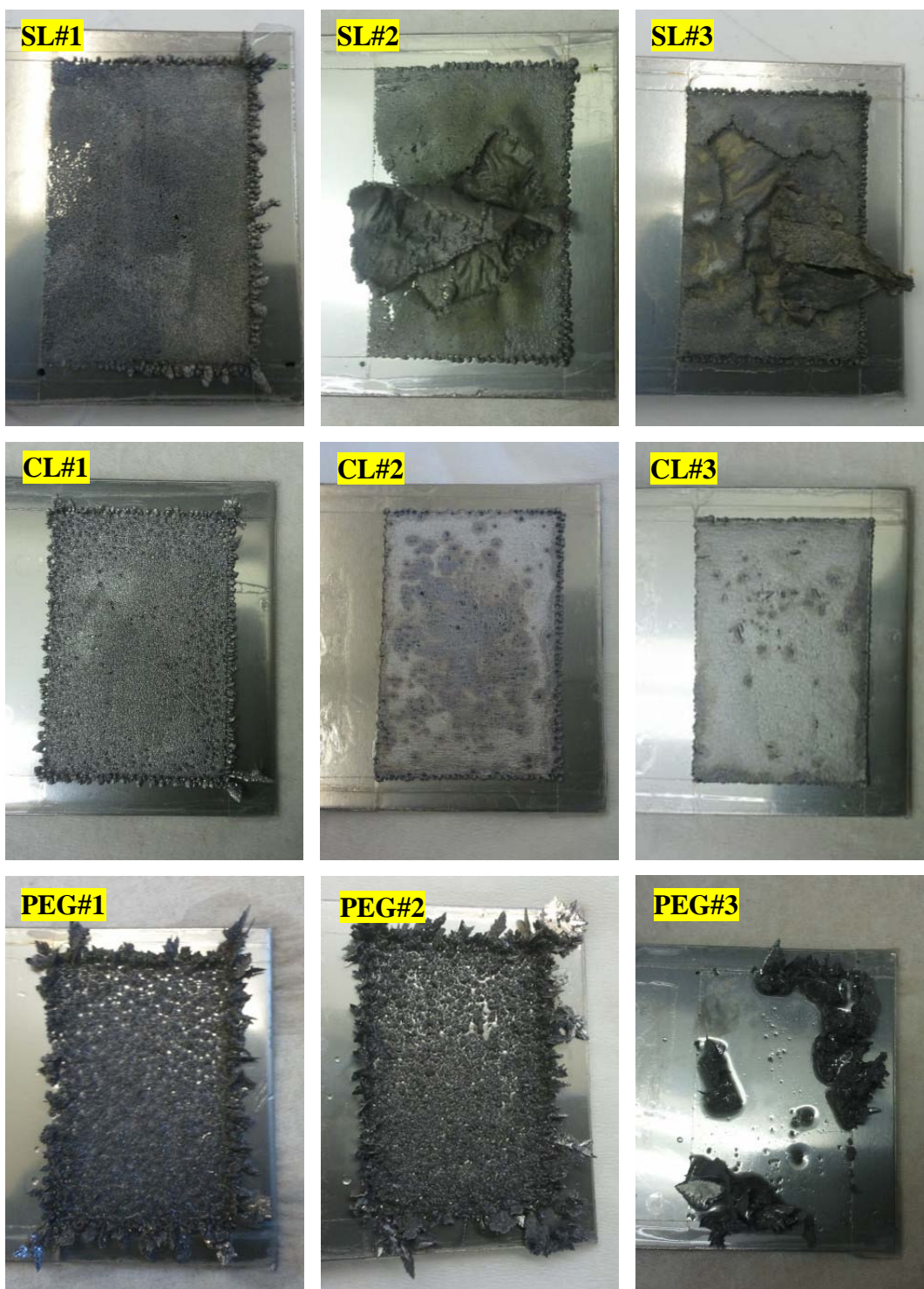
Figure 22   Effects of SL, CL, PEG, PPG concentrations on the morphologies of lead deposits

(3-hour electrowinning duration under conditions: current density=215.8A/m^2, deposition area=6cm^2, circulation flow rate=80ml/min, temp.=40ºC)
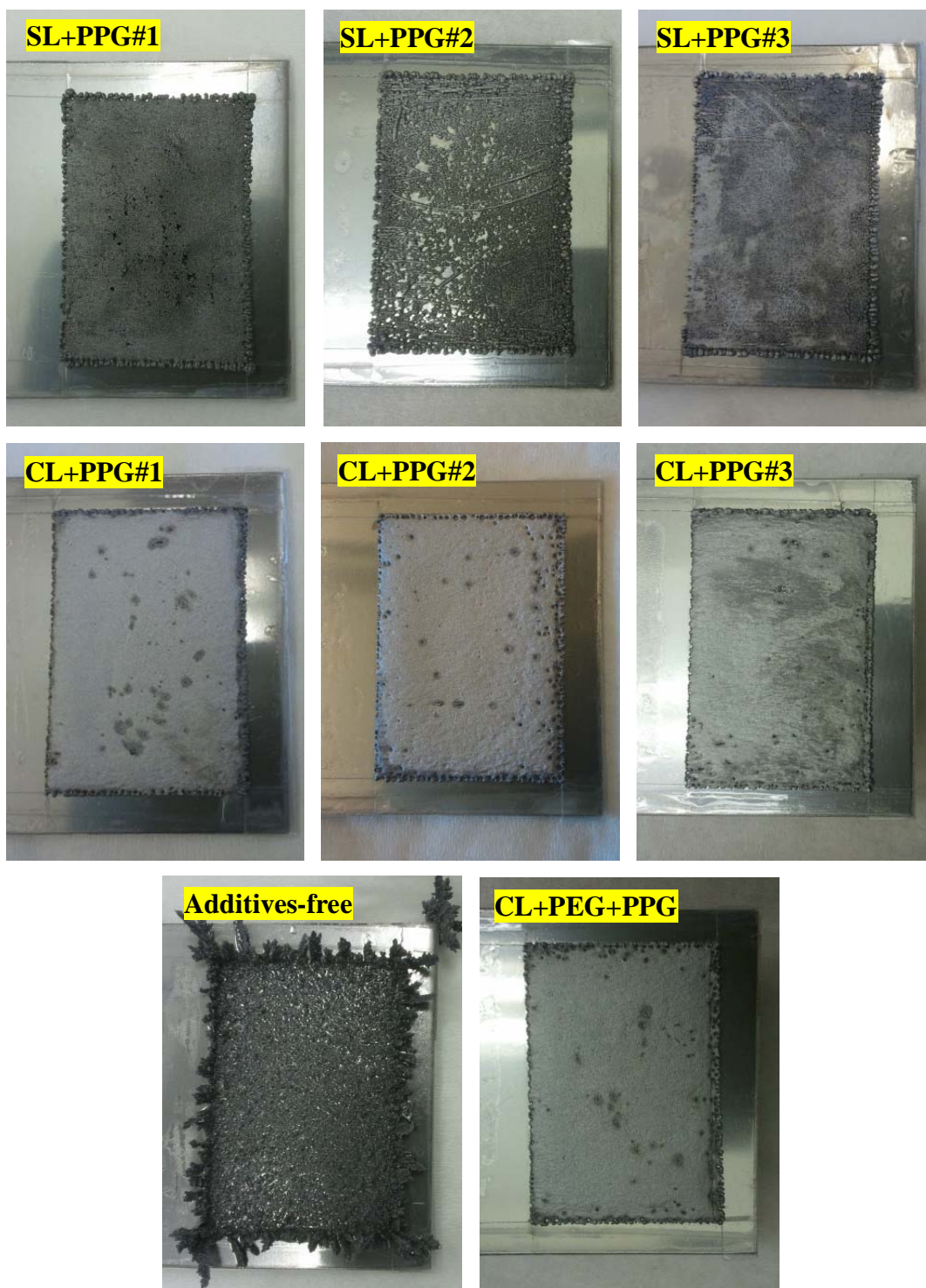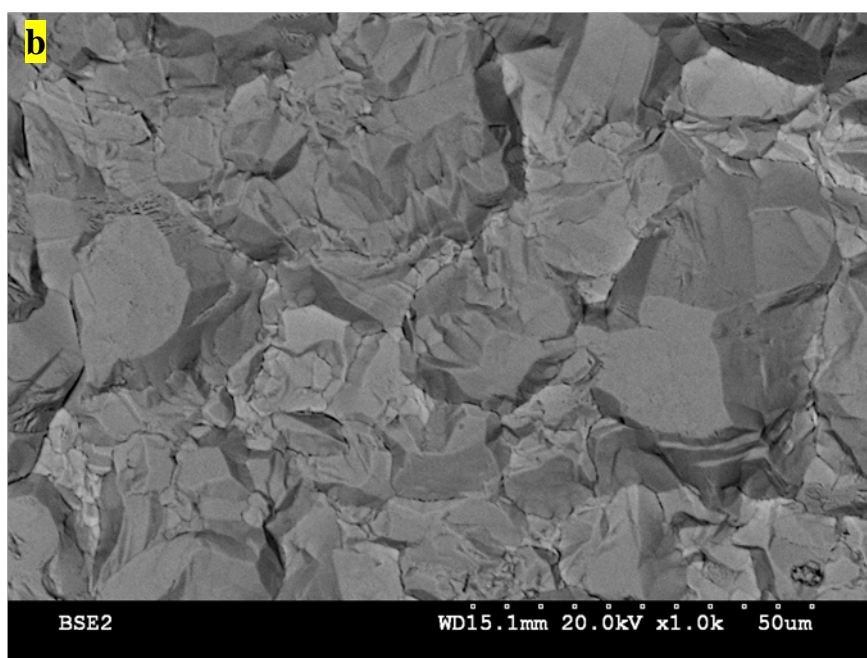
Figure 22 Effects of SL, CL, PEG, PPG concentrations on the morphologies of lead deposits (continued)

