

**A NOVEL METHOD FOR METAL RECOVERY FROM  
ZINC & LEAD SLAGS**

**by**

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**We accept this thesis as conforming  
to the required standard**

**THE UNIVERSITY OF BRITISH COLUMBIA**

**June 2003**

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## ABSTRACT

**Conventional zinc fuming from lead blast furnace slags cannot continue when zinc and lead contents are below 1.5-2.5 wt.% and 0.1-0.5 wt.% respectively, because of solid iron formation, which also causes the formation of accretions, foaming of slag, and contamination of the fume. A new method, electroreduction, was developed in a previous study to recover the heavy metals zinc, lead, indium and germanium from final zinc fumer slag. A series of experiments was also conducted in this study using two types of fumer slag from COMINCO. Zinc content was 4.5wt% in one slag and 1.5wt% in another slag. Experimental data indicated that about 50% of the zinc and most of the lead could be removed from both slags by 90 minute of electrorefining.**

**Following the work on the fumer slags, a study was conducted on the potential to reduce lead and zinc directly from COMINCO's Kivcet slag (containing about 16 wt% zinc and 10 wt% lead) and potentially obviate the need for slag fuming. Metal recovery from the Kivcet slag was examined using the three methods used for the fumer slag study: holding at temperature to allow the divalent iron to reduce the metal ions into the gas phase; equilibration with a copper "getter"; and electroreduction into a liquid copper cathode using a graphite anode.**

**The presence of metallic lead and carbon in the Kivcet slag has a significant influence on the recovery of metal from the slag in subsequent processing. Holding of the slag at temperature permitted the recovery of much of the metallic lead as vapor and some small recovery of zinc as fume. When copper was used as a getter, more zinc and lead were recovered. In electrorefining, lead recovery was much higher than that in equilibrating with copper, but there was no obvious enhancement in zinc recovery. A series of experiments were also conducted in which the Kivcet slag was treated to remove some of the zinc and the lead and then was electro-refined three times. Zinc and lead contents in the final slag decreased to 5.9% and 0.3% respectively. Although most of the lead was recovered, further refining would still be required to capture the remaining zinc metal.**

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## 1. INTRODUCTION

Kivcet slag is produced from the Kivcet process for lead production. There are two stages in the Kivcet process. The first one is an oxidation stage in which fine coal and metal sulfides in the feed burn to form a hot sulphur dioxide gas and the sulfides of lead and zinc are converted to oxides. The oxides, silica and limestone form a semi-fused slag. In the second stage, the lead and zinc oxides are reduced by a "coke checker", which floats on top of the molten slag. Lead bullion and zinc vapor are produced.

In the Kivcet smelter of Trail Operations, Teck Cominco Limited (Trail, British Columbia, Canada), the metal oxides, especially zinc oxide, are not reduced completely in the second stage. Kivcet slag, a by-product of the Kivcet process, is an  $\text{FeO}(\text{Fe}_2\text{O}_3)\text{-CaO-SiO}_2$  system containing 15~20% zinc and 5~11% lead. Trace elements such as antimony, arsenic, indium and germanium are also found in the slag.

Generally, this zinc-bearing lead slag is treated by fuming with coal. Regardless of the fuming method employed, the tail slag from zinc fuming furnaces still contains about 3% zinc and some significant amounts of lead and the trace elements.

Conventional zinc fuming from lead blast furnace slags cannot continue when zinc and lead contents are below 1.5-2.5 wt.% and 0.1-0.5 wt.% respectively, because of solid iron formation, which also causes the formation of accretions, foaming of slag, and contamination of the fume.<sup>1</sup> A new method, electrorefining, was developed in a previous study by Fengxiang He, under the supervision of Professor Ray Meadowcroft, to recover metals from the tail slag.<sup>2</sup> Robert Olson also did some experimental work.<sup>3</sup> A series of experiments were

also conducted in this research with two kinds of fumer slag from COMICO. The experimental data indicated that approximately 50 percent of the zinc and most of the lead in the slag could be recovered by 90 minute of electrorefining.

This present work was designed to determine what would happen when Kivcet slag, containing much higher contents of zinc and lead than the fumer slag, is treated using the same processes. The slag is very similar in many respects to the fumer slag previously tested, but because of the much higher lead and zinc contents, its conductance should be larger than that of the fumer slag. The higher contents of ZnO and PbO also make Kivcet slag more corrosive.

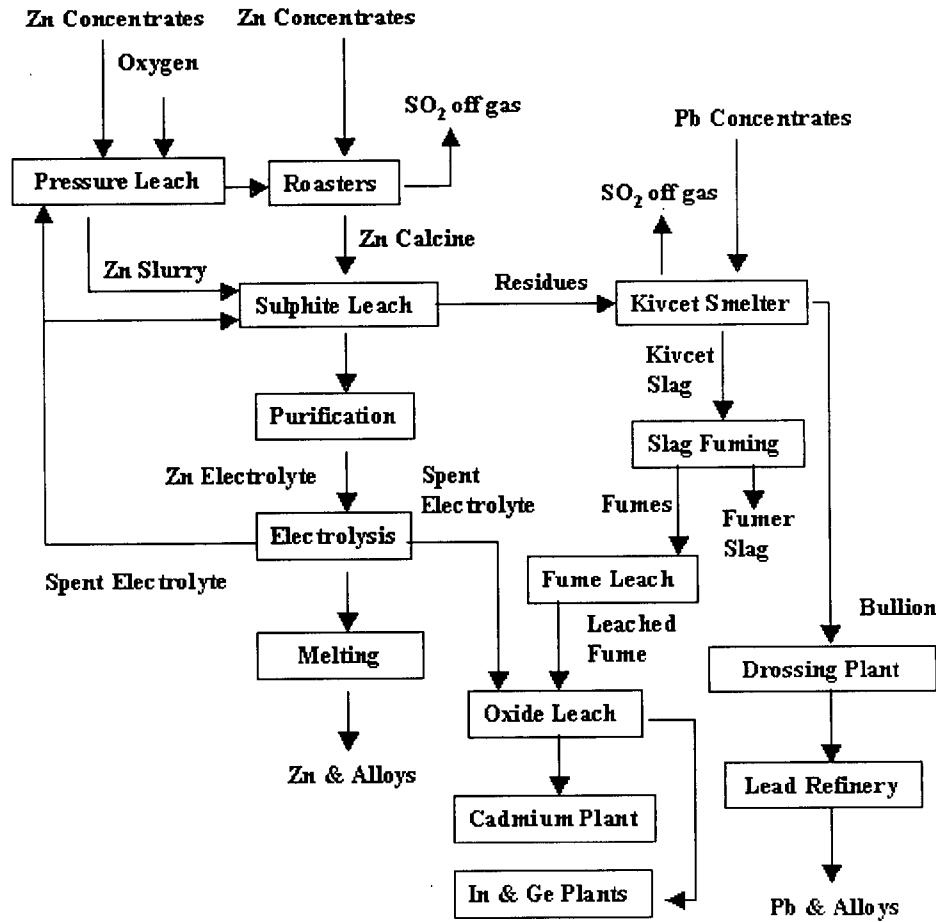
## 2. THE SLAGS FROM COMINCO

COMINCO's integrated lead-zinc smelting complex is located at Trail, British Columbia, Canada. The complex is composed of Zinc Operations and Lead Operations (see Fig. 1). Zinc Operations is a typical roast-leach-electrowinning process. Lead Operations comprises a Kivcet flash smelter and a water-jacketed slag fuming process. Leach residues from the zinc plant, as well as lead concentrate, is treated in the Kivcet smelter and lead bullion is produced. The slag fuming process is employed to recover zinc from Kivcet slag, the by-product of the Kivcet smelter. The fume generated is collected and returned to the zinc plant.

COMINCO's Kivcet flash smelter and slag fuming process was completed in 1997 and started up. The smelter has a lead capacity of 120,000 tonnes per year. In addition, zinc production capacity has increased to 290,000 tonnes per year from 272,000 tonnes. The output of tailing slag from the slag fuming furnaces is 500-600 tonnes per day.<sup>4, 5, 6, 7</sup>

The Kivcet slag and the fumer slag in this study were water quenched at about 1200 °C to a particle size of less than 4 mm. According to the contents of zinc and lead, the tailing slag can be divided into two types: (1) high residue fumer slag, which is under-treated in the fumer and contains about 4.5% zinc, and (2) low residue fumer slag, which is over-treated and contains approximately 1.5% zinc. Table 1 shows slag analysis data (average of two separate samples of each slag) determined by IPL (International Plasma Lab Limited, Vancouver, B.C, Canada). The analyses shown are typical of the analytical deviation that was found in all of the experimental work. It can be seen that the slags is a FeO(Fe<sub>2</sub>O<sub>3</sub>)-CaO-SiO<sub>2</sub> system containing some significant amounts of zinc and lead. Basicity (B=CaO%/(CaO%+SiO<sub>2</sub>)) of the slags is 0.36~0.4. The Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio is about 2.6 in Kivcet slag, 4 in high residue

fumer slag, and 48 in low residue fumer slag. Trace elements such as antimony, arsenic, indium and germanium are also found in the slags.



**Fig. 1: The flow sheet of the Cominco's integrated zinc-lead operations**

**Table 1: Analysis of the slags from Cominco**

Slag Type	Zn (%)	Pb (%)	Sb (ppm)	As (ppm)	Ge (ppm)	In (ppm)	Cu (ppm)	Fe <sup>2+</sup> (%)	Fe <sup>3+</sup> (%)	SiO <sub>2</sub> (%)	CaO (%)	Al <sub>2</sub> O <sub>3</sub> (%)
KIV	15.8	10.2	3275	3027	162	366	3368	17.4	6.7	21.8	13.0	1.6
HRFS	4.5	1.1	1919	210	59	41	3803	28.3	6.9	30.4	18.6	2.8
LRFS	1.5	0.02	603	275	34	<5	4037	30.8	0.6	30.0	19.5	3.4

Legend: KIV-Kivcet slag, HRFS-High residue fumer slag, LRFS-Low residue fumer slag

High residue fumer slag was characterized using SEM, EDX and XRD in a previous study.<sup>2</sup> The results indicated that the slag particles were heterogeneous and the maximum dimension of most of them was less than 3 mm. The particles were very porous because of the water-quench operation. The slag was in a glassy state. Most of the iron was in the slag matrix as ferrous iron. Some of the iron existed in dendritic magnetite. There was also a little iron present as alloy.

Kivcet slag is very similar to fumer slag in many respects. But, because of the much higher lead and zinc contents, the conductance of Kivcet slag should be larger than that of fumer slag. The higher contents of ZnO and PbO also make Kivcet slag somewhat more corrosive.

Since the slag had been in contact with lead bullion and coke in the Kivcet smelter, an attempt was made to determine if the Kivcet slag sample contained metallic lead and carbon. Scanning Electron Microscopy (SEM) analysis indicated that there were numerous bright spots in most of the slag particles. Black spots and cracks were also found. Fig. 2 shows a SEM image of a slag particle that contains a number of bright spots, a black spot and some

cracks. A SEM image of a bright spot is shown in Fig. 3. Two bright spots were analyzed with EDX. The results shown in Fig. 4 and Fig. 5 indicated that the bright spots contained about 80% lead with some arsenic, antimony, zinc, iron and copper, compared to a matrix reading of from 1.5% to 12% lead. Although the analysis of the bright spots could indicate lead oxide, FACT<sup>8</sup> analysis suggests that any metal oxide would be present as the silicate in this very acidic slag. The bright spots are assumed therefore to be metallic lead alloy containing small amounts of the other metals. Previous analytical work at Cominco suggests that up to half of the lead in the slag is present as metallic lead.<sup>7</sup> Fig. 6 shows a SEM image of a black spot. EDX analysis shown in Fig. 7, Fig. 8, Fig. 9 and Fig. 10 indicated that the black spot contained about 98% carbon and some zinc, lead, copper and iron.

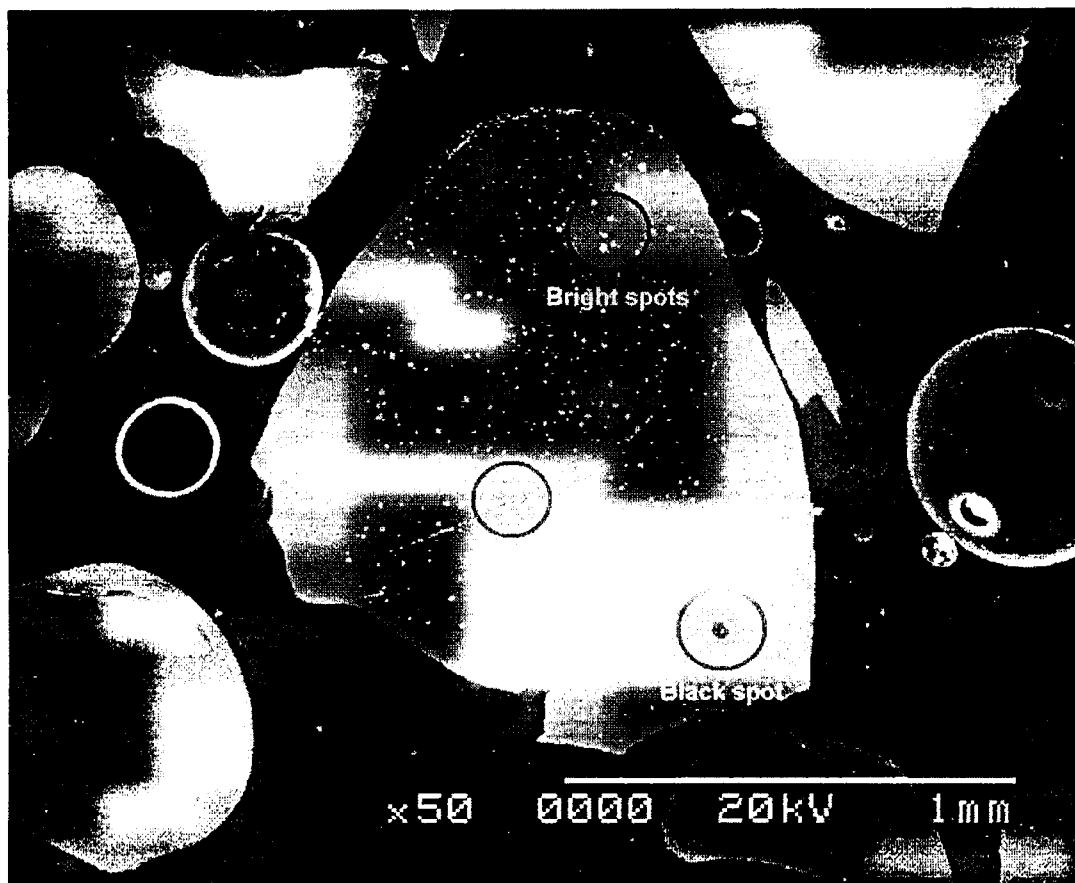
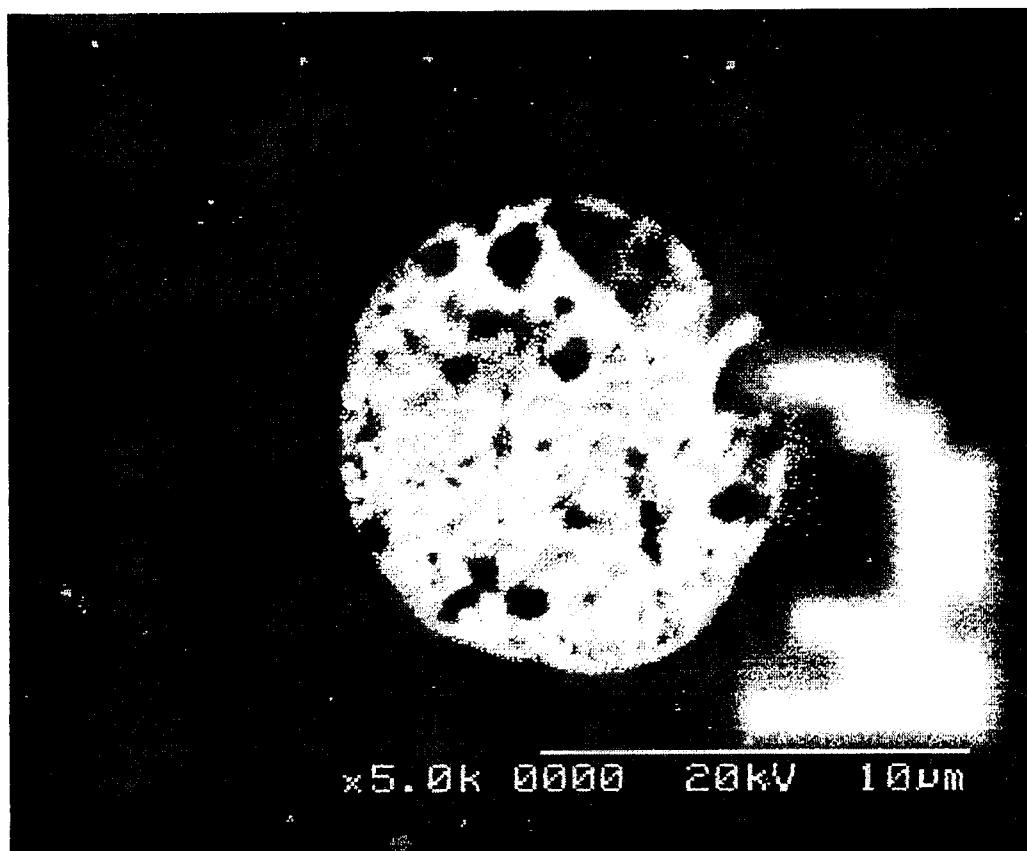
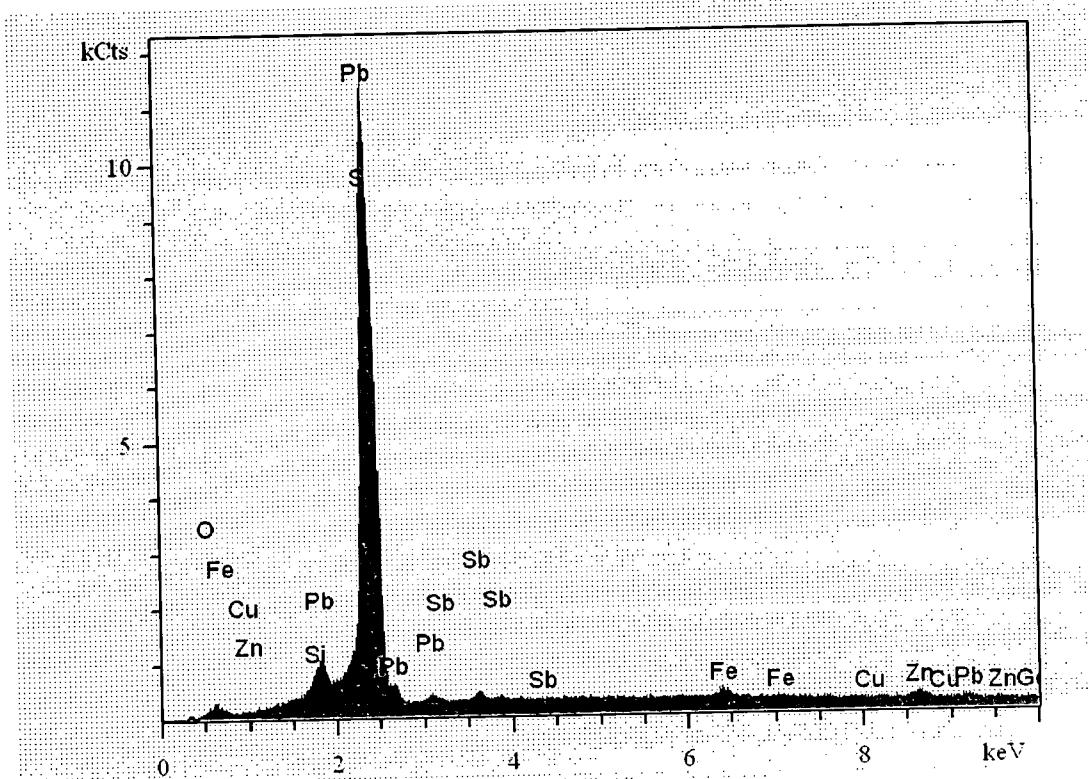