(3-hour electrowinning duration under conditions: current density=215.8A/m², deposition area=6cm²,
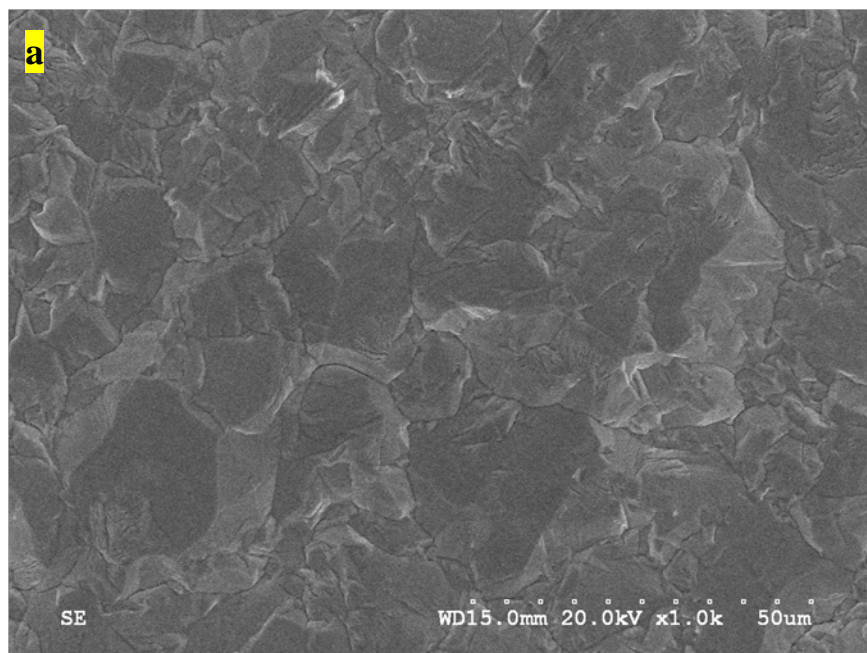
circulation flow rate=80ml/min, temp.=40ºC)

Figure 22   Effects of SL, CL, PEG, PPG concentrations on the morphologies of lead deposits (continued)

(3-hour electrowinning duration under conditions: current density=215.8A/m^2, deposition area=6cm^2,

circulation flow rate=80ml/min, temp.=40ºC)

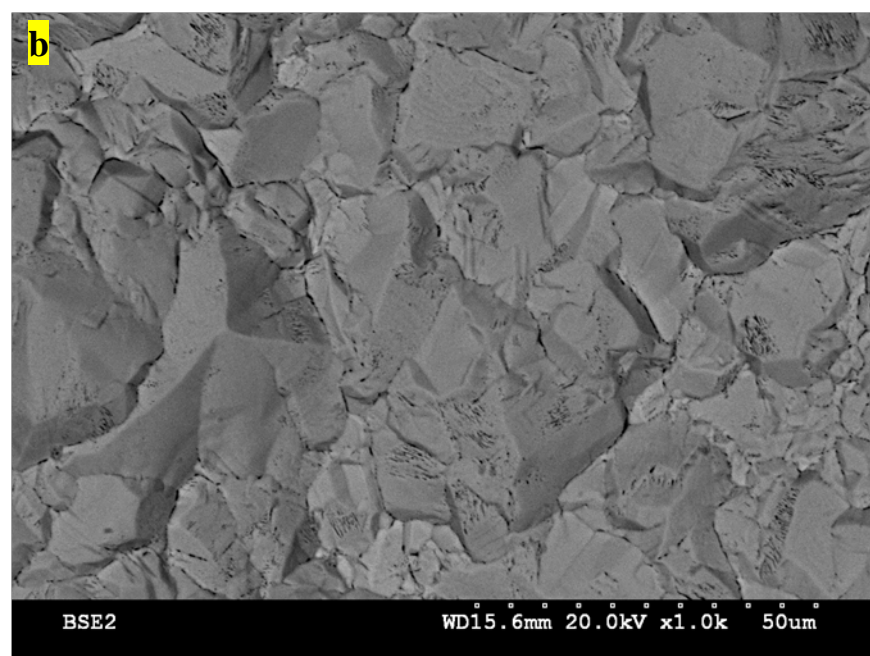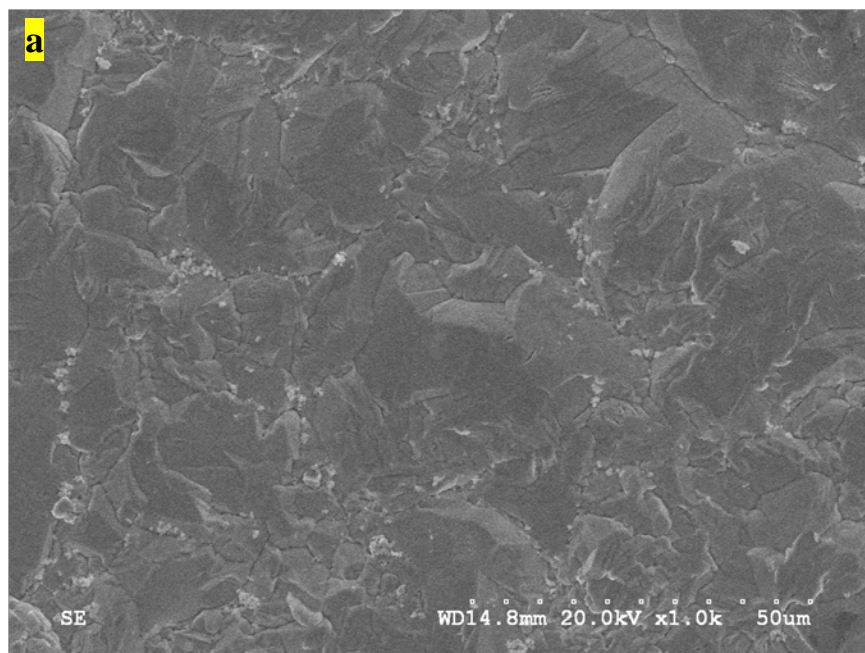**Figure 23   SE (a) and BSE (b) diagrams for sample CL#3**

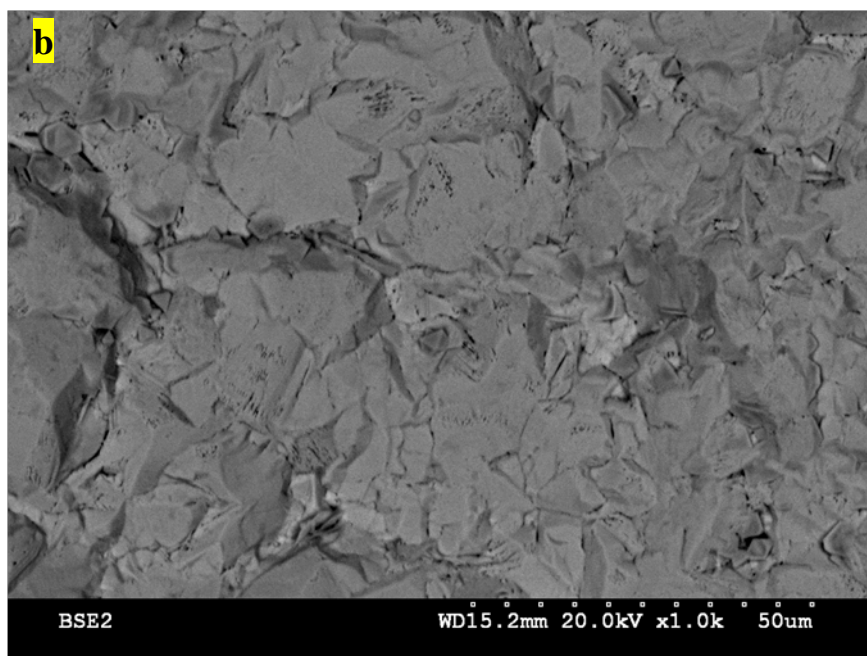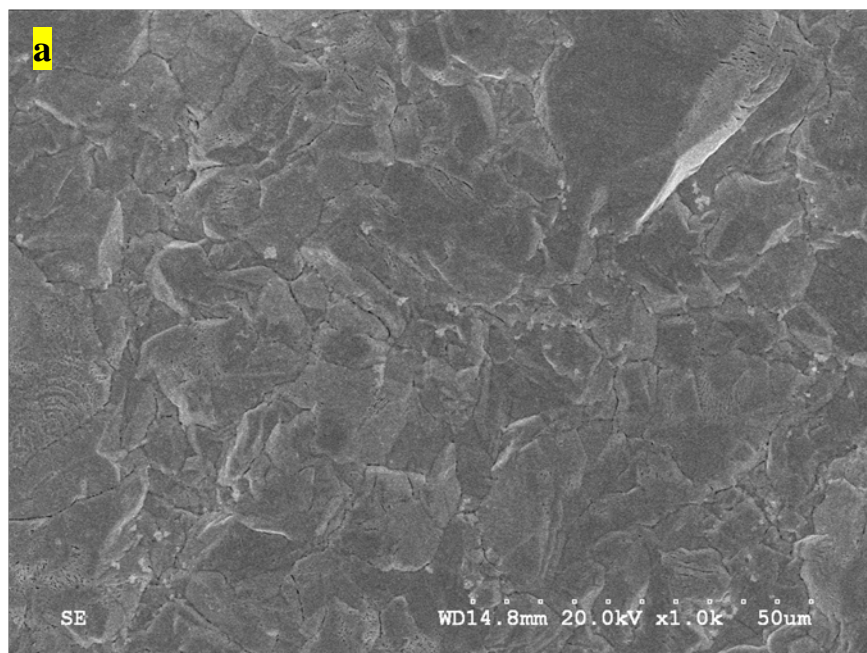**Figure 24   SE (a) and BSE (b) diagrams for sample CL+PEG#1**