Fig. 2: SEM image of a Kivcet slag particle

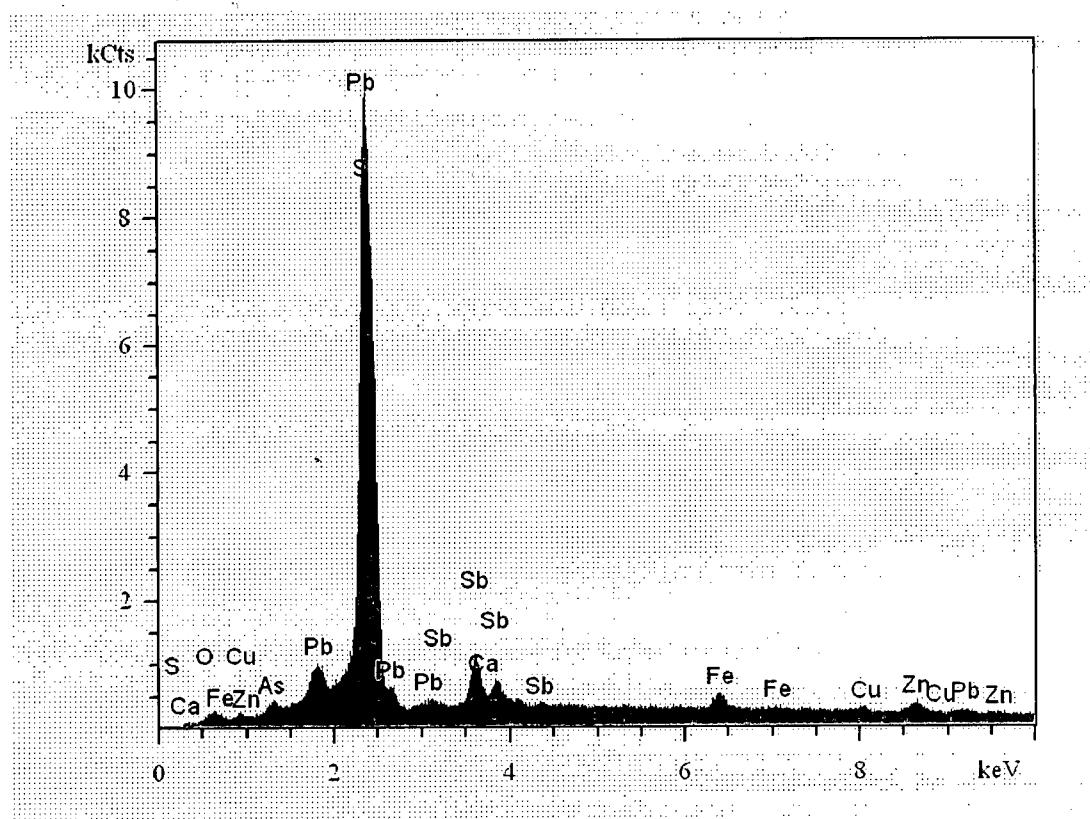


**Fig. 3: SEM image of a bright spot**



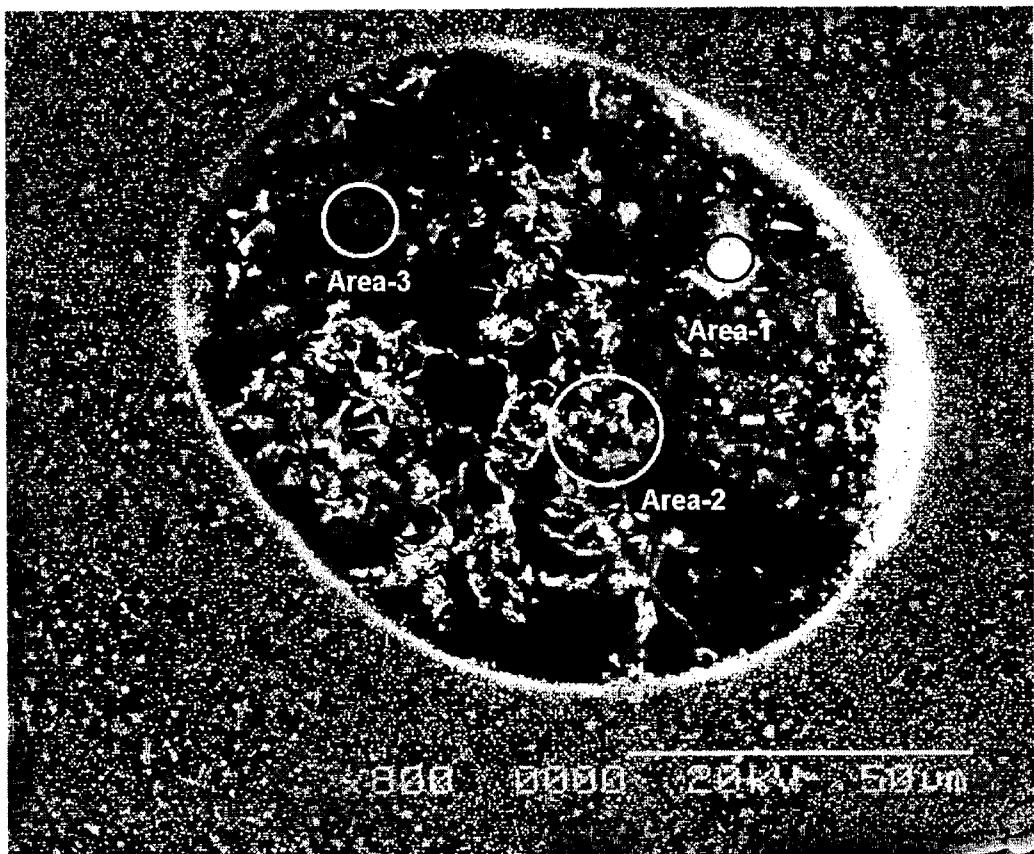
	Concentration
Oxygen	9.67 wt%
Silicon	0.13 wt%
Sulfur	0.00 wt%
Iron	1.28 wt%
Copper	0.00 wt%
Zinc	2.66 wt%
Germanium	2.80 wt%
Arsenic	2.26 wt%
Antimony	0.97 wt%
Lead	80.24 wt%

Fig. 4: EDX analysis of one bright spot

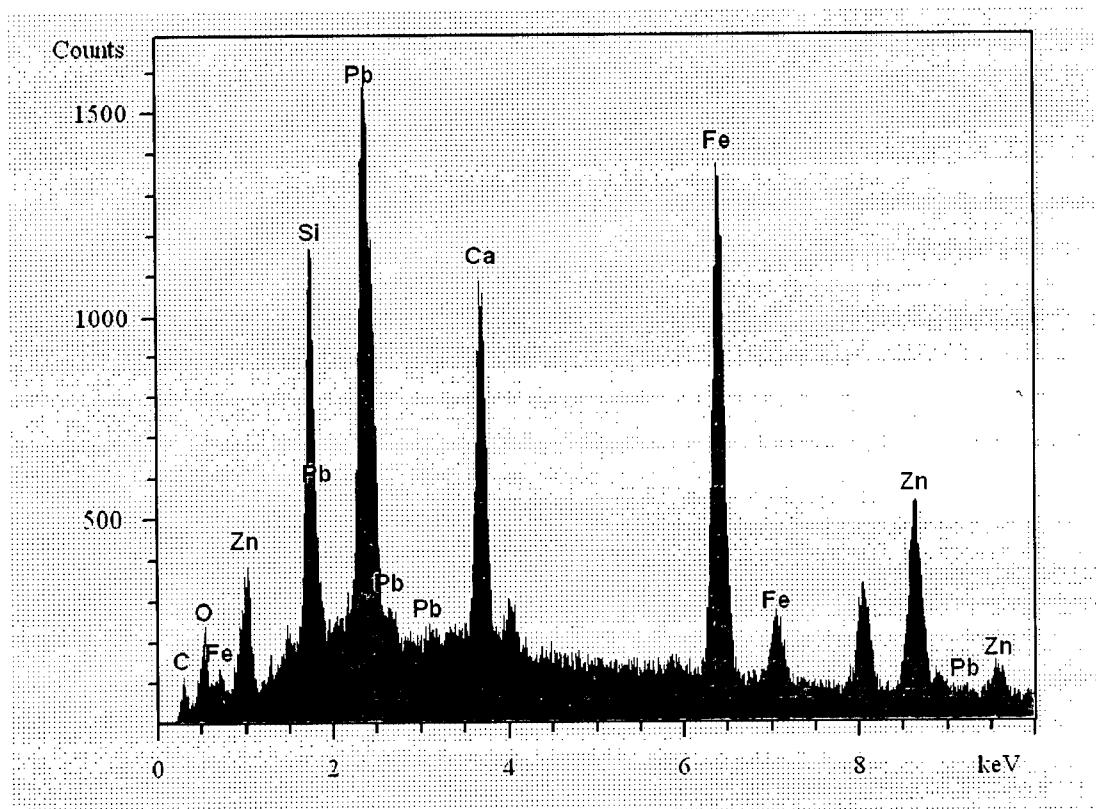


	Concentration
Oxygen	10.06 wt%
Sulfur	0.00 wt%
Calcium	0.25 wt%
Iron	1.52 wt%
Copper	1.25 wt%
Zinc	2.68 wt%
Arsenic	3.43 wt%
Antimony	6.27 wt%
Lead	74.53 wt%

**Fig. 5: EDX analysis of another bright spot**

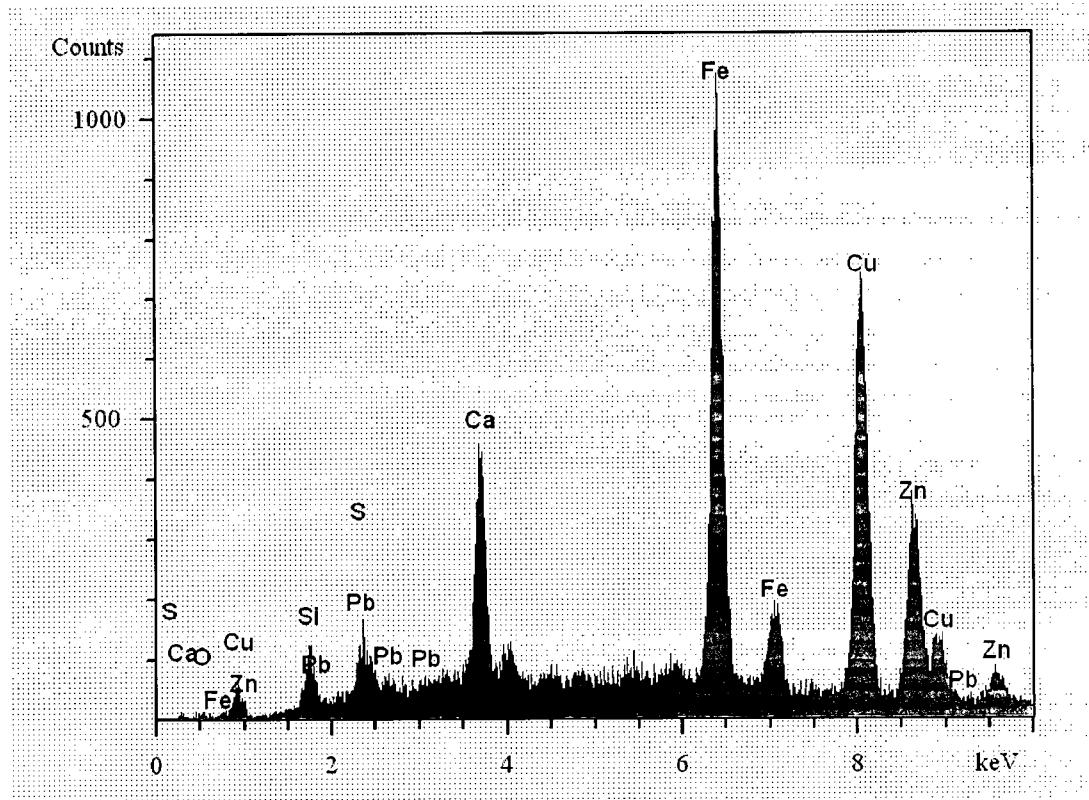


**Fig. 6: SEM image of a black spot**



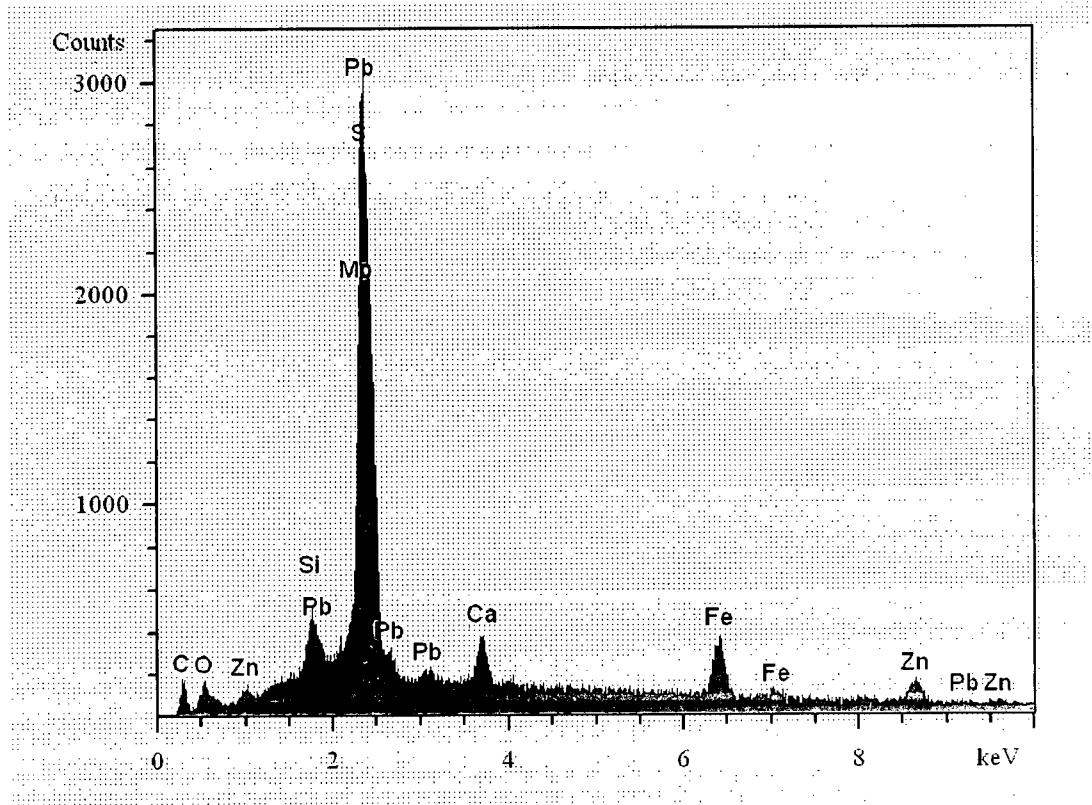
	Concentration
Carbon	98.31 wt%
Oxygen	0.67 wt%
Silicon	0.02 wt%
Calcium	0.06 wt%
Iron	0.22 wt%
Zinc	0.21 wt%
Lead	0.51 wt%