Figure 25   SE (a) and BSE (b) diagrams for sample CL+PPG#1
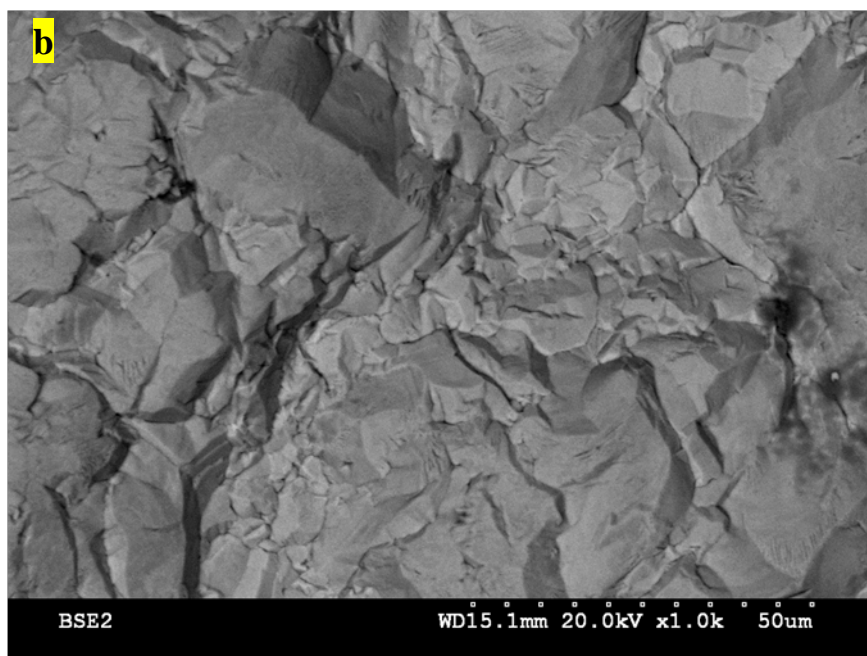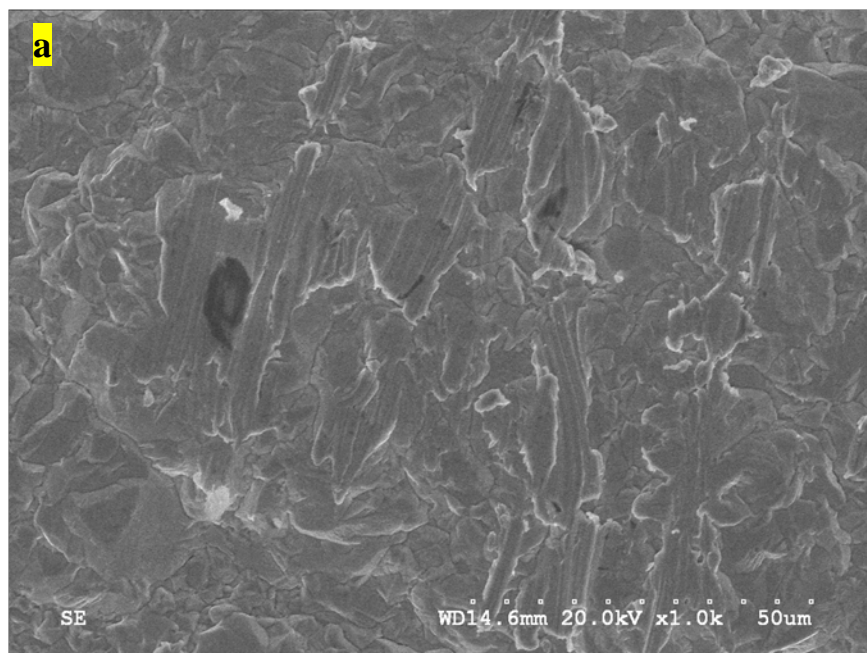
Figure 26   SE (a) and BSE (b) diagrams for sample CL+PEG+PPG

4.4   Optimization for Operating Conditions

Based on the optimal use of additives discussed in **Section 4.3**, the baseline test was determined to be CL#3 for the study of optimizing operation parameters. The composition for the baseline test was: 100 g/L Pb (as $Pb(CH_3SO_3)_2$), 0.5 M free MSA, 2 g/L O-phosphoric acid (85%) and 2.5g/L calcium lignin sulfonate salt. The operating conditions for baseline test were: current density = 215.8A/m^2, temperature= 40 ± 1ºC, circulation flow rate = 80 mL/min.

The operating parameters in this section were organized as shown in **Table 15**. The variable ranges for temperature, concentration of lead ions and protons, and current density were 35~50 ºC, 50~150 g/L, 0.25~1.5 M, 100~250 A/m^2, respectively.

Table 15   Test design for optimizing operation conditions

Variables	Sample NO.		
	#1	#2 (baseline)	#3
Temperature(T)/ºC	35±1	40±1	50±1
Lead concentration(L)/ g.L^{-1}	50	100	150
Acid concentration(A)/M	0.25	0.5	1.5
Current density(CD)/ A.m^{-2}	100	215	250

The cathodic current efficiency and specific energy consumption for each electrowinning test was first evaluated. The results are organized and shown in **Table 16**. As can been seen from the results, higher temperature (from 35ºC to 50ºC), greater concentrations of lead ions (250 g/L Pb^{+2}) and protons (1.5M H$^+$), and lower current density (100 A/m^2) could lead to lower cell voltage under 2V. Particularly, current density has the most remarkable and significant influence on declining the cell voltage. However, low current density limited the production capacity. Therefore, lowering cell voltage through declining current density was hardly worth consideration. Temperature also has significant benefits on decreasing cell voltage. **Equation 3** could shows the influence of working parameters. The cell voltage $\Delta E_{applied}$ can be regarded as a sum of thermodynamic cell voltage, anodic overpotential, cathodic overpotential and the electrolyte Ohmic drop, as shown below:

$$\Delta E_{applied} = \Delta E_{ther\,mod\,ynamic} + (\eta_{S.a} + \eta_{D.a}) + + (\eta_{S.c} + \eta_{D.c}) + IR \qquad \text{Equation 3}$$

thermo. cell voltage: $\Delta E_{ther\,mod\,ynamic} = \Delta E_0 - 2.303RT \log \prod_j a_j^{m_j} / (nF)$ **Equation 4**

activation: $\eta_S = a + b \log i$, where $b = 2.303RT / (\alpha F)$, $a = -b \cdot \log i_0$ **Equation 5**

mass transfer: $\eta_D = 2.303RT \log \left[i_{\lim} / (i_{\lim} - i) \right] / (nF)$ **Equation 6**

Ohmic Drop: $IR = iA \cdot l / (\Lambda_m C)$, where $\Lambda_m = \Lambda_m^0 - KC^{0.5}$ (*very dilute*)   **Equation 7**

$\Lambda_m^0 = \nu_+ \lambda_+^0 + \nu_- \lambda_-^0$, where $\lambda_{i,T}^0 \cong \lambda_{i,298K}^0 \left[1 + 0.02(T - 298) \right]$ **Equation 8**

From **Equation 4 ~ Equation 8**, we can figured out that all the components of applied cell voltage are dependent on temperature. Except the thermodynamic cell voltage, both the overpotential at the electrodes and the Ohmic drop are affected by the current density. The concentrations of electrolyte components have an impact on the thermodynamic cell voltage, diffusion overpotential and the electrolysis cell Ohmic drop. Therefore, we can see that the influence of working parameters on the electrowinning process is very complicated. However, in practice (i.e. electrowinning of copper and zinc), the greatest resistance is due to the solution or electrolyte. The lower voltage at greater concentration of lead ions or protons and higher temperature was possibly due to the increased conductivity of the electrolyte.

Table 16   Experimental data for optimizing operation conditions

Sample #	Cathodic Current Efficiency (%)	Specific Energy Cost (kWh/kg)	Cell Voltage (V)	Sample #	Cathodic Current Efficiency (%)	Specific Energy Cost (kWh/kg)	Cell Voltage (V)
T1	101.19	0.53	2.07	A1	99.86	0.54	2.09
T3	99.86	0.50	1.94	A3	98.53	0.52	1.98
L1	98.53	0.55	2.09	CD1	100.64	0.47	1.84
L3	99.86	0.52	2.02	CD3	99.66	0.53	2.06

The cathodic current efficiency for all tested parameters in MSA based electrolyte was over 98% (See **Table 16**). The various parameters showed only a slight influence on the electrowinning process, indicating that the operating parameters in MSA based electrolyte had wide range of applicability. This flexibility makes MSA based electrolyte easy to operate and thus highly advantageous. The specific energy consumption was around 0.53Wh/kg.

The **Figure 27** displays the influence of operating parameters on the morphologies of lead deposit. Lower temperature (about 35ºC) resulted in smoother surfaces and trim edges (T#1), while at higher temperature about 50 ºC, the surface turned uneven and coarse, and quite a few cavities or holes were formed on the edges of lead deposit (T#3). Low lead concentration (50 g/L as $Pb(CH_3SO_3)_2$) caused obvious uneven deposit surface, while greater lead concentration was capable of trimming the deposit edges. Higher free acid concentration (1.5M) resulted in worse morphology of lead deposit probably due to the low effectiveness of calcium lignin sulfonate in a very acidic environment. This also induced the cathodic side reaction to happen, which generated hydrogen gas bubbles at the cathode and thus diminished the cathodic current efficiency during the electrowinning process. Low current density caused a relatively thin deposit in the same deposition duration (3 hours) that was very brittle and easy to break off, while greater current density had few effects on the macro-morphology of deposit compared to the baseline test.

Some SEM images were taken for lead deposits obtained under different operation parameters. Obviously, high temperature (50ºC) benefited the crystal growth, which made the surface relatively coarse and uneven (**Figure 29**); low lead concentration (100 g/L) caused nodular grains of lead (**Figure 30**); high proton concentration (1.5 M) induced some micro-cracks between the lead crystals (**Figure 33**). However, MSA still possessed a relatively wide feasibility and flexibility on operating conditions. Moderately low temperature (35~40ºC), high lead content (100~150 g/L), low free acid concentration (0.25~0.5 M) and high current density (250 A/m^2) were potentially acceptable in use, contributing to a high current efficiency and a low specific energy consumption.
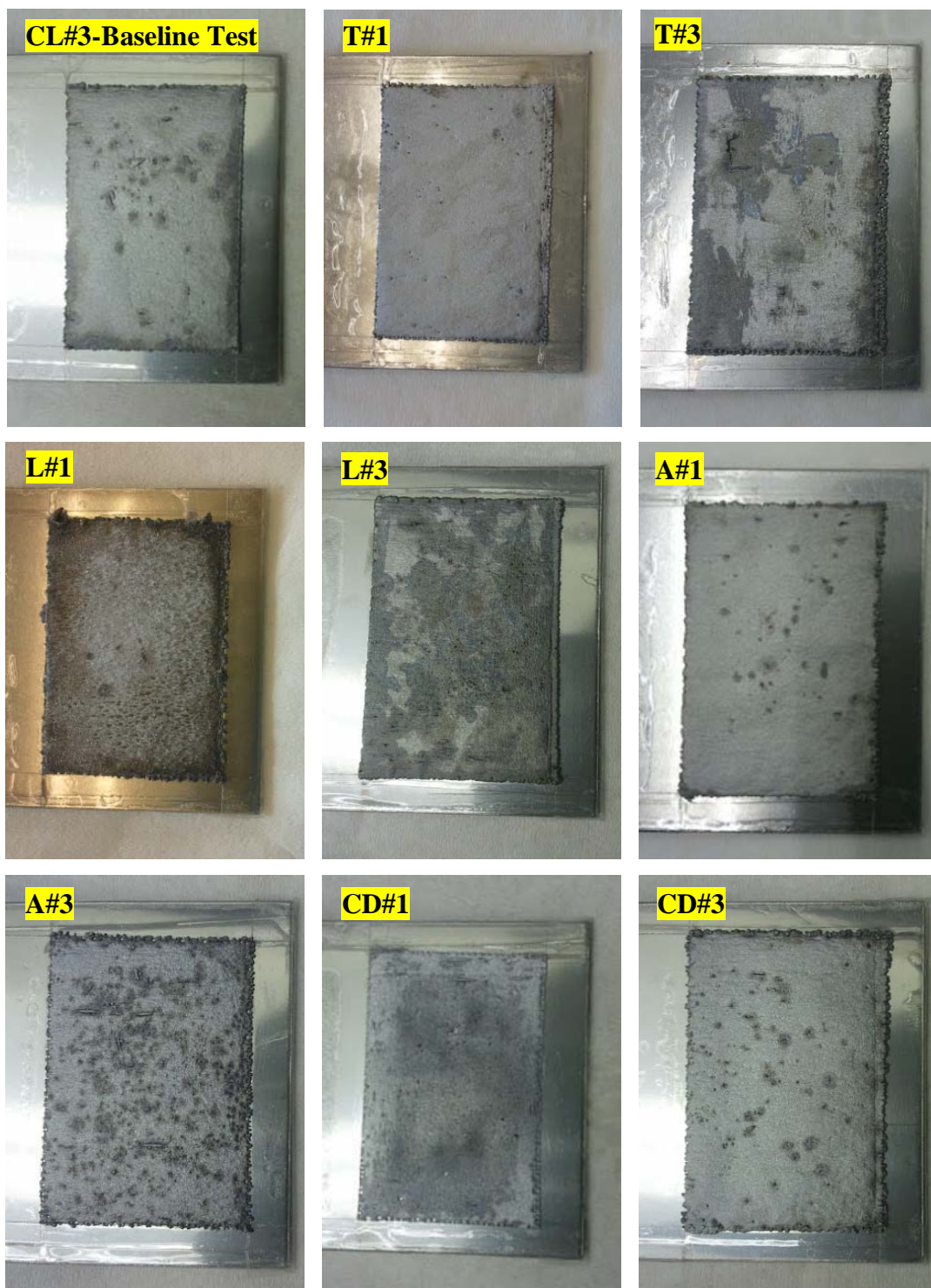
Figure 27   Morphologies of lead deposit under different operation conditions
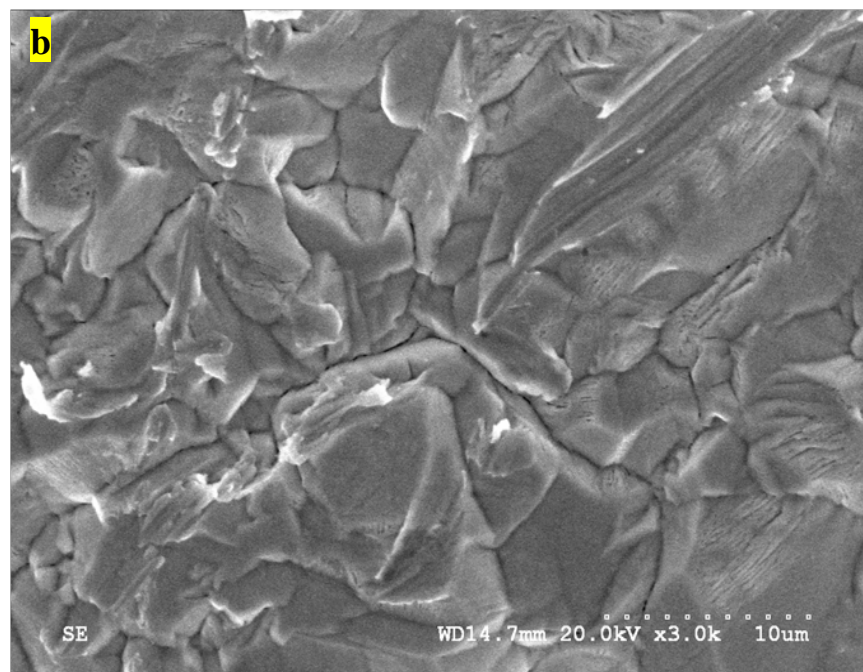
Figure 28   Scanning electron microscope (SEM) diagrams for sample T#1

Figure 29   Scanning electron microscope (SEM) diagrams for sample T#3

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Figure 30   Scanning electron microscope (SEM) diagrams for sample L#1