**Fig. 7: Overall analysis of the black spot (with EDX)**



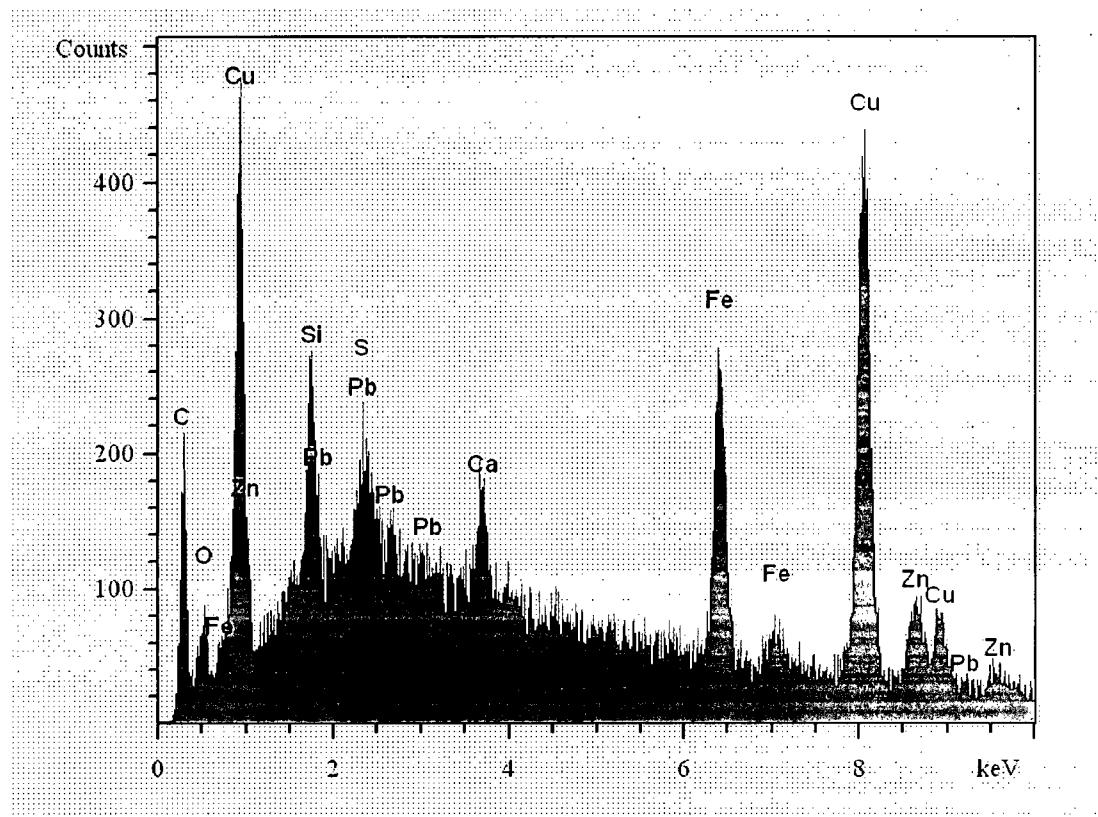
	Concentration
Oxygen	1.68 wt%
Silicon	0.40 wt%
Sulfur	0.00 wt%
Calcium	4.02 wt%
Iron	23.51 wt%
Copper	34.29 wt%
Zinc	20.00 wt%
Lead	16.10 wt%

**Fig. 8: EDX analysis of Area-1 in the black spot**



	Concentration
Carbon	99.49 wt%
Oxygen	0.32 wt%
Silicon	0.00 wt%
Sulfur	0.00 wt%
Calcium	0.01 wt%
Iron	0.03 wt%
Zinc	0.04 wt%
Molybdenum	0.00 wt%
Lead	0.10 wt%

**Fig. 9: EDX analysis of Area-2 in the black spot**



	Concentration
Carbon	99.69 wt%
Oxygen	0.15 wt%
Silicon	0.00 wt%
Sulfur	0.00 wt%
Calcium	0.00 wt%
Iron	0.02 wt%
Copper	0.07 wt%
Zinc	0.02 wt%
Lead	0.04 wt%

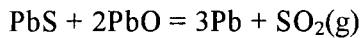
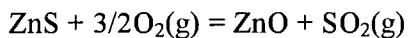
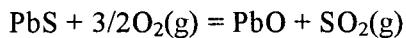
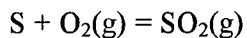
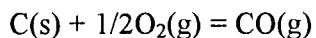
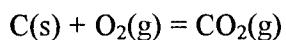
**Fig. 10:** EDX analysis of Area-3 in the black spot

### **3. LITERATURE REVIEW**

#### **3.1. THE KIVCET PROCESS**

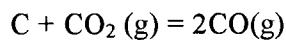
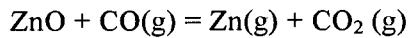
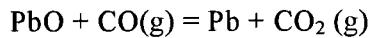
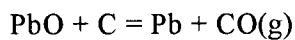
The Kivcet process, also called the Oxygen Flash Cyclone Electro Thermal Process, was developed by VNIITSVETMET Institute in Ust-Kamenogorsk, Kazakhstan, under the supervision of Professor A. Sychev. The first commercial Kivcet unit was installed and operated at the Ust-Kamenogorsk Lead-Zinc Combine (now Kazzinc J. St. Co.) in 1985.<sup>9</sup>

There are two stages in the Kivcet process. In the first stage, lead sulphide concentrate, zinc plant residues, recycle dust, silica, limestone, fine coal and moderately coarse coke are injected at the top of the reaction shaft along with oxygen. The sulfides of lead, zinc and other metals are converted to metal oxides while heating in a fine coal flame. The oxides, silica and limestone form a semi-fused slag, while the gas reaches up to 15% sulphur dioxide. Reactions in this stage are as follows:



In the second stage, the lead and zinc oxides are reduced by a "coke checker", which floats on top of the molten slag. The lead oxide is converted to metal as bullion and zinc gas is

produced. The following reactions occur:



The bullion passes through the molten slag layer under the coke checker and enters the electrothermal settler together with the zinc-bearing slag. In the electrothermal settler, the heat from the graphite electrodes keeps the bullion-slag bath in a molten state. The lighter slag continues to float to the surface and the heavier bullion sinks to the bottom of the settler. This separation enables them to be tapped separately from the furnace.

The bullion produced in the Kivcet furnace is treated further to remove copper, arsenic and antimony. It is then ready for electro-refining.

The slag from the Kivcet furnace is treated in a slag fuming furnace where the zinc in the slag vaporizes to form a zinc oxide fume, which is further treated in a oxide leaching plant to recover the zinc, indium, germanium and cadmium.

The hot sulphur dioxide gas (about 1200 °C) from the reaction shaft is cooled in the waste heat boilers and then passes through the electrostatic precipitator. The final cleaned sulphur dioxide gas is piped to sulphuric acid plants.

### 3.2. OTHER PYROMETALLURGICAL LEAD AND ZINC PROCESSES

Other pyrometallurgical lead and zinc processes include the lead blast furnace (LBF) process,<sup>10</sup> the Imperial Smelting Process (ISP),<sup>1, 11</sup> and the QSL process.<sup>12</sup>

The lead blast furnace is similar to the blast furnace for iron production. Solid sinter, heated coke and refinery skims are fed at the top of the furnace. Preheated air is blown in at the bottom. Molten lead and slag are tapped from the blast furnace into a settler where they are separated. Chemical composition of lead blast furnace slag is shown in Table 2.<sup>10</sup> In the Imperial Smelting Process, the charge is a mixture of cold or warm sinter and hot coke. Molten lead and zinc vapor are produced. The zinc vapor is collected with condensers containing a liquid lead pool. Table 3<sup>1</sup> shows the composition of the slag from the Imperial Smelting Process. The QSL smelter can be used to treat a wide range of lead-bearing materials, such as concentrates, battery paste, slag, Pb/Ag residues, scrap and lead glasses. The main product is lead bullion. The final slag is iron silicate containing about 2% lead.

The slags from the above processes are very similar to the Kivcet slag. If these slags are treated with the methods in this study, the results should be similar to that of the Kivcet slag treatment.

**Table 2: Analysis of typical LBF slag**

Element	Content (wt%)
SiO <sub>2</sub>	27.0
CaO	15.0
Al <sub>2</sub> O <sub>3</sub>	3.0
MgO	5.0
Pb	2.2
Zn	6.0
Fe	24.0
Cu	0.3

**Table 3: Analysis of typical ISP slag**

Element	Content (wt%)
FeO	30 ~ 42
SiO <sub>2</sub>	16 ~ 21
Al <sub>2</sub> O <sub>3</sub>	5 ~ 10
ZnO	5 ~ 10
PbO	0.6 ~ 1
S	1 ~ 3

### 3.3. PYROMETALLURGICAL PROCESSES FOR ZINC-BEARING SLAGS AND RESIDUES

Zinc-bearing slag from non-ferrous smelters, such as lead blast furnaces and Kivcet smelters, is usually treated by a fuming process because both melting and boiling temperatures of zinc are very low, only 419.5 °C and 907 °C respectively. In addition, lead melts at 327 °C and boils at 1740 °C. The earliest experimental work on slag fuming was conducted in Australia by the Sulphide Corporation at Cockle Creek between 1906 and 1920.<sup>13</sup> Commercial development of the process was made by the Anaconda Copper Mining Company and the Consolidated Mining and Smelting Co. in the 1920's.<sup>14, 15</sup> The first slag-fuming furnace was installed at East Helena, U.S.A. in 1927 by the Anaconda Copper Mining Company.

At present, there are many commercial slag fuming processes in the world such as Water-jacketed fuming process,<sup>16, 17, 18</sup> Enviroplas process,<sup>19, 20</sup> Ausmelt process,<sup>19</sup> and Waelz kiln fuming process.<sup>21</sup> In all the above processes, carbon or coal is used as reductant. Zinc and lead oxides are reduced to metallic zinc and lead, which vaporize to fume. The main difference among the above processes lies in heat transfer and furnace structure. Detailed information on the above slag fuming processes has been described in Fengxiang He's thesis.<sup>2</sup>

### **3.4. PROPERTIES OF ZINC-LEAD SLAGS**

#### **3.4.1. Activities of ZnO and FeO in Zinc-bearing Slags**

Many researchers have studied activities of ZnO and FeO in zinc-bearing slag with several methods.<sup>22, 23, 24, 25, 26</sup> Studies also have been done on the activity of zinc in the molten Cu-Zn-Fe ternary system, activity measurements in liquid Cu-Zn-X (X = Pb, Ag, and Au) ternary alloys and the equilibrium between CaO-SiO<sub>2</sub>-FeO<sub>x</sub> slag and Cu-Zn-Fe (iron-saturated) alloy.<sup>27, 28</sup> The results of these studies have been described in Fengxiang He's thesis.<sup>2</sup> In summary, the activity coefficient of ZnO in CaO-SiO<sub>2</sub>-“FeO” slag increases with increasing slag basicity (%CaO/(%CaO+% SiO<sub>2</sub>)). It is nearly independent of zinc concentration.

When iron oxides and zinc oxide coexist in the slag, the activity coefficient of FeO depends on the mole fractions in the slag. It also increases with increasing slag basicity. For zinc blast furnace slag, FeO starts to be reduced when the concentration of ZnO is less than 3 mol%.<sup>1</sup>

### 3.4.2. Conductivity of Zinc-Lead Slags

Conductivity of zinc-lead slags is related closely to the specific conductivities of pure oxides and the ionic nature of the FeO-CaO-SiO<sub>2</sub> system. It has been described in Fengxiang He's thesis. The results are summarized here.

The oxides can be divided into covalent and ionic groups. The important covalent oxides include SiO<sub>2</sub>, GeO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub>, P<sub>2</sub>O<sub>5</sub> and As<sub>2</sub>O<sub>3</sub>. In these oxides, oxygen is bonded so as to form three-dimensional networks. In the liquid state, these oxides have very high viscosities of  $10^5\text{--}10^7$  cP and very low specific conductances of  $10^{-5}\text{--}10^{-6}$  ohm<sup>-1</sup>cm<sup>-1</sup>. The remaining metal oxides are more or less ionic. When liquid, they have viscosities of 10~50 cP and specific conductances greater than 10 ohm<sup>-1</sup>cm<sup>-1</sup>. Table 4<sup>29,30</sup> shows specific conductances of some oxides near their melting points.

**Table 4: Specific conductances of some oxides near their melting points**

Oxide	FeO	Cr <sub>2</sub> O <sub>3</sub>	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>	ZrO <sub>2</sub>	TiO <sub>2</sub>	PbO	SiO <sub>2</sub>
Melting point (°C)	1370	2275	2580	2800	2050	2500	1650	900	1710
Specific conductance (ohm <sup>-1</sup> cm <sup>-1</sup> )	122	65	40	35	15	15	10	0.9	$10^{-5}$

The ionic nature of the “FeO”-CaO-SiO<sub>2</sub> system with CaO/(CaO+SiO<sub>2</sub>) ratios of 0.2~0.6 has been studied by Dickson and Dismukes.<sup>31</sup> The system conducts current by both ionic and nonionic mechanisms. Ionic conductance increases with increasing silica content. When FeO concentration is increased, both ionic and nonionic conductances increase. The increase in

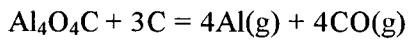
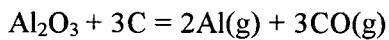
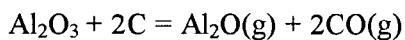
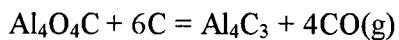
ionic conductance is consistent with the increase in concentration of cations and ionic mobilities. The reason for the increase in nonionic conductance is p-type semi-conduction.

Anode current efficiency increases with decreasing FeO content because of the electrical conduction reactions ( $\text{Fe}^{++} - e = \text{Fe}^{+++}$  at the anode and  $\text{Fe}^{+++} + e = \text{Fe}^{++}$  at the cathode). When FeO concentration is less than 40wt%, anode current efficiency is more than 90%. It does not vary with temperature by any significant degree and gives a realistic measure of the degree of ionic conductance because the amount of oxygen gas produced at the anode is corresponded to the amount of metal produced at the cathode.

According to the above results on the specific conductivities of pure oxides and the ionic nature of the FeO-CaO-SiO<sub>2</sub> system, the total electrical conductances of the fumer slag and the Kivcet slag in this study are estimated to be approximately 0.5 ohm<sup>-1</sup>cm<sup>-1</sup> and 2.6 ohm<sup>-1</sup>cm<sup>-1</sup> respectively. The Kivcet slag has a higher electrical conductance because it contains higher contents of zinc and lead oxides. The ionic conductances in the three slags account for more than 90%.

### 3.5. THE HALL-HEROULT PROCESS

Carbon is usually used as reductant in pyrometallurgical processes for metal production. But aluminum cannot be produced by this method. When alumina reacts with carbon,  $\text{Al}_4\text{O}_4\text{C}$ , but not Al, is the primary product. All of the following reactions might occur:



H. Davy was the first person who attempted to decompose alumina electrolytically.<sup>32</sup> In 1807, he melted it with current from a battery. Some aluminum was reduced, but it alloyed with the iron leads. R. W. Bunsen and S. C. Deville produced aluminum electrolytically by using fused sodium-aluminum chloride, but it was not a practical process. The aluminum chloride was continually used up. It also volatilized from the molten salt. This resulted in an increase of sodium chloride content and thus raised the melting point of the electrolyte. Increasing the electrolyte temperature increased the volatilization losses.

Charles Martin Hall successfully solved the problem. On February 23, 1886, he electrolyzed a solution of alumina in molten cryolite ( $\text{Na}_3\text{AlF}_6$ ) and produced shining globules of aluminum at his home.<sup>32</sup> The key of his invention was the discovery of a fused electrolyte which dissolved alumina in substantial quantities and possessed a higher stability than the alumina.

In addition, his technique had other advantages such as a reasonably low melting point, a low operating voltage of about 6 volts, and a specific gravity low enough to permit pure aluminum to sink through the electrolyte and be protected.

Paul L. T. Heroult applied for and was granted a French patent on the electrolysis of alumina in cryolite on April 23, 1886. On April 15, 1887, he got another French patent on a different process, which only produced aluminum alloys.<sup>32</sup> Pure alumina in a carbon-lined furnace was fused electrothermally by heat from an electric current. A large carbon anode was suspended in the furnace. A layer of molten copper in the bottom of the furnace was used as cathode. Electrolytically reduced aluminum went into the molten copper to form an aluminum bronze alloy. The alloy could be tapped out of the bottom of the furnace. Copper and alumina were added at the top. Two years later, Heroult found that the furnace used for the aluminum bronze alloy could be employed in the alumina-cryolite process to produce pure alumina.

#### **4. OBJECTIVES**

The first purpose of this study is to reconfirm the feasibility of recovering the heavy metals Zn, Pb, In and Ge from final zinc fumer slags by an electrorefining technique which was developed in previous study. A series of experiments was conducted with two types of fumer slag from Cominco.

The second objective was to determine what would happen when Kivcet slag, containing much higher contents of zinc and lead than the fumer slags, is treated using the same processes. Kivcet slag is very similar in many respects to the fumer slag previously tested, but because of the much higher lead and zinc contents, its conductance should be higher than that of the fumer slag. The higher content of ZnO and PbO also made Kivcet slag more corrosive.

## 5. FACT CALCULATION ON THE KIVCET SLAG

The potential changes possible in this system were examined using thermodynamic calculations made with FACT software<sup>8</sup>. Table 5 shows the calculation results on 250 grams of Kivcet slag. Half of the lead in the original slag was assumed to be metallic. Carbon content was assumed to be 0.23%, a value which was derived from some of the subsequent experimental data.

At 1250 °C, when the system pressure was set to 1 atmosphere, all of the carbon was converted to 0.21 grams of CO and 1.80 grams of CO<sub>2</sub> at equilibrium, resulting in a CO pressure of 0.142 atmospheres and a CO<sub>2</sub> pressure of 0.773 atmospheres. About 0.19 grams of zinc and 0.32 grams of lead were also found in the gas phase, giving a zinc pressure of 0.056 atmospheres and lead pressure of 0.029 atmospheres. The activities of ZnO and PbO in the slag were 0.149 and 0.016 respectively. The metallic lead in the slag increased from 11.55 grams to 14.92 grams, indicating that very little vaporization of the liquid lead occurred and some lead oxide was reduced to liquid lead. The amount of FeO increased from 50.75 grams to 60.34 grams, while the weight of Fe<sub>2</sub>O<sub>3</sub> decreased from 21.75 grams to 11.09 grams. Some Fe<sub>2</sub>O<sub>3</sub> was reduced to FeO. Although the FeO/Fe<sub>2</sub>O<sub>3</sub> weight ratio was only about 5.4 at equilibrium, the ratio of FeO activity (0.498) to Fe<sub>2</sub>O<sub>3</sub> activity (0.014) was as high as 35.6, giving the divalent iron ion a reasonable reduction potential. These results suggest that there is considerable potential for the further loss of zinc and lead to the gas phase.