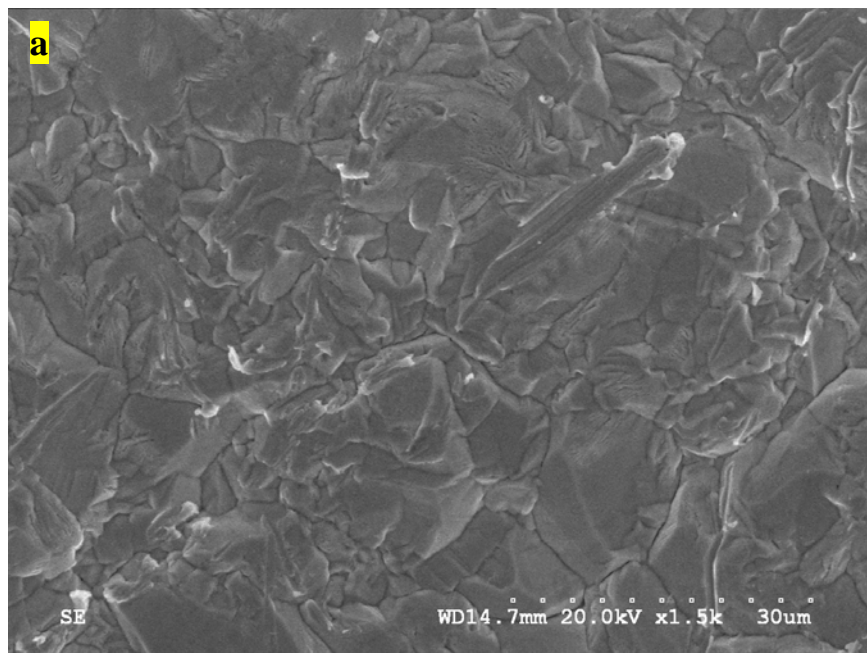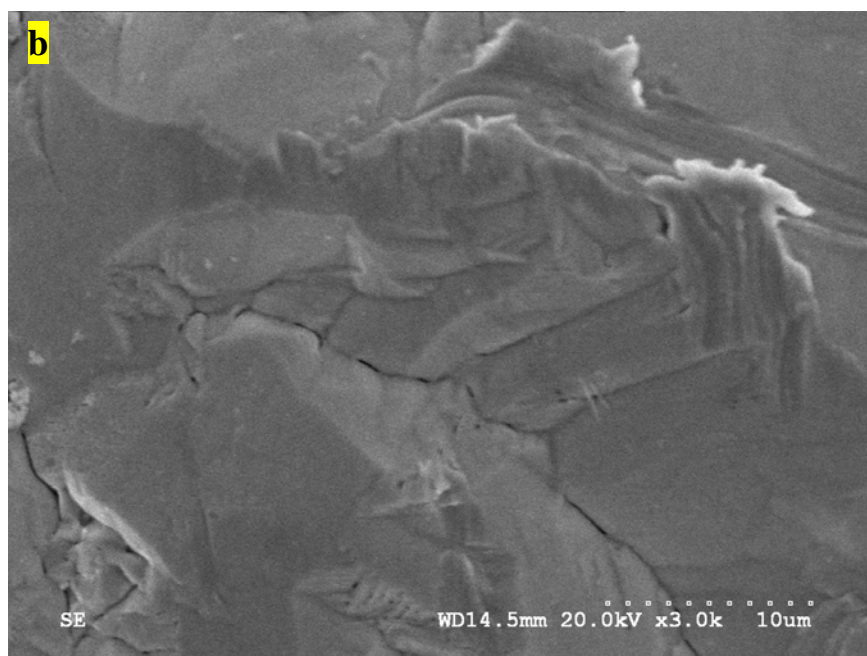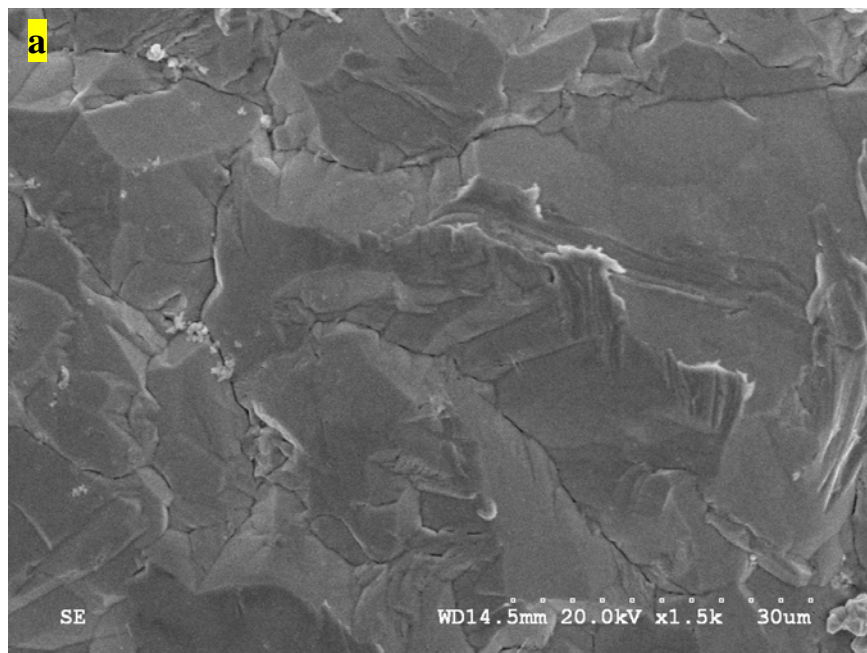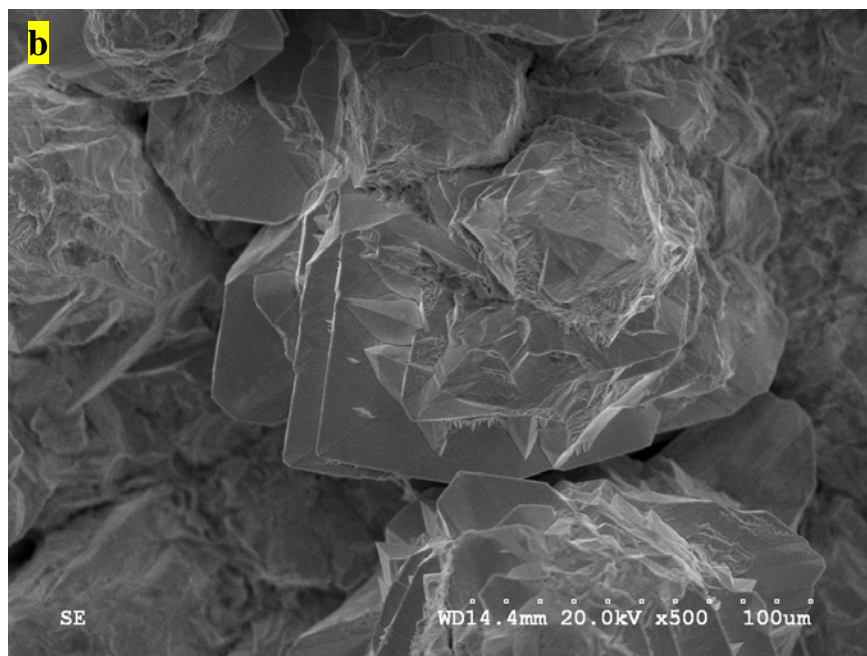**Figure 31   Scanning electron microscope (SEM) diagrams for sample L#3**