**Table 5: Results of FACT calculation on the Kivcet slag**

250g Kivcet Slag + Ar													
Gas phase					Liquid Slag					Liquid Lead			
Ar gram	Zn gram	Pb gram	CO gram	CO2 gram	ZnO activity	PbO activity	FeO activity	Fe <sub>2</sub> O <sub>3</sub> activity	Cu <sub>2</sub> O activity	Pb gram	Zn gram	Fe gram	Cu gram
0	0.19	0.32	0.21	1.80	0.149	0.016	0.498	0.014	0.000	14.92	0.01	0.00	0.19
40	2.64	6.84	0.15	1.88	0.137	0.023	0.471	0.017	0.000	4.40	0.00	0.00	0.06
80	3.71	10.38	0.12	1.93	0.131	0.024	0.452	0.021	0.000	0.00	0.00	0.00	0.00
120	4.18	11.03	0.10	1.97	0.127	0.022	0.435	0.024	0.000	0.00	0.00	0.00	0.00
160	4.54	11.47	0.08	1.99	0.124	0.020	0.423	0.027	0.000	0.00	0.00	0.00	0.00
200	4.83	11.82	0.07	2.01	0.122	0.019	0.413	0.030	0.000	0.00	0.00	0.00	0.00
250g Kivcet Slag + 200g Ar + 100g Crucible													
Gas phase					Liquid Slag					Liquid Lead			
Ar gram	Zn gram	Pb gram	CO gram	CO2 gram	ZnO activity	PbO activity	FeO activity	Fe <sub>2</sub> O <sub>3</sub> activity	Cu <sub>2</sub> O activity	Pb gram	Zn gram	Fe gram	Cu gram
200	1.15	4.31	0.04	2.06	0.057	0.014	0.238	0.019	0.000	0.00	0.00	0.00	0.00
250g Kivcet Slag + 200g Ar + 100g Crucible + 150g Copper													
Gas phase					Liquid Slag					Liquid Copper			
Ar gram	Zn gram	Pb gram	CO gram	CO2 gram	ZnO activity	PbO activity	FeO activity	Fe <sub>2</sub> O <sub>3</sub> activity	Cu <sub>2</sub> O activity	Pb gram	Zn gram	Fe gram	Cu gram
200	1.36	2.99	0.05	2.05	0.052	0.007	0.232	0.014	0.014	9.19	0.53	0.02	143.4

If argon was introduced into the above system at 1250 °C, the amount of metallic lead in the slag decreased sharply, while the weight of lead in the gas phase increased dramatically.

Activities of ZnO and FeO in the slag decreased, while Fe<sub>2</sub>O<sub>3</sub> activity increased with the loss of Zn to the gas phase. When the amount of argon in equilibrium with the slag was set to 200 grams, almost all of the carbon was converted to CO<sub>2</sub>. The amount of lead in the gas phase at 11.82 grams was very closed to that (11.55 grams) of metallic lead in the original slag. The amount of PbO at equilibrium was almost equal to that in the original slag. The activity of

ZnO dropped to 0.122 and 4.83 grams of zinc went into the gas phase. At the same time, FeO activity decreased to 0.413, while  $\text{Fe}_2\text{O}_3$  activity increased to 0.030. Clearly the divalent iron ion available in the slag can reduce zinc oxide. If the zinc and lead in the gas phase are removed continually, some zinc and lead in the slag can be recovered just by holding at temperature.

When a FACT analysis was done of slag heated to 1250 °C in a fireclay crucible (36%  $\text{Al}_2\text{O}_3$  and 57%  $\text{SiO}_2$ ), 100 grams of the crucible were assumed to dissolve into 250 grams of the slag. In this case, activities of all the above oxides decreased as the total weight of the slag increased. When 200 grams of argon was introduced into the system, only 1.15 grams of zinc and 4.31 grams of lead went into the gas phase at equilibrium. The amount of PbO in the slag increased from 12.40 grams to 20.20 grams and no metallic lead was present in the slag. The amount of FeO increased to 66.92 grams, while that of  $\text{Fe}_2\text{O}_3$  decreased to 3.78 grams. Apparently, some  $\text{Fe}_2\text{O}_3$  was reduced by metallic lead. Although the FeO/ $\text{Fe}_2\text{O}_3$  wt% ratio increased to 17.7, the ratio of FeO activity to  $\text{Fe}_2\text{O}_3$  activity decreased to 12.5 because the dissolved crucible increased the  $\text{Fe}_2\text{O}_3$  activity coefficient from 0.347 to 1.626, while it decreased the FeO activity coefficient from 1.695 to 1.149. Divalent iron ions lost some of their reduction potential. The activity coefficients of ZnO and PbO were also decreased from 0.617 and 0.348 to 0.384 and 0.221 respectively. The dissolved crucible had significant influence on the metal recovery. On a commercial scale, where the surface to volume ratio of the slag is much lower, the ratio of dissolved refractory in the slag should be much lower and the influence will be smaller.

In the FACT analysis of the above system equilibrated with 150 grams of copper, the amount of zinc in the gas phase increased to 1.36 grams, while that of lead decreased to 2.99 grams.

At the same time, about 0.53 grams of zinc and 9.19 grams of lead were recovered into the liquid copper. The amount of lead oxide at equilibrium was very close to that in the original slag. Most of the metallic lead went into the liquid copper. Using copper, a greater quantity of zinc and lead can potentially be removed from the slag. Some  $\text{Fe}_2\text{O}_3$  was reduced to  $\text{FeO}$  by copper. The weight of the copper decreased by 6.6 grams and activity of  $\text{Cu}_2\text{O}$  in the slag increased from 0 to 0.014.

In the case of 0.1% Zn, Pb and Fe in a Cu-Zn-Pb-Fe melt, the ratio of Fe activity to Zn activity is apparently 296. Also, the Fe activity is 15 times higher than the Pb activity. There should therefore be a thermodynamic driving force for zinc and lead to enter the liquid copper without much iron.

## 6. EXPERIMENTAL

### 6.1. EXPERIMENTAL APPARATUS

A schematic diagram of the experimental apparatus is shown in Fig.11. The detailed information on the different parts of the apparatus is given below.

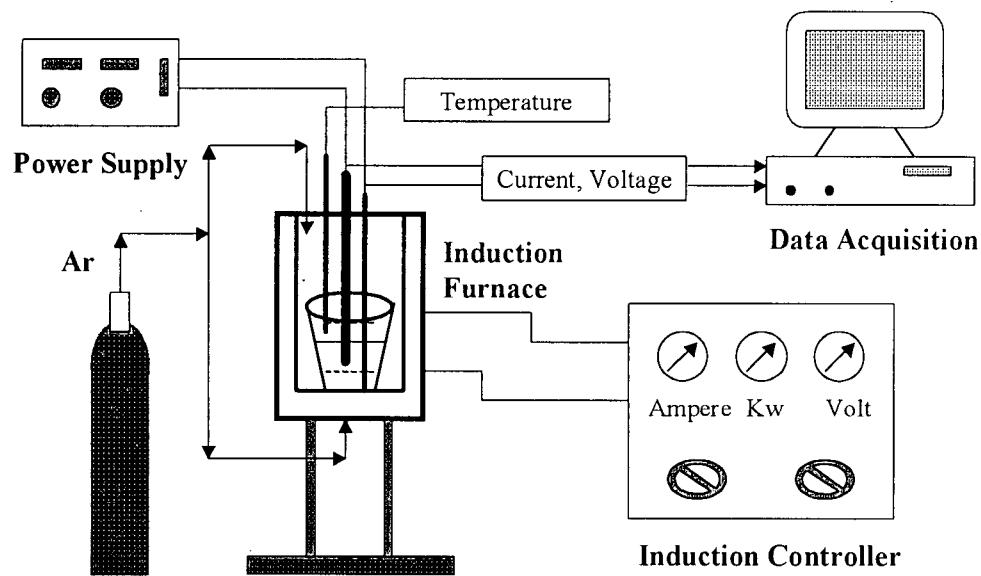


Fig. 11: Schematic diagram of the experimental apparatus

### *Induction Furnace*

A self-constructed induction furnace (Fig.12) was employed to melt the slags. A graphite bushing (labeled '13' in Fig.12,  $5\frac{1}{4}$ "(O.D.)  $\times 3\frac{3}{4}$ "(I.D.)  $\times 9$ "(L), supplied by National Electrical Carbon Canada, Edmonton, AB, Canada) was used as the heating element of the furnace. This heating element combined with the MgO ring (labeled '7') and the alumina ring (labeled '14'), separated the furnace into two chambers. The inner chamber was the place inside the graphite bushing, which was used as the working space for the crucible assembly. The outer chamber was the space between the graphite bushing and the refractory bucket (labeled '5'), which served as insulation and graphite bushing protection.

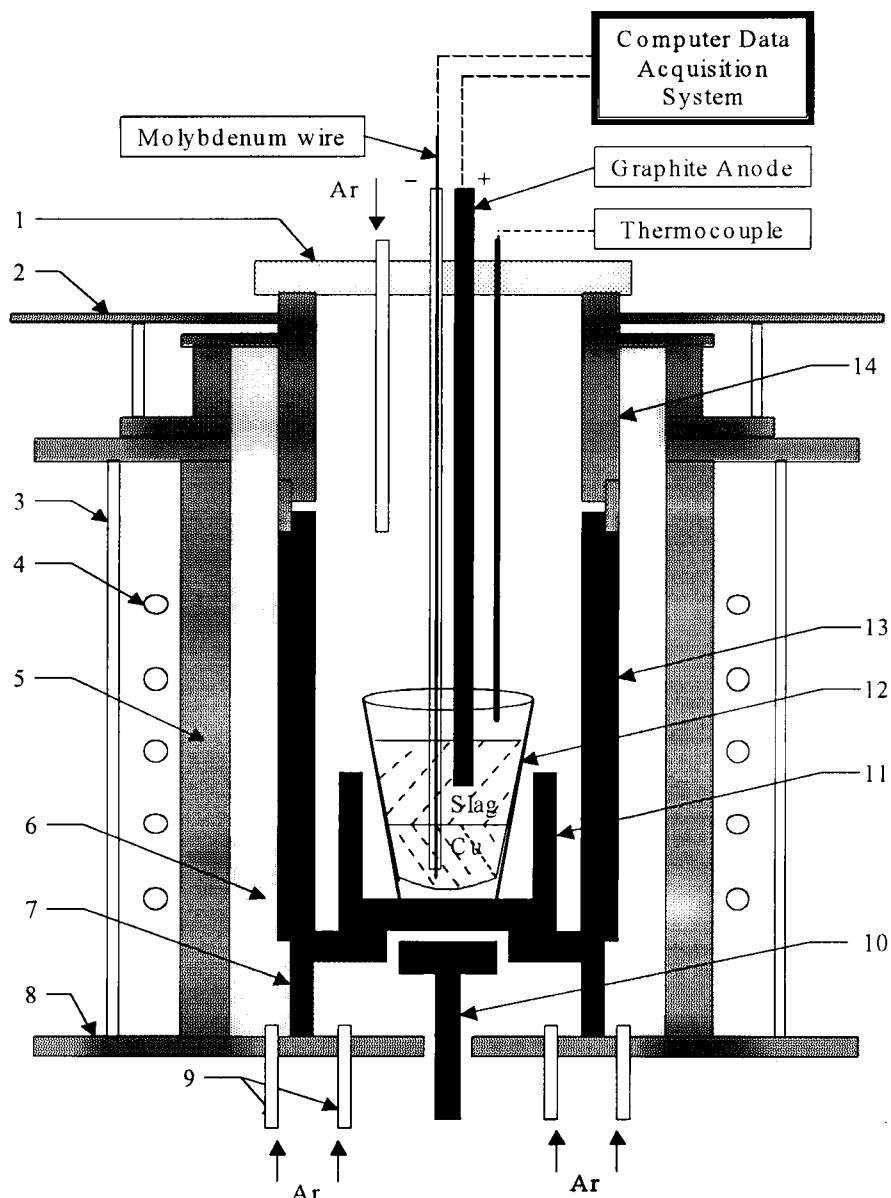
A fireclay crucible (labeled '12') containing the slag was placed in a graphite cup (labeled '11') inside the inner chamber. In the cases of a leak of molten slag, a slag overflow from the crucible, and a melting of the crucible, the graphite cup could hold the molten materials to protect the furnace. A thermocouple was placed above the slag surface to measure the temperature. The outer chamber was filled with coarse alumina powder (labeled '6'), which was used as an insulator. The average size of the alumina powder was about 2.1 mm.

Argon was introduced into the inner chamber through the three jets located in the bottom fiber plate (labeled '8') and one jet in the top refractory cover (labeled '1') to protect the bath from oxidation and to reduce the oxidation of the graphite bushing. A second stream of argon was introduced into the outer chamber through another three jets located in the bottom plate to protect the graphite bushing. Flow rate of the argon streams were controlled with a mass flow controller.

In the electroreduction trials, a graphite rod (10 mm in diameter) was used as the anode immersed into the liquid slag. The graphite anode was more mechanically stable than the platinum ring, which was used in the previous study<sup>2</sup>. Separate runs indicated that the extent of reaction between the graphite rod and the slag when no current was applied was negligible. The cathode is a liquid copper melt with a Mo electrode (0.8 mm in diameter), sheathed in alumina except where immersed in the copper. FACT<sup>8</sup> calculation indicated that in the case of 0.1% zinc, lead and iron in a copper melt at 1250 °C, iron activity was about 296 times and 15 times higher than zinc and lead activities respectively. In addition, at this temperature the solubility of Mo in Cu is negligible and no wear of the Mo electrode was noticed in any of the trials.

The electrodes were placed to the desired position with a XYZ Movement Controller. A computer-based data acquisition system (supplied by Keithley Instruments, Data Acquisition Division, Taunton, MA, USA) was employed to record voltage and current readings from the DC power supply. The data acquisition card could obtain data at different frequency and saved it in an ASCII format. This format data could be imported into Excel spreadsheets.

At the end of the experiment, a graphite shaft was used to push the graphite cup holding the crucible to the furnace top so that it could be removed from the furnace.

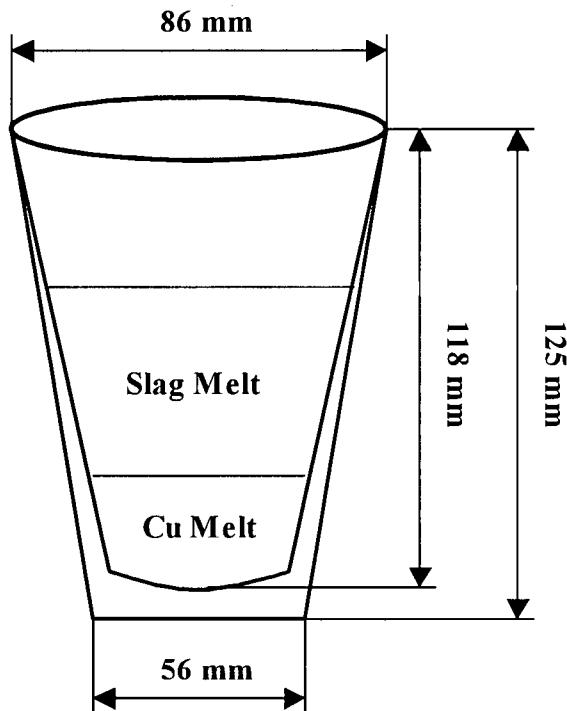


**Fig. 12: Induction furnace** (1) furnace cover, (2) top plate, (3) side support stands, (4) induction coils, (5) refractory bucket, (6) coarse alumina powder, (7) MgO ring, (8) bottom plate, (9) argon inlet tubes, (10) graphite shaft, (11) graphite cup, (12) fireclay crucible, (13) graphite bushing, (14) alumina ring

***Crucible***

The crucible used was a fireclay material analyzing 36% Al<sub>2</sub>O<sub>3</sub> and 57% SiO<sub>2</sub> with Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> as the major contaminants. This composition should be almost exactly half mullite (Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>) and half silica. This material was chosen after trying a variety of refractory materials in the previous study on fumer slag. The slag is acidic, with a CaO/SiO<sub>2</sub> ratio less than 1, but it is not saturated with either SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>. Consequently, the slag dissolves any basic refractory within minutes but also attacks expensive quartz or alumina refractories very substantially. The cheaper fireclay used was also attacked by the fumer slag, but no more than alumina or quartz. Kivcet slag is similar to the fumer slag in this respect, but is more corrosive due to higher ZnO and PbO contents. In the analysis of results, the change in slag composition because of crucible erosion is considered and discussed.

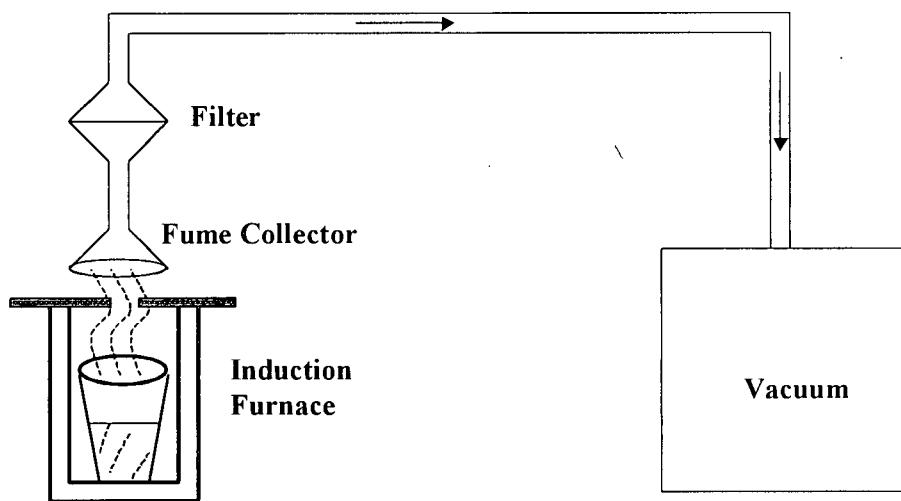
The crucible is conical in shape, 118 mm in depth, with a diameter of 86 mm at the top and 56 mm at the bottom (see Fig. 13).



**Fig. 13: Assembly of the crucible**

#### ***Fume Collection Device***

A simple fume collection device was made to collect fume (Fig. 14). A vacuum cleaner was used to produce a force. The off-gas entered a collector, which was made of glass. Then it passed through a filter and the particles in the gas were collected on a filter paper (8 um).



**Fig. 14: Schematic diagram of the fume collection device**

## 6.2. METHODOLOGY

The experiments in this study can be divided into roughly 2 categories:

1. Metal recovery from the slags under different conditions
2. Electrical resistance measurement

### 6.2.1. Metal Recovery

At first, a series of runs were conducted with two fumer slags to confirm the results of the previous study. In that study, only limited chemical analysis had been done and the extent of reaction with the crucible was not apparent. This produced results that gave an apparent greater recovery of zinc but masked the differences between the different experimental techniques used. For this study, Cominco volunteered to pay for all the chemical analyses, including a reasonably complete element analysis of each slag sample and the ratio of  $\text{Fe}^{++}$  to  $\text{Fe}^{+++}$ . This permitted a much more detailed analysis of the experimental results.

The first fumer slag had a high residual content and reflected an inadequate processing in the fuming furnace. All metals of interest, zinc, lead, germanium and indium, were present at above average levels. The second fumer slag had a very low residual level, considerable below the normal average for this process. The analyses of these initial slags are given in Table 1. The trials with the two types of fumer slag were of three types:

1. Slag was heated at  $1250^{\circ}\text{C}$ . for 2 hours to determine if either zinc or lead would volatilize and to determine the extent of reaction with the crucible.

2. Slag (generally 250grams) was melted with 150 grams of copper at 1250° C. to determine the extent of redistribution of Zn, Pb, In and Ge without use of voltage and to compare with results obtained from FACT analysis.
3. Slag (200-250 grams) and copper were melted and subjected to a voltage of 5 volts to determine if the cleaning of Zn, Pb, In and Ge from the slag was enhanced.

Next, Kivcet slag was treated using the same processes to see what would happen. Analysis of the original Kivcet slag is also shown in Table 1. As mentioned above, Kivcet slag is more corrosive than fumer slag. When substantial quantities of Kivcet slag were melted, it was necessary to add some amount of ground crucible to the starting slag powder to prevent the slag from eating through the crucible wall.

The runs using the Kivcet slag can be divided into the following groups:

- Melting Kivcet slag (250 or 500 grams) at 1250 °C for 2 hours to see if either zinc or lead could be recovered without using a reductant.
- Melting a charge-mixture (250 grams of Kivcet slag + 25 grams of crucible powder) at 1250 °C for 90 minutes to determine how much zinc and lead can be recovered.
- Equilibrating 275 grams of the charge-mixture with 150 grams of copper at 1250 °C for 90 minutes to define the distribution of the recovered Zn and Pb.
- Melting the charge-mixture and copper at 1250 °C with 5 volts applied to determine if metal recoveries would be enhanced.
- In an attempt to simulate a counter flow process, Kivcet slag was treated to remove some of the zinc and the lead and then was electro-refined with new

copper three times to determine the zinc and lead contents that could be reached.

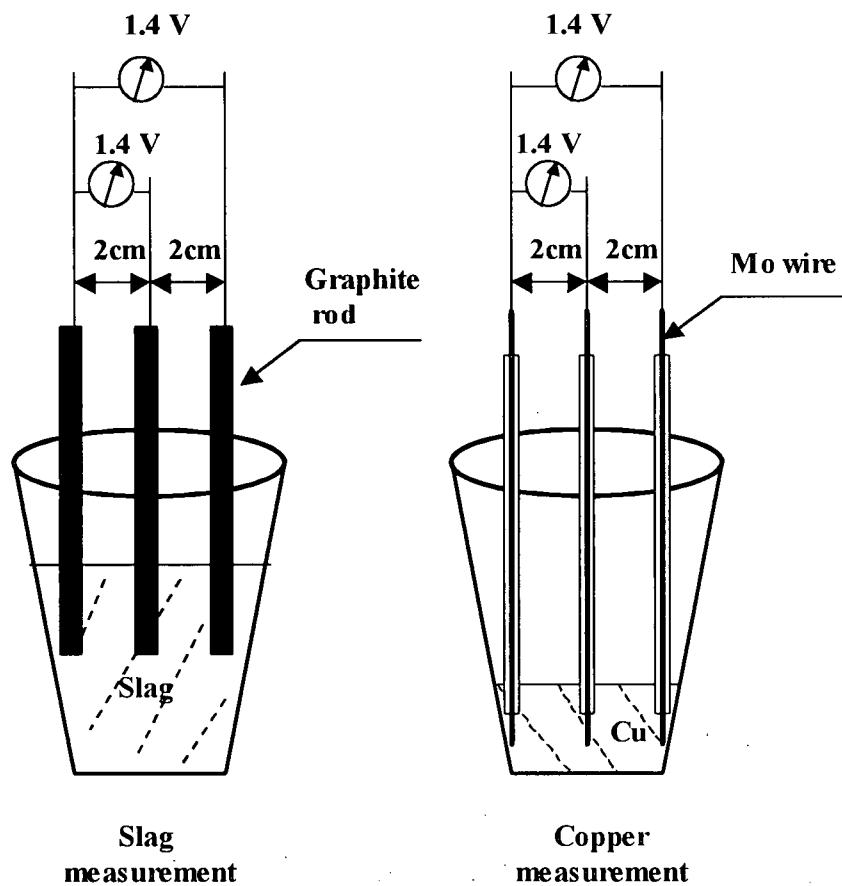
In all experiments, the slag temperature was 1250 to 1270 °C with about a 10-20 °C temperature difference between the slag and the thermocouple. Holding time at this temperature was 90 or 120 minutes. A slag sample was taken with a steel rod every 15 to 30 minutes. A fume sample was collected in some runs. A sample of the copper button was only taken after the run was finished and the slag was cooled to room temperature. The slag samples, the fume samples and the copper buttons were sent to IPL for chemical analysis.

### 6.2.2. Electrical Resistance Measurement

Firstly, a series of experiments were conducted to measure the electrical resistances of the liquid slags. As shown in Fig.15, two graphite rods (10 mm in diameter) were immersed into the liquid slag at 1250 °C. The distance between the graphite rods was 2 cm. A voltage of about 1.4 volts was applied across the graphite rods for about 10 minutes. Then the distance between the graphite electrodes was increased to 4 cm. The same voltage was applied for 10 minutes again. After that, the graphite rods were lifted out of the liquid slag and their tips contacted each other for 10 minutes with the same applied voltage. The voltage and the current in each step were recorded with the computer-based data acquisition system.

Next, the resistance of liquid copper at 1250 °C was measured with a similar method to that in the slag resistance measurement. The graphite rods were replaced by two pieces of molybdenum wire (0.8 mm in diameter) sheathed in alumina except for the part contacting the liquid copper (see Fig.15).

Finally, the total resistance in electrorefining was measured. As shown in Fig.16, a graphite rod was immersed into the liquid slag and used as the anode. The tip of the graphite rod was 2 cm away from the slag-copper interface. A molybdenum electrode was immersed into the liquid copper. The distance between the molybdenum electrode tip and the slag-copper interface was also 2 cm. A voltage of 5 volts was applied across the graphite anode and the molybdenum electrode for about 10 minutes. The voltage and the current were recorded with the data acquisition system.



**Fig. 15: Schematic diagram of slag and copper resistance measurement**

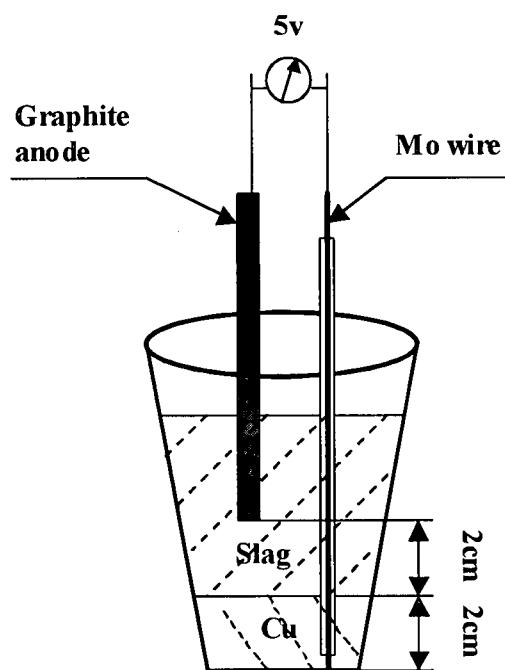


Fig. 16: Schematic diagram of resistance measurement in electrorefining

## 7. RESULTS AND DISCUSSION

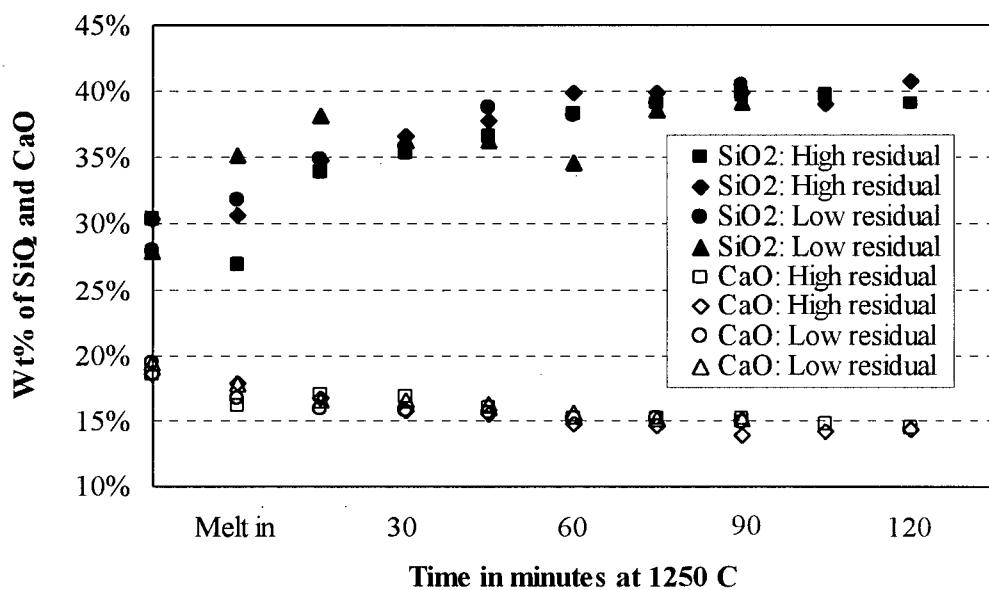
### 7.1. METAL RECOVERY

#### 7.1.1 Metal Recovery from the Fumer Slags

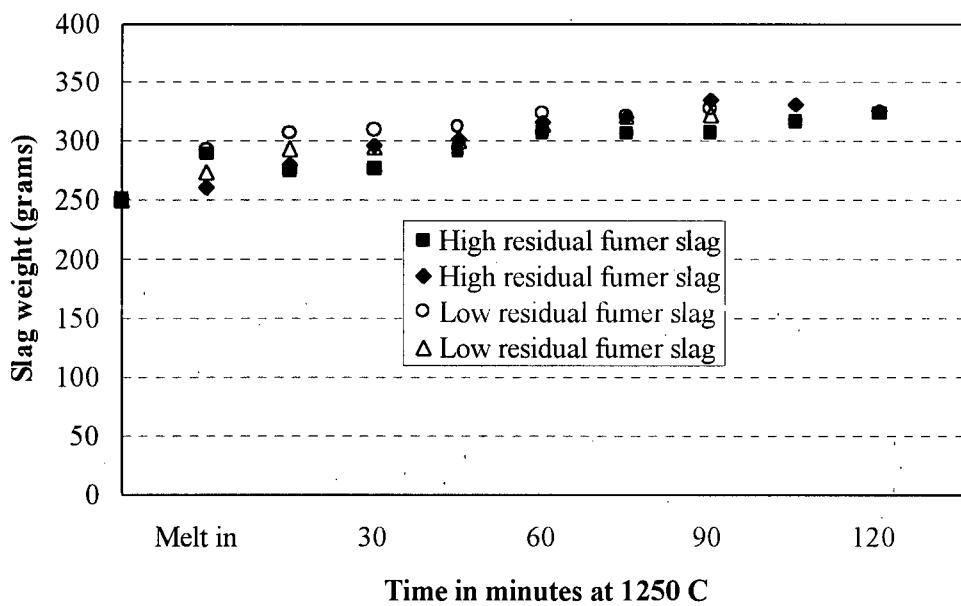
Two types of fumer slag, high residual and low residual, were treated in the experiments.

During all the runs, there was a reaction between the slag and the crucible that appeared to reach equilibrium after about one hour or less. Fig. 17 shows the change in CaO and SiO<sub>2</sub> contents of the slag with time in slag reheating with no copper. The rate of change is decreasing with time. It is possible by using the CaO analysis to calculate the weight of the final slag. Fig. 18 indicates that an initial 250 grams of slag reaches a fairly uniform weight of 320 grams after over two hours of processing at temperature. The exact dilution factor was considered in all calculations of metal loss from the slag during processing.

The most important aspect of the crucible dissolution is the impact of the higher silica and alumina on the activity of the zinc and lead oxide in the slag. The FACT software suggests that the initial slag has a ZnO and PbO activity of 0.029 and 0.0037 respectively. After dissolution of the crucible to the values noted, these activities have been reduced to 0.015 and 0.0018, a reduction of almost exactly fifty percent. Since the change in slag composition in an industrial system, with a much lower surface to volume ratio, would be much lower, it might be expected that the results reported below represent a worst case scenario.



**Fig. 17: The change in CaO and SiO<sub>2</sub> contents of fumer slags with time**



**Fig. 18: Increase in the weight of fumer slags with time**

### ***Slag remelting with no copper***

A number of runs were conducted at 1250 °C using 250 grams of fumer slag melted in a fireclay crucible. As soon as the slag melted, there was a substantial display of fume and the analysis of the slag altered considerable over a two hour period as shown in Fig. 19, that gives the apparent slag composition with time of duplicate runs with the high residual fumer slag. This graph is misleading in that it ignores the dilution effect of the crucible erosion. The actual percentage of the original zinc and lead that are removed is shown in Fig. 20, where this factor is considered. Surprisingly, roughly thirty percent of the zinc and fifty percent of the lead have been removed simply by allowing the slag to equilibrate at temperature. In these runs, the combined weight of zinc and lead vaporized from 250 grams of slag is calculated at roughly 4.2 grams. The weight loss of the slag and crucible, after correcting for sample weights, was 5.5 and 7.1 grams for the two runs shown. The fume collected from these runs, see Table 6, was a mixture of very white crystals with a yellow tinge, and small black glass particles. The latter were clearly small slag particles ejected into the gas phase during melting. The overall analysis of the fume indicated about 10-20 percent slag and over 80 percent lead and zinc oxides in roughly equal amounts. It should be noted that the Ge and In analyses of the fume were roughly 200 and 400 ppm respectively, indicating a recovery of these elements to the fume of over 10 percent.

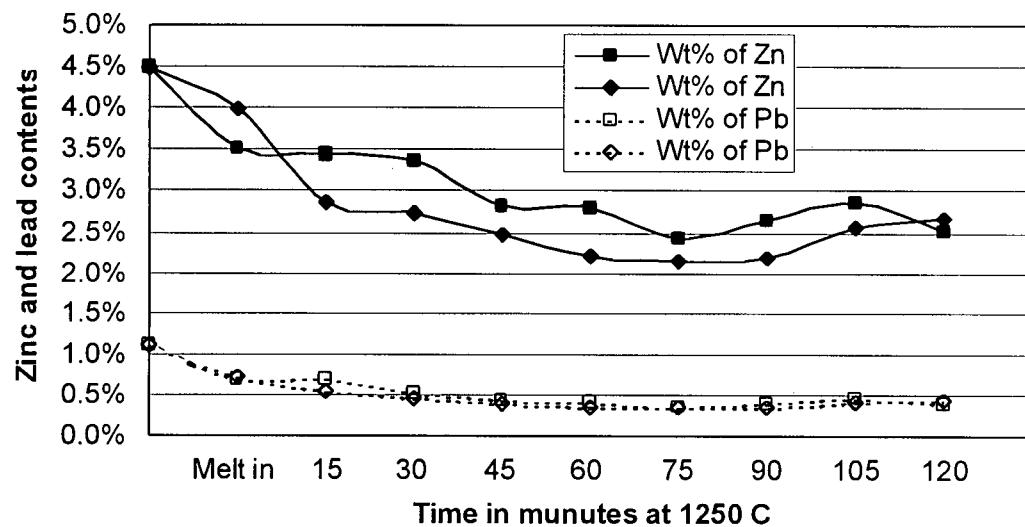


Fig. 19: Analysis of Zn and Pb in the high residual fumer slag, uncorrected

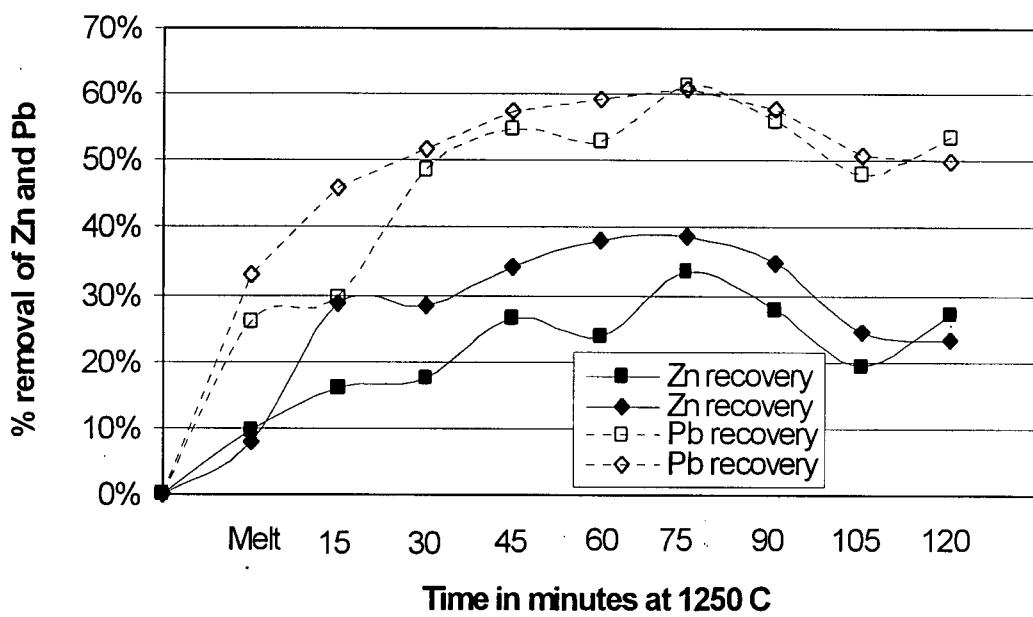


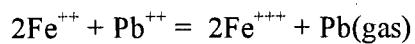
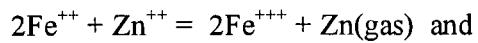
Fig.20: Zinc and lead loss by slag reheating-High residual

**Table 6: Fume analysis - Fumer slag**

Slag type	Condition	Zn%	Pb%	Ge ppm	In ppm
High Residual	After heating	23.0	36.5	206	360
	After heating with Cu	32.3	27.5	179	501
Low Residual	After heating	31.4	12.8	647	481

When the low residual fumer slag was remelted, the lead removal was near zero and the zinc removal over 30 percent as shown in Fig. 21. The low lead removal is not surprising since the original content of lead in this slag was just over 0.03 percent. It is interesting to note that even though the zinc content in this slag is one-third that of the high residual fumer slag, the zinc removal is still substantial. The weight loss of the slag and crucible in these runs was lower than the high residual runs, being 1.9 and 3.6 grams for the duplicate runs. In the fume, the zinc to lead ratio was roughly 3/1 and these two materials represented just over half of the fume. The initial analysis for In and Ge was very low in this slag and it appeared that all of these metals reported to the fume. However, at the 20-40 ppm level, the analysis is not reliable enough to calculate the percent removal.