Figure 32   Scanning electron microscope (SEM) diagrams for sample A#1
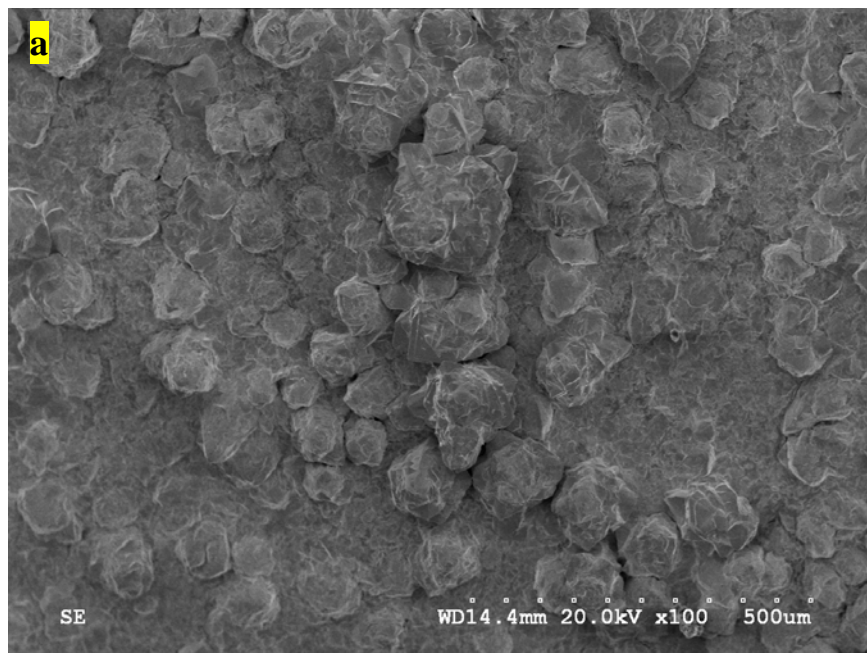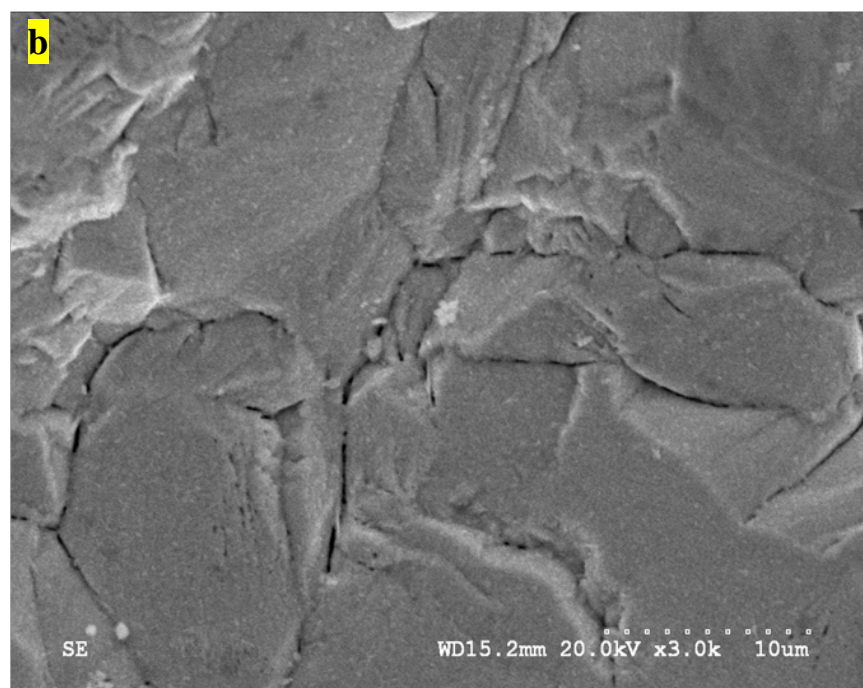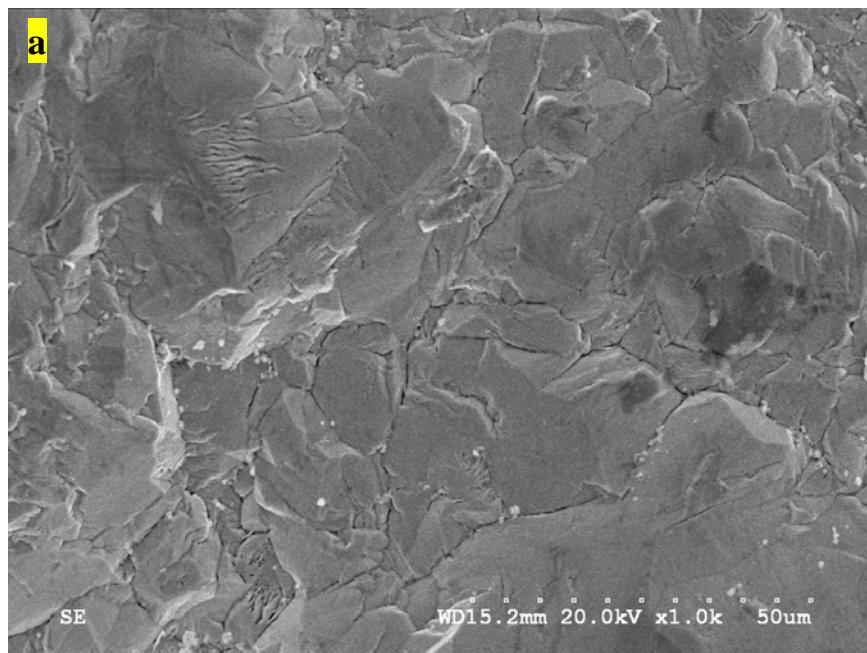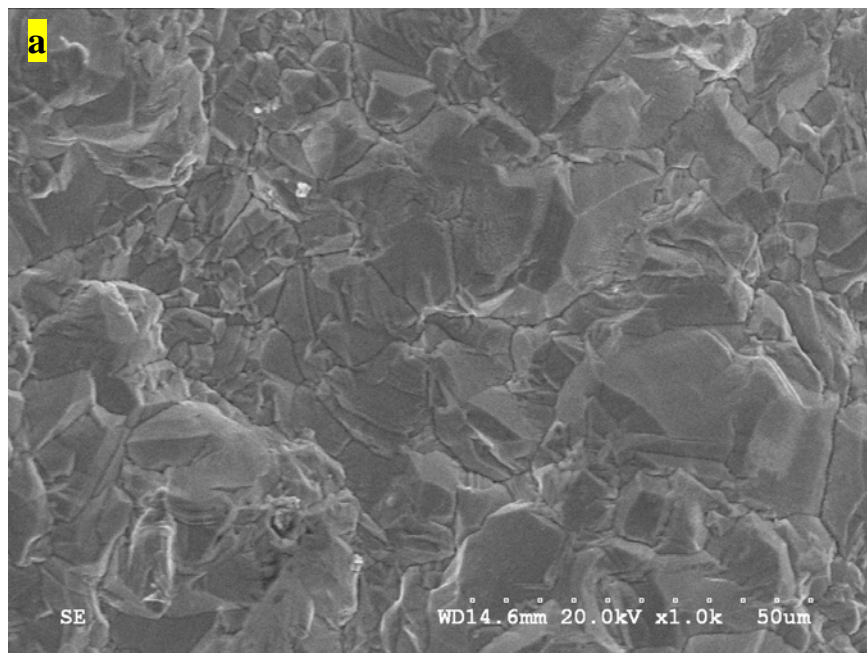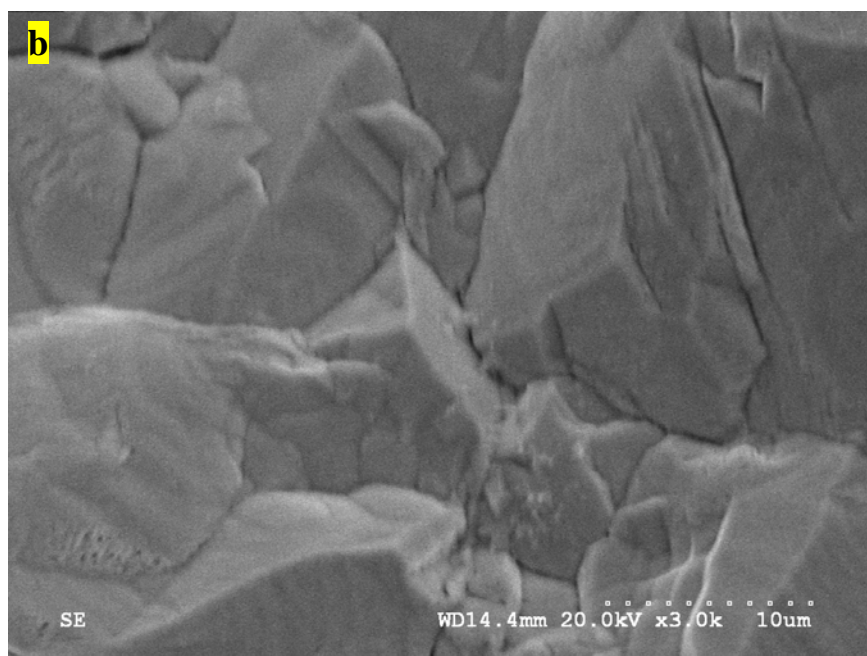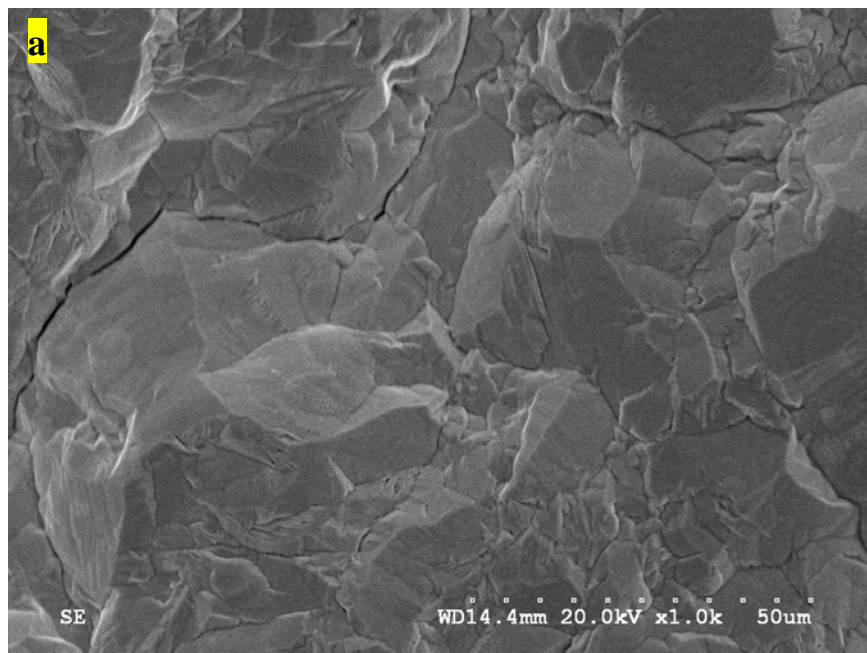
Figure 33　Scanning electron microscope (SEM) diagrams for sample A#3
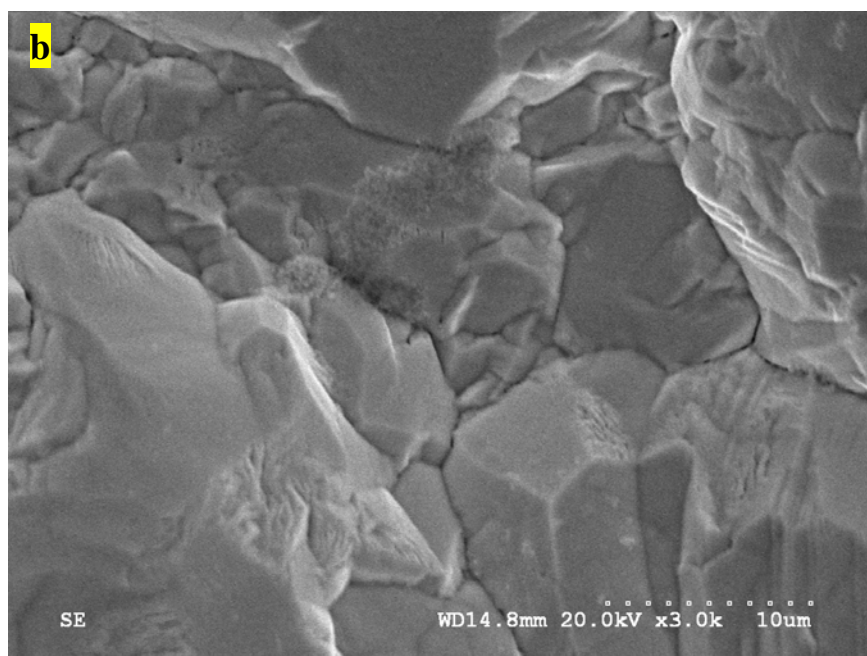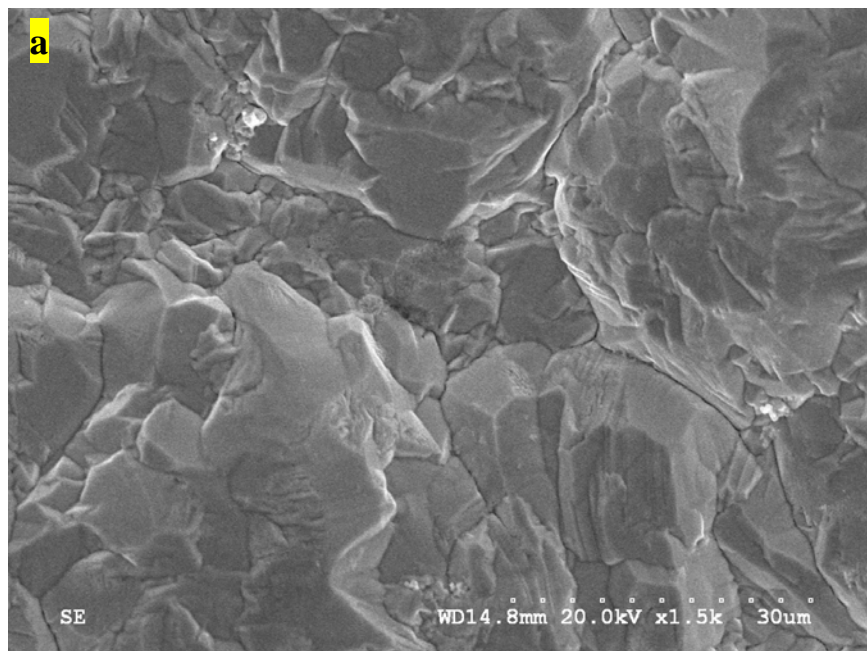
Figure 34   Scanning electron microscope (SEM) diagrams for sample CD#3

4.5   Summary

The following points can be summarized from this work:

(1) Lignin sulfonate salts significantly suppressed the dendritic growth of lead deposit. The resulting smooth layer presents a weakly interlaced structure. Compared to SL, CL displayed greater inhibiting influence and thus bettered the morphology of the lead deposit. The optimal concentration of CL was around 2.5g/L.