In the slag, the divalent iron ion is the only reductant present in a substantial amount. The reactions



appear to take place readily in the first thirty minutes of melting. Analysis of the high residual fumer slag using FACT indicates that the pressure of Zn over the slag at melt-in should be 0.002 atmospheres and the pressure of Pb, 0.001 atmospheres. These values drop to 0.0001 and 0.00007 respectively after crucible dissolution. Given the extent of the fume and the high loss of lead and zinc, these calculated values would appear to be a trifle low.

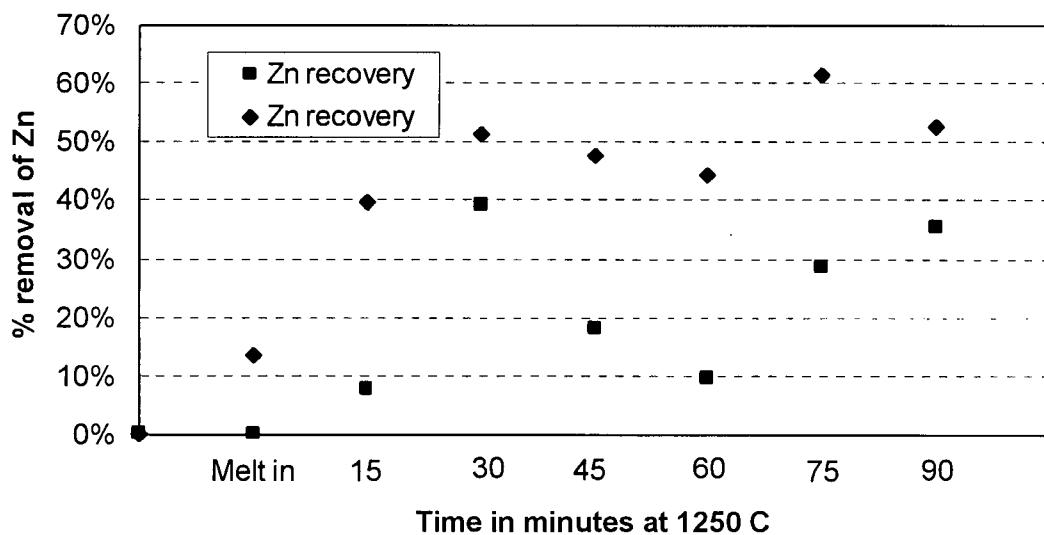


Fig.21: Zinc loss by slag reheating -Low residual

Since in the reduction of lead and zinc from the slag the electrical charge balance must be maintained, a calculation was made of the gram-ion equivalents of the major ionized species, zinc, lead, copper, and iron, both divalent and trivalent. The balance, shown in Table 7, was generally consistent, but the variability was high. The analysis for divalent and trivalent iron appears to be one of the less reliable ones and scatter in the results is quite large which is unfortunate when divalent iron is the major reductant in the slag. (An analysis was done on the initial slags to determine if there was residual carbon from the fuming process. The amount found was under 0.05 percent.)

**Table 7: Ion equivalents in the fumer slags**

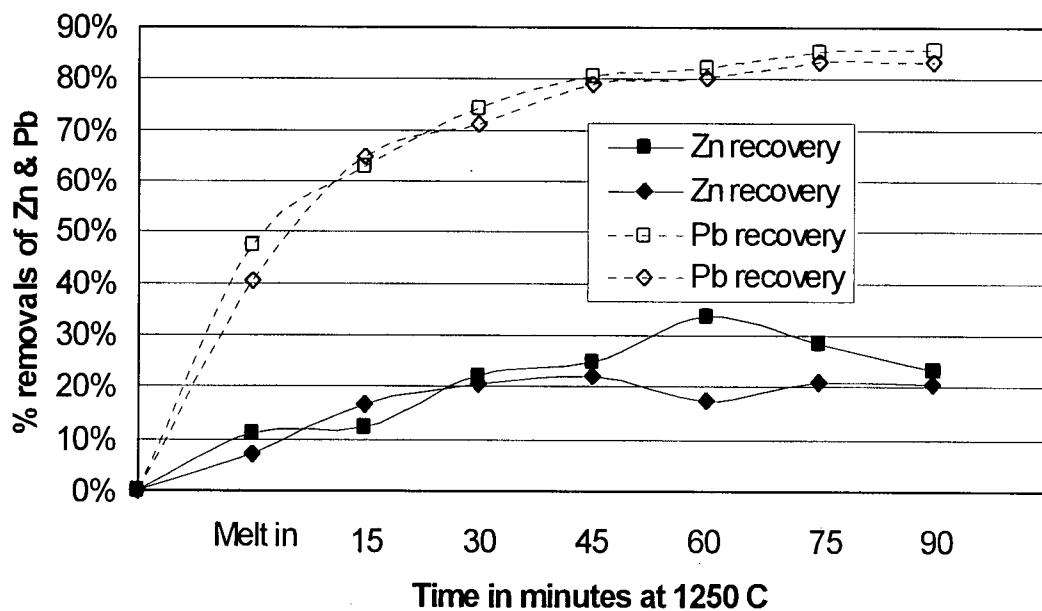
Slag type	Conditions	Cu	Zn	Pb	Fe	I*t/96487	Sum
High Residual	As received	0.015	0.343	0.026	2.753		3.137
	After heating	0.008	0.257	0.013	2.819		3.096
	After heating with Cu	0.037	0.268	0.004	2.908		3.217
	After electroreduction	0.021	0.183	0.002	2.739	0.202	3.146
Low Residual	As received	0.016	0.117	0.000	2.747		2.880
	After heating	0.009	0.066	0.001	3.195		3.271
	After heating with Cu	0.025	0.063	0.000	3.219		3.307
	After electroreduction	0.029	0.057	0.000	2.660	0.148	2.895

***Slag remelting with copper with no current applied***

A series of runs were made at 1250° C with no current applied using 250 grams of fumer slag with 150 grams of copper. The zinc and lead loss from the high residual fumer slag, shown in Fig. 22, indicates clearly the combined effect of fuming of the slag and the removal of zinc to the copper. After roughly sixty minutes, a relatively constant value appears to have been reached. At the end of the two runs shown, between 20 and 30 per cent of the zinc had been removed from the slag and over 80 percent of the lead. Had all of this zinc and lead reported to the copper, the copper should analyze 1.78 per cent zinc and 1.50 percent lead. The analysis of the copper is shown in Table 8. It is seen that the actual analyses for zinc and lead are roughly 0.3 and 1.0 percent respectively with an iron content of 0.11 percent. It would appear that roughly 80 percent of the zinc lost and 30 percent of the lead lost, or roughly 3.8

grams of metals, have reported to the fume. The actual weight loss to the fume in these runs averaged 3.5 grams with zinc and lead in the fume analyzing in the ratio of 2.5 to 1 (Table 6). Considering the vagaries of the analysis, the agreement is very good. The copper analysis of the slag after equilibration increased to 0.69 percent from 0.38 percent.

It can be seen that a small fraction of the indium reports to the copper in the high residual fumer slag case. However, the majority of both the indium and germanium report to the fume.



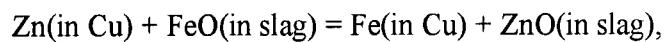
**Fig. 22: Zinc and lead loss with copper getter-High residual**

**Table 8: Copper button analysis – Fumer slag**

		Copper button composition				
Slag type	Condition	Zn %	Pb %	Fe %	Ge ppm	In ppm
High Residual	After heating with Cu	0.34	1.09	0.11	<5	73
	After electroreduction	1.77	0.81	0.90	<5	59
Low Residual	After heating with Cu	0.43	0.05	0.57	15	7
	After electroreduction	0.64	0.04	2.5	67	<5

Analysis of this system using FACT is difficult since the equilibrium volume of gas passing over the system is difficult to estimate. However, ignoring the gas phase, FACT suggests that the zinc, lead and iron content of the copper would be 0.10, 0.81 and 0.014 weight percent respectively and that the copper content of the final slag would be 2 percent. However, the zinc and lead vapor pressures would be the same as calculated for the no copper case and there would obviously be a significant loss of these metals to the fume. These calculated values are all substantially lower than the actual recoveries, indicating that the reduction potential in the system is greater than indicated by the apparent  $\text{Fe}^{++}/\text{Fe}^{+++}$  ratio. However, the actual electrical equivalence in Table 7 shows a reasonable balance.

FACT calculation indicated that at 1250 °C the activity coefficients for iron and zinc at infinite dilution in the copper melt were 19.9 and 0.077 respectively. Using the formula

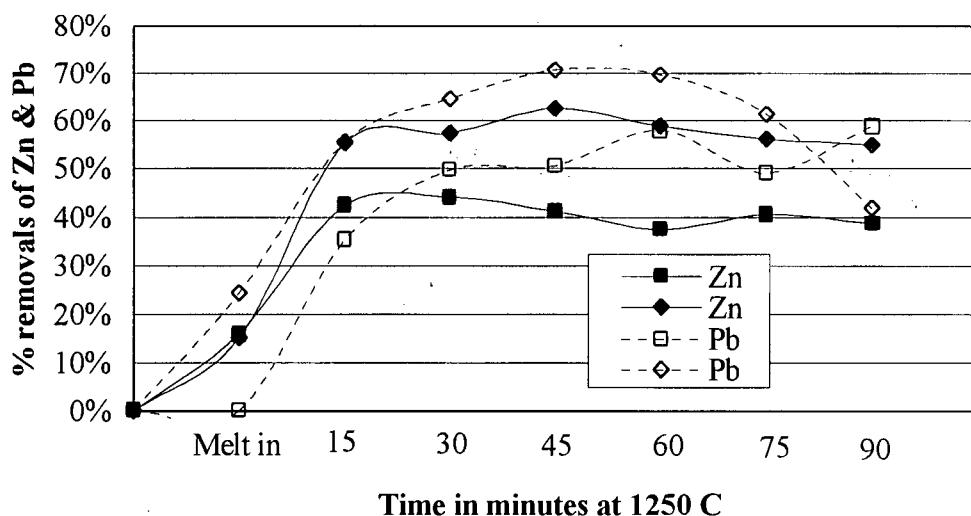


it can be calculated that the ratio of zinc to iron in the copper should be:

$$\frac{\%Zn}{\%Fe} = 28.5 \frac{a_{ZnO}}{a_{FeO}}$$

If the activity coefficients of the oxides are assumed to be equal, the ratio of zinc to iron in the copper for this slag should be 3.9. Using the activity coefficients for ZnO and FeO from the FACT software for this slag composition (0.326 and 1.072 respectively), the ratio should be 1.03. The actual ratio, from Table 8, is 3.1.

Runs made with the low residual fumer slag also showed a substantial removal of zinc, in the order of 50 percent, as seen in Fig.23. The initial lead content was very low (0.03%) but the final lead content also appeared to be lowered to about 0.01 percent. Of the roughly 1.8 grams of zinc that was removed from the slag (average of two runs), some 0.65 grams was recovered in the copper and over 1 gram was removed in the fume. This corresponds to the overall weight loss in the experiments. Copper loss to the slag was very low.



**Fig.23: Zinc and lead loss with copper getter-Low residual**

Analysis of this system using FACT<sup>8</sup> suggested that, ignoring the gas phase, the copper would analyze 0.05 percent zinc and 0.02 percent iron and that the slag would increase to 1.6% Cu. Again the actual results would appear to indicate that the conditions in the experimental furnace are considerably more reducing than indicated by the initial  $\text{Fe}^{++}/\text{Fe}^{+++}$  ratio. However, in this case, the ion equivalent balance (Table 7) is not good and it appears that a high percentage of divalent iron has been oxidized with very little material apparently being reduced.

#### ***Slag Remelting with Copper with 5 volts Applied***

In this series of runs, 5 volts was applied across the electrodes shown in Fig. 12 and the results were collected as in the previous series. A typical curve of current and voltage versus time is shown in Fig. 24. In all cases, after a very brief lag, the current reached a high point and then slowly decreased, presumably as the mobile ions in the slag were depleted. The curve for zinc loss in the high residual fumer slag is compared to zinc loss with no voltage in Fig. 25. After the initial melt in, it is seen that the zinc loss is greater at all times for the case in which current is applied. In this case, a sample was also taken of the slag after the crucible and slag had cooled in contact with the copper. As seen, there was a marked reversion of zinc into the slag after the voltage was removed, indicating that the voltage had indeed created a new equilibrium. The iron and zinc contents of the copper buttons recovered after the runs were much higher than those from the runs with no voltage and the ratios of zinc to iron were much lower. The lead content of the copper was lower with voltage applied, even though the lead removal from the slag was marginally higher with voltage applied as seen in Fig. 26. The electrical equivalence of the slag after treatment is seen in Table 7 where the contribution

of current times time has been considered along with the valence change of the elements. It appears that the contribution of the applied voltage is significant but not as impressive as hoped.