(2) The glycol-type additives (PEG and PPG) did not considerately benefit the lead electrowinning process in MSA based electrolyte. Even the synergistic use of the glycol-type additives with CL worsened the morphology of the lead deposit compared to the use of CL alone, since many fine grains dispersed between the lead crystals were generated. Therefore, glycol-type agents are not recommended for lead-MSA electrolyte.

(3) A wide range of operating conditions for the ferric-free Pb-MSA electrowinning process are feasible: 100~150 g/L Pb(as $Pb(CH_3SO_3)_2$), 0.25~0.5 M free MSA, current density 215.8~250 A/m^2 and temperature 35~40ºC.

(4) The cathodic current efficiency and specific energy consumption under the optimal electrolysis conditions were around 99% and 0.53kWh/kg, respectively.

5 Chapter: A Proposed Process for Lead Production

The results of the present work demonstrated that both the extraction of lead from cerussite concentrate from Magellan Mine with methane sulfonic acid (MSA) and lead electrowinnig from MSA based electrolyte were very feasible at bench scale. MSA extracted lead rapidly from cerussite concentrate. The parameters of lead electrowinning in MSA baths also exhibited a wide range of useful conditions, which was similar to the Betts Elctrorefinning Process. Based on these results, a commercial process based on MSA solution may be a promising alternative. A simplified flowsheet for lead production from cerussite concentrate MSA medium is proposed (See **Figure 35**).

The first step involves in acid leaching of the cerussite concentrate from Magellan Mine with methane sulfonic acid. At the end of leaching process, the leach slurry is subjected to a solid-liquid separation process (i.e. thickening, filtration, centrifugation or cycloning) with incorporation of washing in order to give a first solid residue and an impure leachate.

Minor amounts of lead sulphate (anglesite) are present in the concentrate or ore and it is insoluble in MSA solution, but it can be converted to lead carbonate by recovering the first leaching residue and treating it with a source of soluble carbonate (i.e. sodium carbonate). This desulfurization or carbonation treatment converts lead sulphate to lead carbonate for a subsequent leaching operation with MSA. The sodium sulphate solution from this desulfurization treatment may be a saleable by-product. The second leach residue (containing lead carbonate formed from lead sulfate) is followed by the acidic leaching step.

The second step in the process involves purification of the impure leachate. The lead methane sulfonate solution from the first step may be purified by pH adjustment (with base, and oxidants might be required to oxidize some impurity ions for easy-precipitation) to eliminate the impurities (i.e. Fe^{+3}, Al^{+3}, Cr^{+3}) and by cementation with metallic lead powder or scrap to remove more noble impurities such as copper in order to remove the impurities to produce a suitable solution prior to electrolysis production.

The third step in recovery of lead is electrowinning operated in an undivided cell containing anodes and cathodes. The anodes may be formed of graphite and the cathode may be formed from stainless steel. Lead is recovered as metal at the cathode and oxygen is evolved at the anode by electrolysing the purified lead methane sulfonate solution. The lead-depleted electrolyte containing methane sulfonic acid may then be recycled to the leaching process.
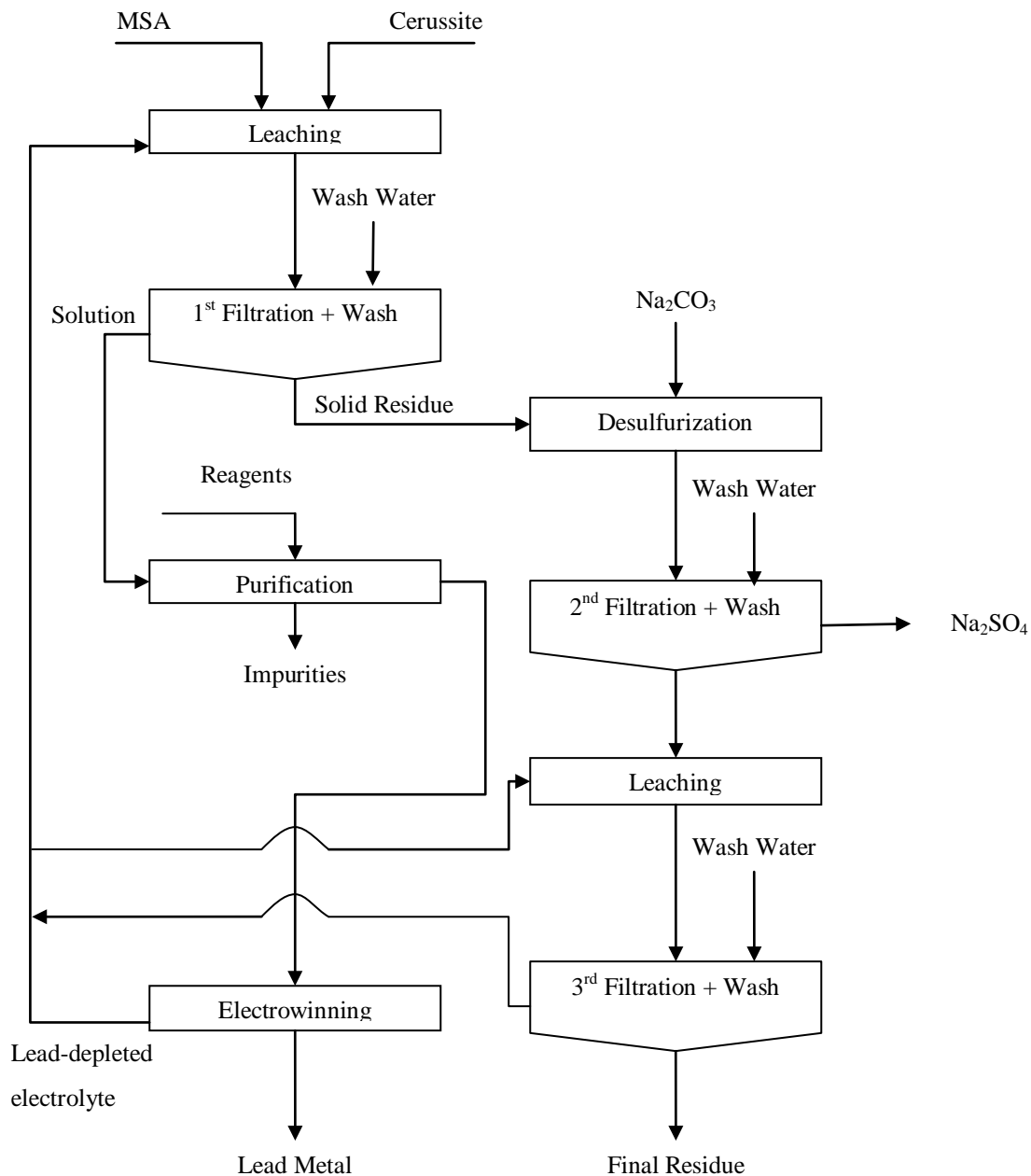

Figure 35   Proposed flowsheet for lead recovery from cerussite concentrate in MSA based solution

6 Chapter: Conclusions

The following overall conclusion can be summarized from this work:

(1) Methane sulfonic acid is very feasible to treat cerussite concentrate at ambient conditions; the kinetics process is fast and can be completed during a very short time (600s) for most experiments in this study. Sufficient stirring speed, higher temperature, finer particle size and higher MSA concentration can significantly increase the kinetics process. Solid concentration in the range from 20g/L to 200g/L does not affect the final lead extraction. At the solid concentration of 200g/L, the lead content in the solution is around 100g/L, which is very competitive to that in the Betts Process for lead electrorefining.

(2) The remaining lead in the leached residue is mainly as anglesite, accounting for approximately 15% of the total initial lead content. This part of the lead in the residue can be recovered by the desulfurization process through transforming $PbSO_4$ to $PbCO_3$, followed by MSA re-leaching treatment. The total lead extraction via a "Leaching-Desulfurization-Washing-Leaching" route is about 98%.

(3) The synergistic and individual uses of four selected additives including two lignin sulfonate salts and two glycol-type agents were first evaluated. Among the four additives, calcium lignin sulfonate (CL) displays the best inhibiting influence and most improves the morphology of the lead deposit; while the glycol-type additives (PEG and PPG) do not take effect in lead electrowinning process in MSA based medium.

(4) The operating parameters including temperature, concentration of lead ions and protons, current density are then investigated based on the previous study on optimizing the use of additives. It is observed that the operation parameters for Pb-MSA electrowinning process hold relatively wide varying ranges: 100~150g/L Pb(as $Pb(CH_3SO_3)_2$), 0.25~0.5M free MSA, current density 215.8~250A/m^2 and temperature (35~40)±1℃.

(5) The values of cathodic current efficiency and specific energy consumption for most electrolysis tests are around 98% and 0.53kWh/kg, respectively, which are very competitive to those obtained in fluosilicate or fluoborate medium.

(6) MSA based electrolyte is a promising alternative medium to directly treat lead-bearing oxide concentrate (i.e. cerussite). Therefore, based on the results obtained in this study, a proposed process with a simplified flowsheet is given.

7   Chapter: Recommendation for Future Work

(1) The fundamental study of cementation process by adding lead powder to purify the leachate should be conducted; cementation efficiency and the remaining impurity content in leachate should be evaluated.

(2) More effective additives should be selected and tested in lead electrowinning process with the incorporation of lignin sulfonate salts. Aloe extract is first proposed.

(3) The fundamental kinetics study of dissolution of galena concentrate in ferric methane sulfonate lixiviant should be undertaken to elucidate the characteristics and the mechanism.

(4) The behaviour of sulphide sulphur, which is probably oxidized to elemental sulphur and sulphate ions during the leaching process, should be investigated since sulphate reacts with lead ions to generating white precipitates of lead sulphate. This precipitation will result in lower lead extraction.

(5) The lead electrowinning from the electrolyte containing Pb-MSA, free acid and Fe^{+3}/Fe^{+2} redox couple should be studied in a divided cell with a diaphragm. Such a study would greatly assist in determining the commercial feasibility of the process.

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Appendices

Appendix A: Thermodynamic Calculations

For a redox reaction, OX+ne- = RED,   K= {RED}/{OX}{e-}^{n}

$$-n \cdot \log\{e^-\} = \log K + \log \frac{\{RED\}}{\{OX\}}$$

Define $-\log\{e^-\} = pe$

Therefore, $n \cdot pe = \log K + \log \frac{\{RED\}}{\{OX\}}$ **Equation 9**

Thermodynamic data used was from the Pankow[28]. The data used is complied in **Table 17**.

The sample calculations shown below are for the calculation.

Table 17   Thermodynamic date used (25°C/1 atm)

Reaction#	Reactions	logK
A-1	$PbO_{2(s)} + 4H^+ + 2e^- = 2H_2O + Pb^{+2}$	49.2
A-2	$Pb^{+2} + 2e^- = Pb_{(s)}$	-4.26
A-3	$PbO_{(s)} + 2H^+ = Pb^{+2} + H_2O$	12.7
A-4	$Pb^{+2} + H_2O = PbOH^+ + H^+$	-7.7
A-5	$PbOH^+ + H_2O = Pb(OH)_2 + H^+$	-9.4
A-6	$Pb(OH)_2 + H_2O = Pb(OH)_3^- + H^+$	-11.0
A-7	$PbCO_{3(s)} = Pb^{+2} + CO_3^{-2}$	-12.8
A-8	$Pb_3(CO_3)_2(OH)_{2(s)} + 2H^+ = 3Pb^{+2} + 2CO_3^{-2} + 2H_2O$	-18.8
A-9	$H_2CO_3 = H^+ + HCO_3^-$	-6.35
A-10	$HCO_3 = H^+ + CO_3^{-2}$	-10.33
A-11	$H^+ + e^- = \frac{1}{2} H_{2(g)}$	0
A-12	$\frac{1}{4} O_{2(g)} + H^+ + e- = \frac{1}{2} H_2O$	20.78

For example, to calculate the equilibrium constants for other reactions:

A-4

$Pb^{+2} + H_2O = Pb(OH)^+ + 3H^+$ $\log\beta_1$=-7.7

A-13

$Pb^{+2} + 2H_2O = Pb(OH)_2 + 3H^+$ $\log \beta_2$=(-7.7)+(-9.4)=-17.1

A-14

$Pb^{+2} + 3H_2O = Pb(OH)_3^- + 3H^+$ $\log \beta_3$=(-7.7)+(-9.4)+(-11.0)=-28.1

For total lead content Pb_T,

$$[Pb^{+2}]+[PbOH^+]+[Pb(OH)_2]+[Pb(OH)_3^-]=Pb_T$$

Refer to the **Reaction A-4**, **A-13 and A-14**,

$$[Pb^{+2}]\left(1+\frac{\beta_1}{[H+]}+\frac{\beta_2}{[H+]^2}+\frac{\beta_3}{[H+]^3}\right)=Pb_T \qquad \text{Equation 10}$$

Define $1+\dfrac{\beta_1}{[H+]}+\dfrac{\beta_2}{[H+]^2}+\dfrac{\beta_3}{[H+]^3}=Q$, thus $[Pb^{+2}]Q=Pb_T$

A.1 Hydrolysis Reactions

For PbO, refer to the **Reaction A-3**, $[Pb^{+2}]=10^{12.7}[H^+]^2$

$$\log[Pb^{+2}]=12.7-2\,pH \qquad \text{Equation 11}$$

For PbCO$_3$, refer to the **Reaction A-7**, $[Pb^{+2}]=10^{-12.8}/[CO_3^{-2}]=10^{-12.8}/\left(\alpha_2 C_T\right)$

$$\log[Pb^{+2}]=-12.8-\log\alpha_2-\log C_T \qquad \text{Equation 12}$$

where, $\alpha_2=\dfrac{1}{\dfrac{[H^+]^2}{K_1 K_2}+\dfrac{[H^+]}{K_2}+1}$, $\qquad K_1=10^{-6.35},\ K_2=10^{-10.33}$

For Pb$_3$(CO$_3$)$_2$(OH)$_2$, refer to the **Reaction A-8**,

$$[Pb^{+2}]=\left(10^{-12.8}[H^+]^2/[CO_3^{-2}]^2\right)^{1/3}=\left(10^{-12.8}[H^+]^2/\left(\alpha_2 C_T\right)^2\right)^{1/3}$$

$$\log[Pb^{+2}]=-6.27-\frac{2}{3}pH-\frac{2}{3}\log\alpha_2-\frac{2}{3}\log C_T \qquad \text{Equation 13}$$

According to the **Equation 10~Equation 13** to indentify the Pb(II) species and the transition pH value in the pe-pH diagram. The thermo-stable species of Pb(II) were determined to be Pb^{+2}, $PbCO^3$, Pb$_3$(CO$_3$)$_2$(OH)$_2$, PbO, Pb(OH)$_3^-$.

A.2 Half Reactions

For PbO$_2$/Solution boundary, for example PbO$_2$/Pb^{+2}:

Refer to **Reaction A-1**, **Equation 9 and Equation 10**,

$$2\,pe=49.2-\log Pb_T+\log Q-4\,pH$$

For PbO$_2$/Solid boundary, for example PbO$_2$/PbCO$_3$:

Refer to **Reaction A-1**, **Reaction A-7**, **Equation 9 and Equation 10**

$$2pe = 62.0 - \log \alpha_2 - \log C_T - 4pH$$

For Solution/Pb boundary, for example Pb^{+2}/Pb:

Refer to **Reaction A-2**, **Equation 9 and Equation 10**,

$$2pe = -4.26 + \log Pb_T - \log Q$$

For Solid/Pb boundary, for example PbCO$_3$/Pb:

Refer to **Reaction A-2**, **Reaction A-7**, **Equation 9 and Equation 10**

$$2pe = 62.0 - \log \alpha_2 - \log C_T - 4pH$$

A.3   Water Lines

Hydrogen line:

For $p_{H_2} = 1atm$, $pe = -pH$

Oxygen line:

For $p_{O_2} = 1atm$, $pe = 20.78 - pH$

Appendix B: Lead Content Distribution

To determine the lead content in different lead-bearing compounds from cerussite concentrate (-150+75um), the mineral phase composition and specific element contents are required and also can be analyzed by XRD and ICP-ES, respectively (See **Table 5**, **Table 6** and **Table 7**).

As can be seen from **Table 5**, lead compounds include carbonate, sulphate, hydroxide and their mixture (i.e. susannite and leadhillite), as well as sulfide. Each lead ion is associated with one carbonate ion, or one sulphate ions, or two hydroxide ions, or one sulfide ion. Meanwhile sulphur simply comes from sulfide and sulphate. Based on these facts, the lead content distribution can be figured out.

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B.1   Lead Content in Sulphate and Sulfide:

The sulphate content (m_{SO_4}) in the cerussite concentrate was tested 4.42%; the sulphur

content ($m_{S(VI)}$) from sulphate was calculated as following:

$$m_{S(VI)} = \frac{M_S}{M_S + 4 \times M_O} \times m_{SO_4} = \frac{32.26}{32.06 + 4 \times 15.999} \times 4.42\% = 1.475\%$$

The total sulphur content in cerussite concentrate ($m_{S(total)}$) was 1.53%. The sulphur content

from sulfide ($m_{S(II)}$) was obtained:

$$m_{S(II)} = m_{S(total)} - m_{S(VI)} = 1.53\% - 1.475\% = 0.055\%$$

Then the lead content in sulphate and sulfide can be calculated:

$$m_{Pb-S(VI)} = \frac{M_{Pb}}{M_S} \times m_{S(VI)} = \frac{207.20}{32.06} \times 1.475\% = 9.533\%$$

$$m_{Pb-S(II)} = \frac{M_{Pb}}{M_S} \times m_{S(II)} = \frac{207.20}{32.06} \times 0.055\% = 0.355\%$$

B.2   Lead Content in Carbonate and Hydroxide

The inorganic carbon in the cerussite concentrate was in the form of CO_3^{2-}, and this part of

carbon was tested as CO_2 gas. The carbon content in CO_2 gas was:

$$m_C = \frac{M_C}{M_C + 2 \times M_O} \times m_{CO_2} = \frac{12}{12 + 2 \times 15.999} \times 11.81\% = 3.221\%$$

The lead content associated with carbonate was:

$$m_{Pb-C} = \frac{M_{Pb}}{M_C} \times m_C = \frac{207.20}{12.00} \times 3.221\% = 55.617\%$$

The total lead content in cerussite concentrate with specific particle size range (-150+75um)

($m_{Pb(total)}$) was 67.12%. The lead content in hydroxide was obtained:

$$m_{Pb-OH} = m_{Pb(total)} - m_{Pb-C} - m_{Pb-S(II)} - m_{Pb-S(VI)} = 67.12\% - 55.617\% - 0.355\% - 9.533\% = 1.615\%$$

B.3   Lead Distribution

$$p_{Pb-S(VI)} = \frac{m_{Pb-S(VI)}}{m_{Pb(total)}} \times 100\% = \frac{9.533\%}{67.12\%} \times 100\% = 14.20\%$$

$$p_{Pb-S(II)} = \frac{m_{Pb-S(II)}}{m_{Pb(total)}} \times 100\% = \frac{0.355\%}{67.12\%} \times 100\% = 0.53\%$$

$$p_{Pb-C} = \frac{m_{Pb-C}}{m_{Pb(total)}} \times 100\% = \frac{55.617\%}{67.12\%} \times 100\% = 82.86\%$$

$$p_{Pb-OH} = \frac{m_{Pb-OH}}{m_{Pb(total)}} \times 100\% = \frac{1.615\%}{67.12\%} \times 100\% = 2.41\%$$

The lead content distribution was summarized in **Table 8**.