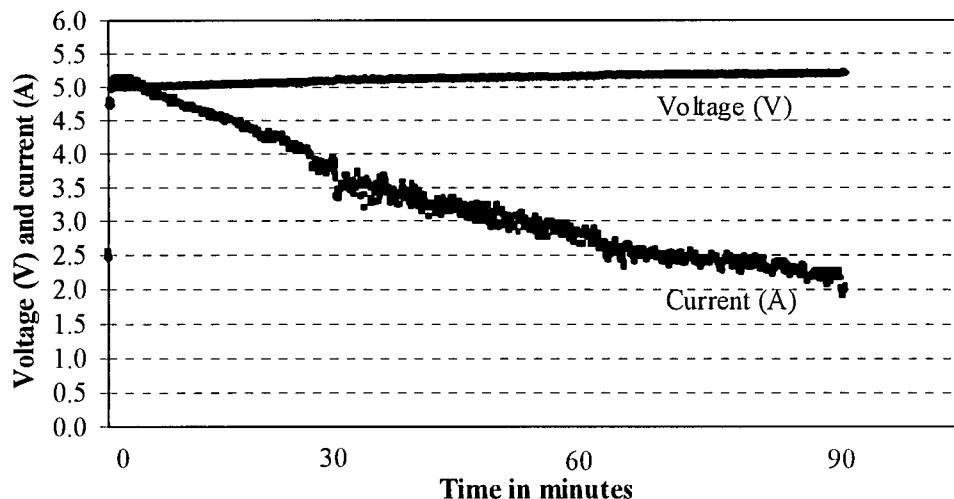


Fig. 24: Typical Current-Voltage-Time record

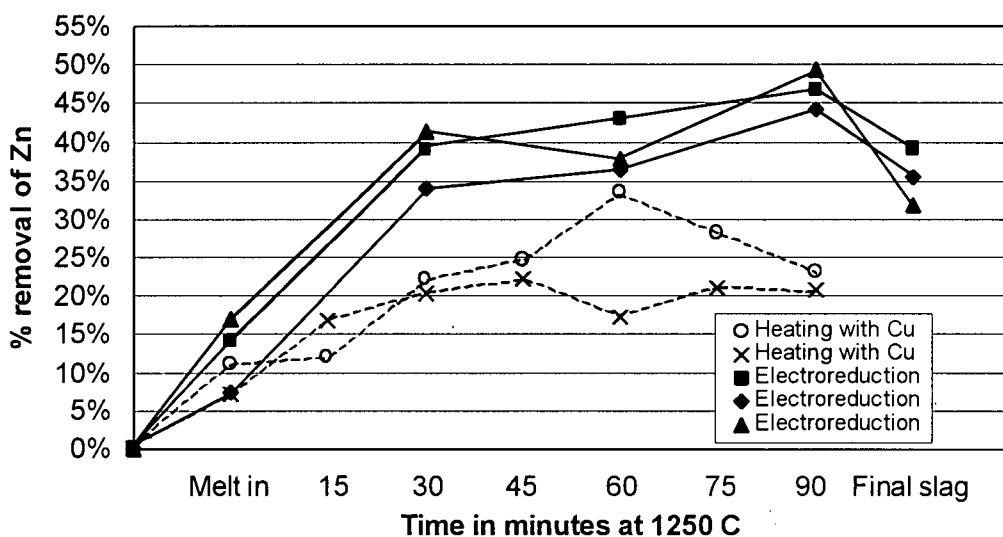


Fig. 25: Comparison of zinc recoveries - High residual electroreduction

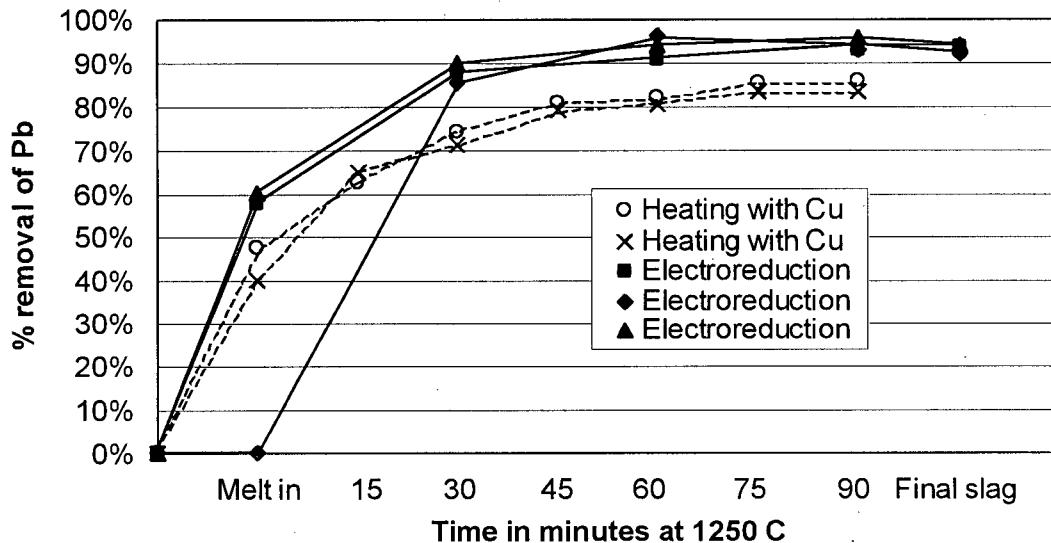


Fig. 26: Comparison of lead recoveries - High residual electroreduction

Electroreduction of the low residual fumer slag didn't give a positive benefit. The loss of zinc from the slag, shown in Fig. 27, was perhaps marginally improved but the difference is certainly within the limits of analysis.

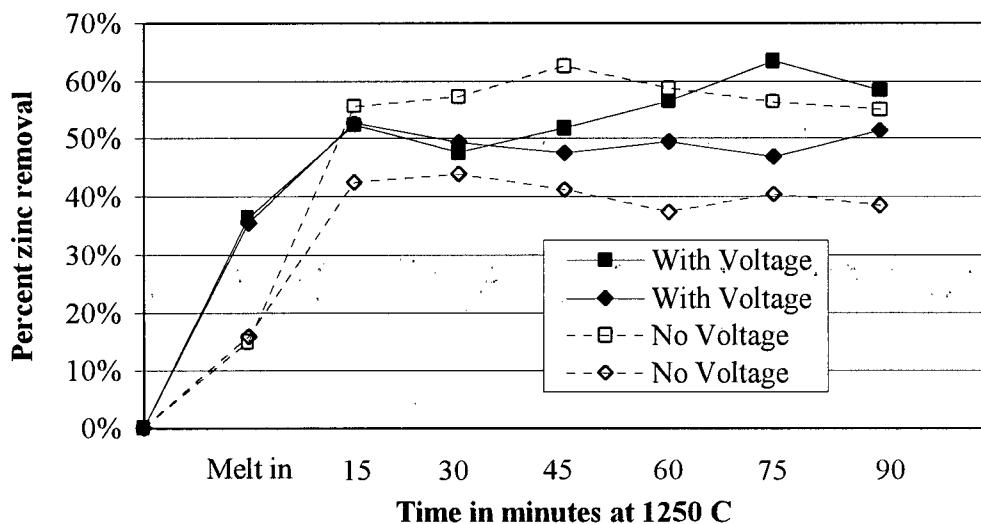


Fig. 27: Comparison of zinc recoveries - Low residual electroreduction

Considering the coulombs passed in the electroreduction of the two slags, it can be calculated that the current efficiency for the high residual fumer slag case was 95.6 percent and for the low residual case was 90.1 percent. This is very similar to the values predicted by Dickson and Dismukes<sup>31</sup> for slags with a low basicity.

***Comparison of the results in this study and in previous study***

Table 9 shows the zinc content in the high residual fumer slag before and after 90 minutes of treatment in this study and in the previous study. Zinc concentration dropped to 2.4~2.6% after melting with and without copper in this study. This agrees with the result of about 2.5% in the previous study. However, wt% of zinc decreased to a lower level of 1.93% after electrorefining 90 minutes in this study. Actual zinc recovery (about 47%) was higher than those (20~35%) in the runs with no current applied, indicating that the current enhanced the removal of zinc from the slag. In the previous study the effect of the current on zinc recovery from the high residual fumer slag was not clear. A possible reason was that the slag analysis was not accurate enough. However, in the case of a synthetic slag (Slag1, ZnO%=4.33) in the previous study<sup>2</sup>, a voltage of 5 volts decreased the zinc content to a lower level (about 0.8%) than those (1.3-1.5%) with no voltage applied.

**Table 9: Zinc content in high residual fumer slag before and after treatment (90 minutes)**

	In this study	In the previous study
Original high residual fumer slag	4.5%	4.5%
After melting without Cu	2.42%	About 2.5%
After equilibrating with Cu	2.57%	About 2.5%
After electrorefining	1.93%	About 2.5%

In the case of low residual fumer slag in this study, about 55% of the zinc was recovered by electrorefining. Zinc concentration in the slag decreased to about 0.55% and stabilized at this level. No experiment was conducted with low residual fumer slag in the previous study. But in the electroreduction runs using another synthetic slag (Slag2, ZnO%=1.98), which was similar to low residual fumer slag, it was found that zinc could not be removed from the slag when its content was lowered to about 0.45%. The results in both studies are similar.

Analysis of the copper buttons in the runs using high residual fumer slag in this study indicated that (1) with current passing, more zinc and iron were deposited in the copper melt than without current applied, and the concentration of zinc was nearly double that of iron; (2) lead, germanium and indium can also be collected in the copper melt, and there was no significant difference for their concentration in the cases with and without current passing (Table 8). This agrees well with the result in the previous study. In the runs using low residual fumer slag in this study, the current also enhanced the thermodynamic driving force for removal of zinc and iron to the copper melt. However, iron content was much higher than that of zinc because the wt% of zinc in the slag was quite low.

Fume was observed in all runs in both studies. The main contents of the fume were zinc and lead oxides in roughly equal amounts. Concentrations of germanium and indium in the fume were much higher than those in the slag.

In the electrorefining runs in both studies, voltage increased slightly during the whole melting period, while current increased a little in the first several minutes and then decreased slowly. In this study, current efficiency was calculated based on the difference in the total ion equivalents of zinc, lead, iron (divalent and trivalent) and copper in the slag before and after

treatment. The calculation results of more than 90% was higher than that (68%) in the previous study, in which the current efficiency was calculated according to the zinc concentration difference in the slag and the iron concentration difference in the copper before and after treatment.

### 7.1.2. Metal Recovery from the Kivcet Slag

#### *Melting Kivcet Slag*

A series of runs was conducted using different amounts of slag. The slag dissolved some of the silica and alumina in the fireclay crucible at high temperature. In the case of 250 grams of original slag, silica content in the slag increased to 34.6% (average of two runs, see Fig. 28) after 120 minutes. At the same time, CaO concentration decreased to 10.2% and slag basicity dropped to 0.23. The amount of Ca in the slag was assumed to be stable. Slag weight calculations based on Ca analysis indicated that an apparent equilibrium between the slag and the crucible was reached after about 75 minutes (see Fig. 29). The weight of final slag generally increased by about 30%.

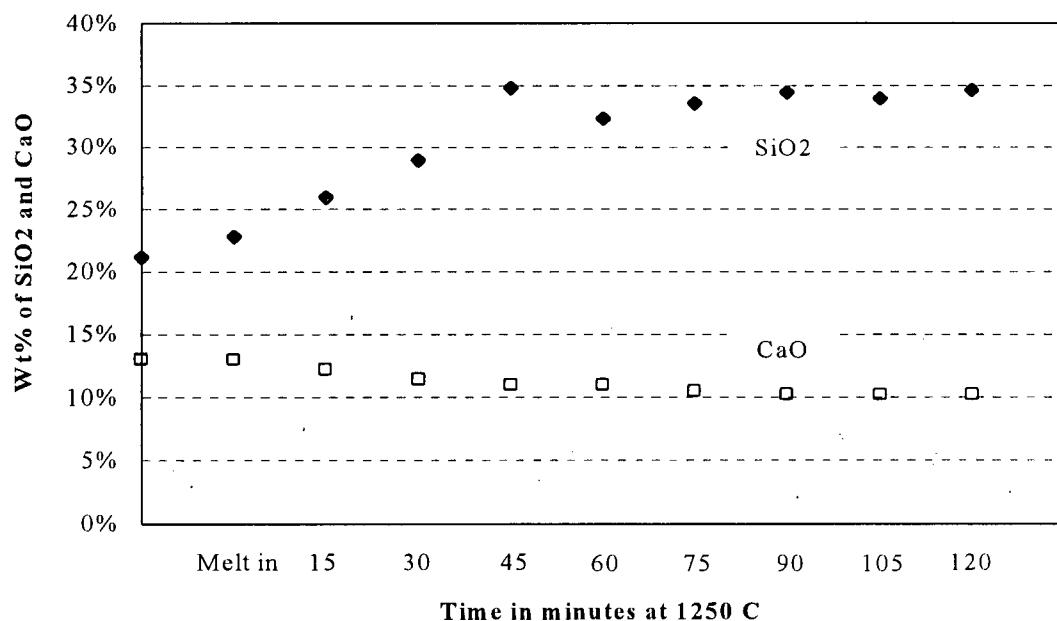
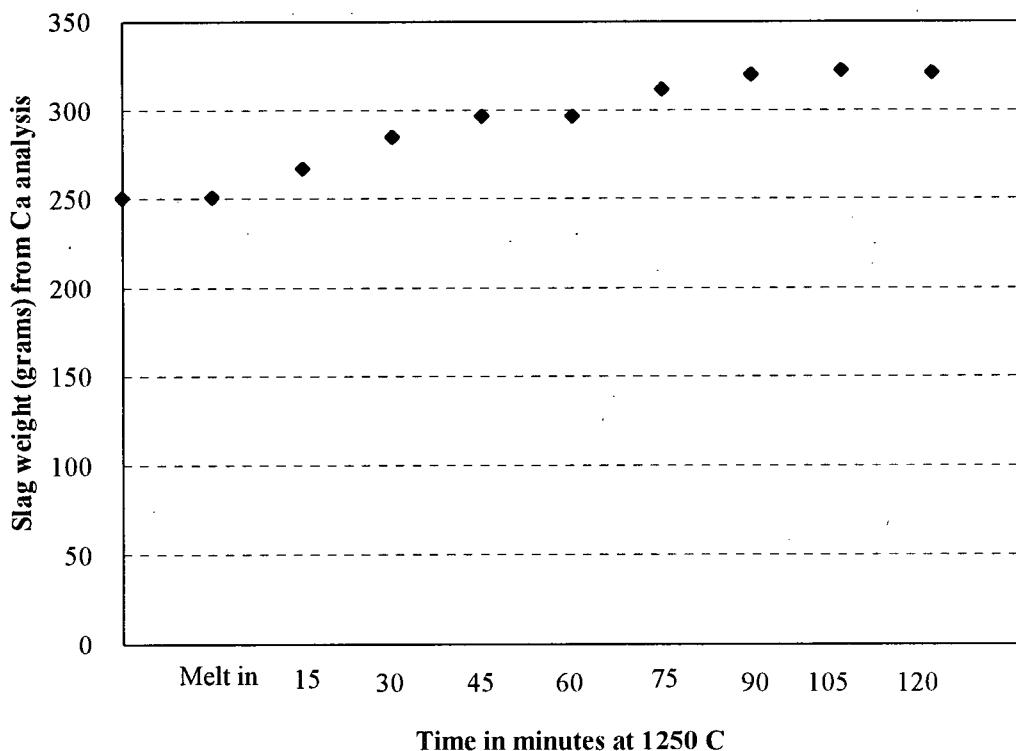


Fig. 28: Change of SiO<sub>2</sub> and CaO contents in the Kivcet slag



**Fig. 29: Increase of slag weight with time - Kivcet**

Black fume was observed over the furnace when the temperature reached about 1100 °C. This fume contained some fine slag, which was ejected into the gas phase during heating and melting. After 30 minutes, the black fume was replaced by gray fume, a mixture of zinc and lead oxides. Significant amounts of white and yellow powders were found on the brick used as a furnace cover. Overall analysis (see Table 10) indicated that the powder contained about 28% zinc and 26% lead. The Ge, In, Sb and As concentrations in the fume fell in a range of 350 to 12500 ppm, indicating a fair recovery of these elements to the gas phase.

**Table 10: Analysis of the fume – Kivcet**

Zn (%)	Pb (%)	As (ppm)	Sb (ppm)	In (ppm)	Ge (ppm)
28.4	26.1	12443	4104	832	350

In an initial run using 500 grams of slag, a leak of molten slag occurred and some liquid material entered the graphite cup. After that run, ground crucible powder was added to the slag mixture to prevent potential leakage.

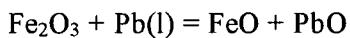
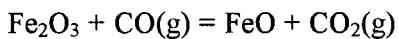
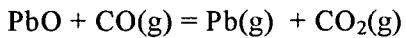
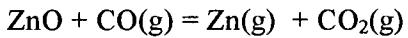
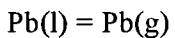
### ***Melting a Charge- Mixture Without Copper***

To make a charge-mixture with the composition shown in Table 11, 250 grams of Kivcet slag were mixed with 25 grams of crucible powder. The charge-mixture was heated to 1250 °C and held at this temperature for 90 minutes. The weight of final slag increased to 358 grams (average of two runs), indicating that crucible dissolution still occurred. But the crucible stayed intact and no molten slag entered the graphite cup. This slag weight increase was considered in the calculation of metal recoveries.

**Table 11: Analysis of the charge-mixture and the final slags**

	Zn (%)	Pb (%)	Sb (ppm)	As (ppm)	In (ppm)	Ge (ppm)	Cu (ppm)	Fe <sup>2+</sup> (%)	Fe <sup>3+</sup> (%)	SiO <sub>2</sub> (%)	CaO (%)	Al <sub>2</sub> O <sub>3</sub> (%)
Original	14.0	8.4	2616	2141	653	121	3177	14.5	6.6	26.4	12.0	3.5
After holding without Cu	9.9	5.3	1664	1196	421	35	2156	14.8	4.6	37.2	9.5	10.7
After holding with Cu	9.5	5.0	1703	971	391	51	5553	14.3	3.8	35.6	9.4	11.2
After electrorefining	10.7	3.6	1083	598	365	53	8459	16.6	2.3	35.3	11.0	9.7

In the slag, some of the metallic lead vaporized directly to the fume. Zinc and lead oxides were reduced by carbon to their metals, which also reported to the fume. During the period from melt-in to 90 minutes, the amount of trivalent iron ions decreased, while that of divalent iron ions increased. Some Fe<sub>2</sub>O<sub>3</sub> was reduced to FeO. Possible reactions were:

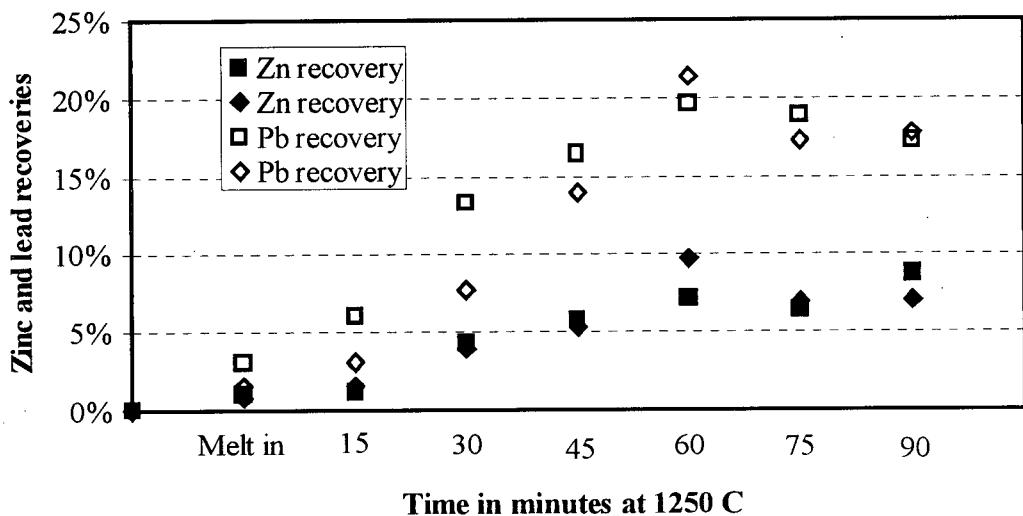


Metal recoveries in Fig. 30 indicated that chemical equilibrium was reached after 60 minutes.

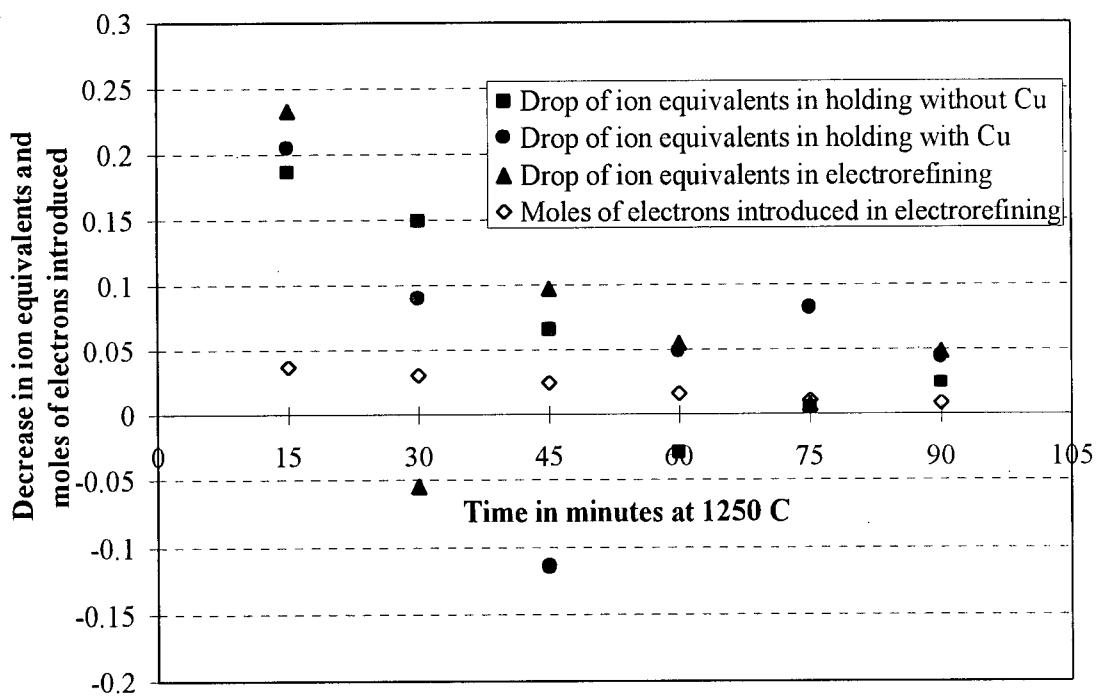
About 8.4% of the zinc and 20.5% of the lead (average) were removed at the apparent equilibrium. These recoveries were lower than those to be expected commercially since the activities of the zinc and lead oxides have been reduced by the addition of crucible material. After 90 minutes, zinc and lead contents in the slag decreased from 14.0% and 8.4% to 9.9% and 5.3% respectively (see Table 11). About 3.0 grams of zinc and 4.0 grams of lead reported to the fume. The total weight loss of the two metals was very closed to the overall weight loss of 10.2 grams. The difference was likely the weight of fine slag ejected during melting.

The total ion equivalents in the slag were calculated using the analysis received from IPL and assuming that all of the metals of interest in the slag were in the ionic state. When the charge was heated from room temperature to 1250 °C, the total ion equivalents at melt-in, assuming all ionic metals, was 3.90. After melt-in, the total ion equivalents decreased as shown in Fig. 31. Since in any reaction, the charge balance must be maintained, it is clear that the metallic lead and the carbon in the slag are involved and are influencing the charge balance calculation. If it is assumed that half of the original lead present is metallic, the weight of

carbon required to give an equal charge balance is 0.58 grams or 0.23% of the Kivcet slag.



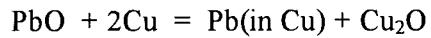
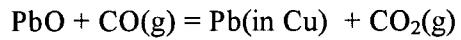
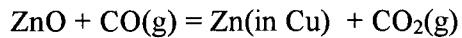
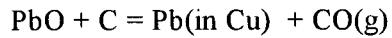
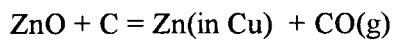
**Fig. 30: Metal recoveries in the holding runs without copper – Charge mix**



**Fig. 31: Decrease in ion equivalents during different melting period and moles of electrons introduced in electrorefining – Charge mix**

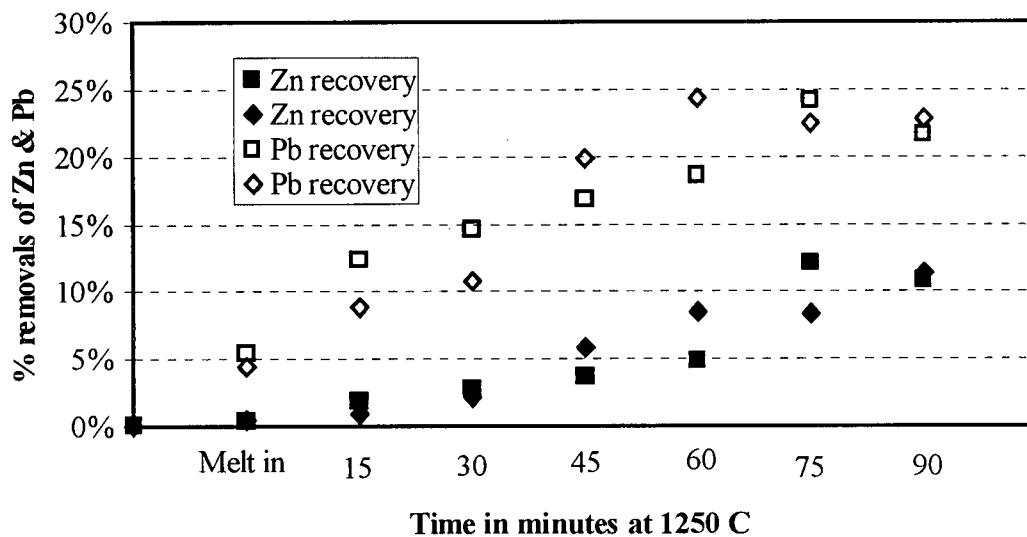
### *Equilibrating With Copper*

When 275 grams of the charge-mixture were melted with 150 grams of copper, the recovered zinc and lead reported to both the fume and the copper button. Reactions (1) to (7) were still possible, as well as the reactions:



After about 75 minutes, slag reduction, shown in Fig. 32, reached an apparent equilibrium at which about 10% of the zinc and 23% of the lead were recovered. A slightly higher metal recovery was obtained by using a copper getter.

Again, the total ion equivalents after melt-in decreased in a similar manner to the runs without copper (see Fig. 31). After 90 minute of melting, the total ion equivalents in the final slag was 0.27 lower than that in the original charge. The amount of carbon calculated to be in the slag, after considering metallic lead, was similar to that in holding without copper.



**Fig. 32: Metal recoveries in the holding runs with copper – Charge mix**

The weight of the copper button increased by 1.5 grams (average) with the composition shown in Table 12. The lead concentration at 1.4%, although lower than the result of FACT calculation (6%), was about 4 times higher than that of zinc and 133 times higher than that of iron. The copper loss to the slag was also lower than calculated above, only about 1.3 grams compared to the FACT calculation of 6.6 grams. As discussed earlier, the FACT calculation is sensitive to the amount of argon gas available to and in equilibrium with the system. In the experimental work, although the total volume of argon used was measured, the fraction in equilibrium with the system was not.

**Table 12: Analysis of the copper buttons – Charge mix**

<b>Conditions</b>	<b>Pb (%)</b>	<b>Zn (ppm)</b>	<b>Sb (ppm)</b>	<b>As (ppm)</b>	<b>In (ppm)</b>	<b>Ge (ppm)</b>	<b>Fe (ppm)</b>	<b>Cu</b>
Holding with copper	1.4	3143	492	512	214	<5	105	Remainder
Electrorefining	5.6	7731	2283	2195	404	<5	742	Remainder

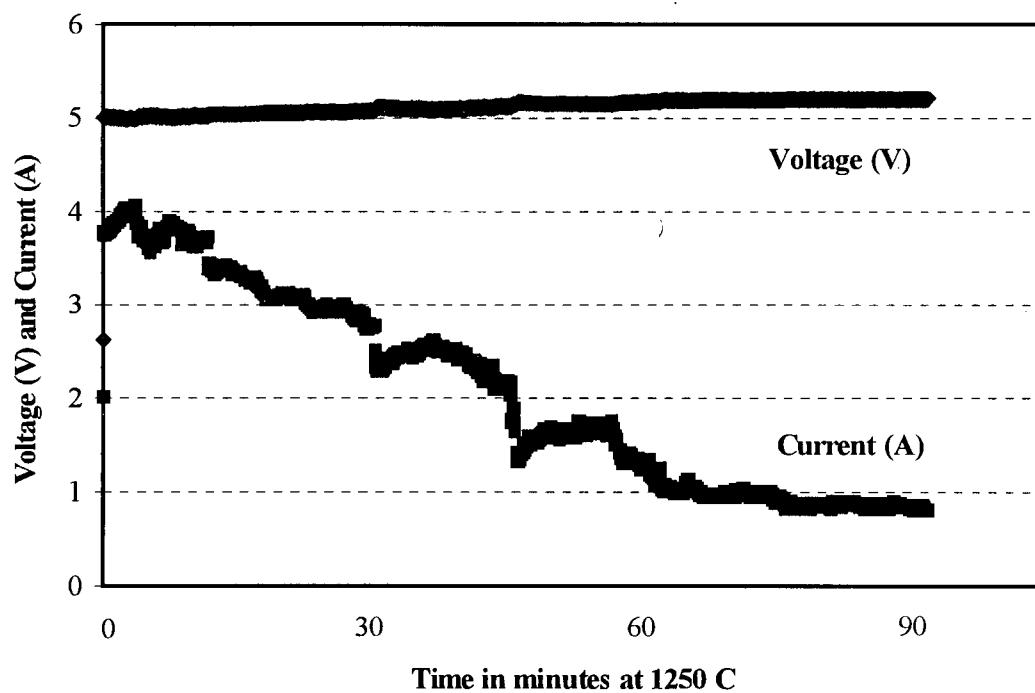
Zinc and lead balances shown in Table 13 indicated that, after 90 minutes, about 3.8 grams of zinc (9.8%) reported to the fume, while only 0.5 grams of zinc (1.3%) entered the copper button. However, the amount of lead in the fume (3.0 grams) was only slightly higher than that (2.1 grams) in the copper button. Although zinc activity in the copper melt is very low at 1250 °C, as indicated by the FACT calculation, both melting and boiling temperatures of zinc are very low, only 419.5 °C and 907 °C respectively, resulting in much more zinc in the fume. The melting point of lead is only 327 °C. Its boiling point, however, is 1740 °C. In addition, the lead activity at this concentration in the copper melt is also quite low. The total weight of the two metals in the fume was 6.8 grams, corresponding to an overall weight loss of 12 grams in the experiments.

**Table 13: Zinc and lead balance in holding with copper and electrorefining – Charge mix**

<b>Holding with copper</b>								
	Total		In the fume		In the copper		In the slag	
	Grams	%	Grams	%	Grams	%	Grams	%
Zinc Balance	38.4	100	3.8	9.8	0.5	1.3	34.1	89.0
Lead Balance	23.1	100	3.0	13.0	2.1	9.2	18.0	77.8
<b>Electrorefining</b>								
	Total		In the fume		In the copper		In the slag	
	Grams	%	Grams	%	Grams	%	Grams	%
Zinc Balance	38.4	100	3.4	8.8	1.2	3.2	33.8	88.0
Lead Balance	23.1	100	2.9	12.8	8.9	38.5	11.3	48.7

***Electrorefining with 5 volts***

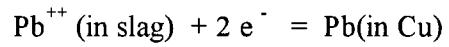
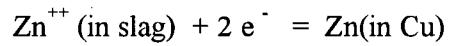
In the electroreduction runs, 275 grams of the charge-mixture and 150 grams of copper were melted and subjected to a voltage of 5 volts for 90 minutes. Similar to the electroreduction of fumer slags, the voltage increased slightly during the whole electrorefining period, while the current increased a little in the first five minutes and then decreased slowly (see Fig. 33).



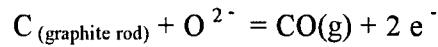
**Fig. 33: Typical potential and current in electrorefining – Charge mix**

In electrorefining, all of the reactions noted above might occur, as well as the half-cell reactions:

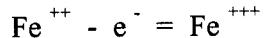
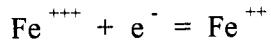
#### Cathode



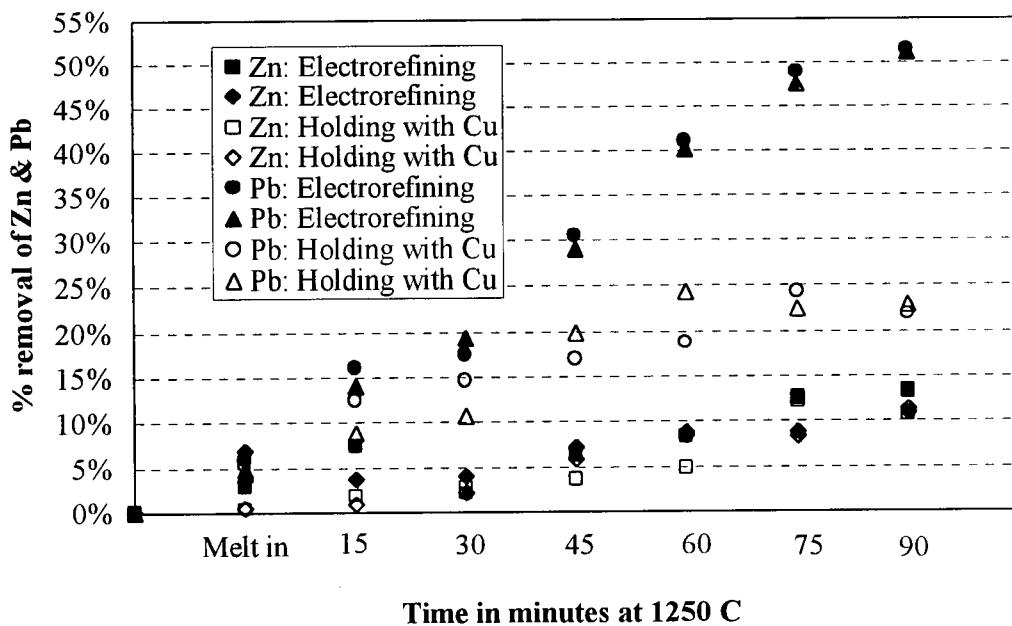
#### Anode



and the electronic conduction reactions:



Zinc and lead were still being removed from the slag after 90 minutes. About 3.4 grams of zinc had reported to the fume. This was nearly 3 times that (1.2 grams) in the copper button. However, the amount of lead in the fume at 3.0 grams was only about one third of that (8.9 grams) in the copper (see Table 13). The total weight of the zinc and lead in the fume was 6.4 grams, with an overall weight loss of 12.1 grams. Metal recoveries were compared with those in equilibrating with copper (see Fig. 34). The voltage applied clearly enhanced lead recovery. However, the effect on zinc recovery was not significant.

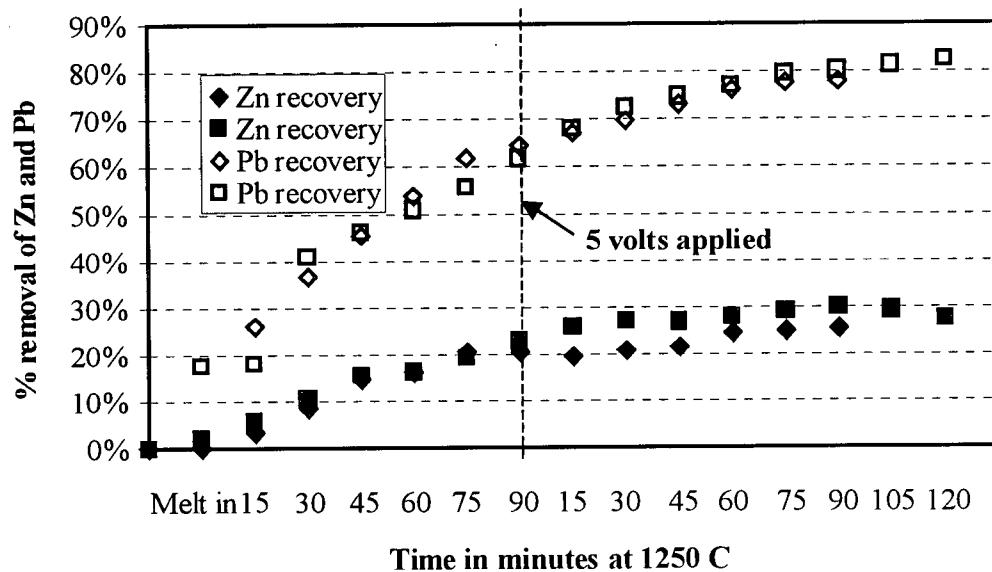


**Fig. 34: Comparison of metal recoveries in electrorefining and equilibrating with copper – Charge mix**

The weight of the copper button increased to 158.9 grams (average) with the composition shown in Table 12. Concentrations of lead, zinc, iron and the trace elements were much higher than those with no current applied, indicating a significant effect of the current. The copper loss was also quite low, only 2.1 grams.

As shown in Fig. 31, the moles of electrons per minute introduced decreased continually over the 90 minute period, although the voltage increased a little. Because of the metallic lead and carbon in the slag mentioned above, the decrease in the total ion equivalents from melt-in to 60 minutes was larger than the moles of electrons supplied. After 90 minutes, the total ion equivalents of the recovered Pb, Zn, Fe, As and Sb in the copper button, after being adjusted by that of the copper loss, was 0.12, very closed to the total amount of the electrons introduced (0.13 moles).

If the Kivcet slag was equilibrated with copper at 1250 °C for 90 minutes and then 5 volts was applied, zinc and lead continued to be removed from the slag. There was, however, no sharp change in metal recovery at the time when the voltage was applied. Fig. 35 shows the zinc and lead recoveries in this case.



**Fig. 35: Reduction of Kivcet slag in the electrorefining runs in which 5 volts was applied after 90 minutes**

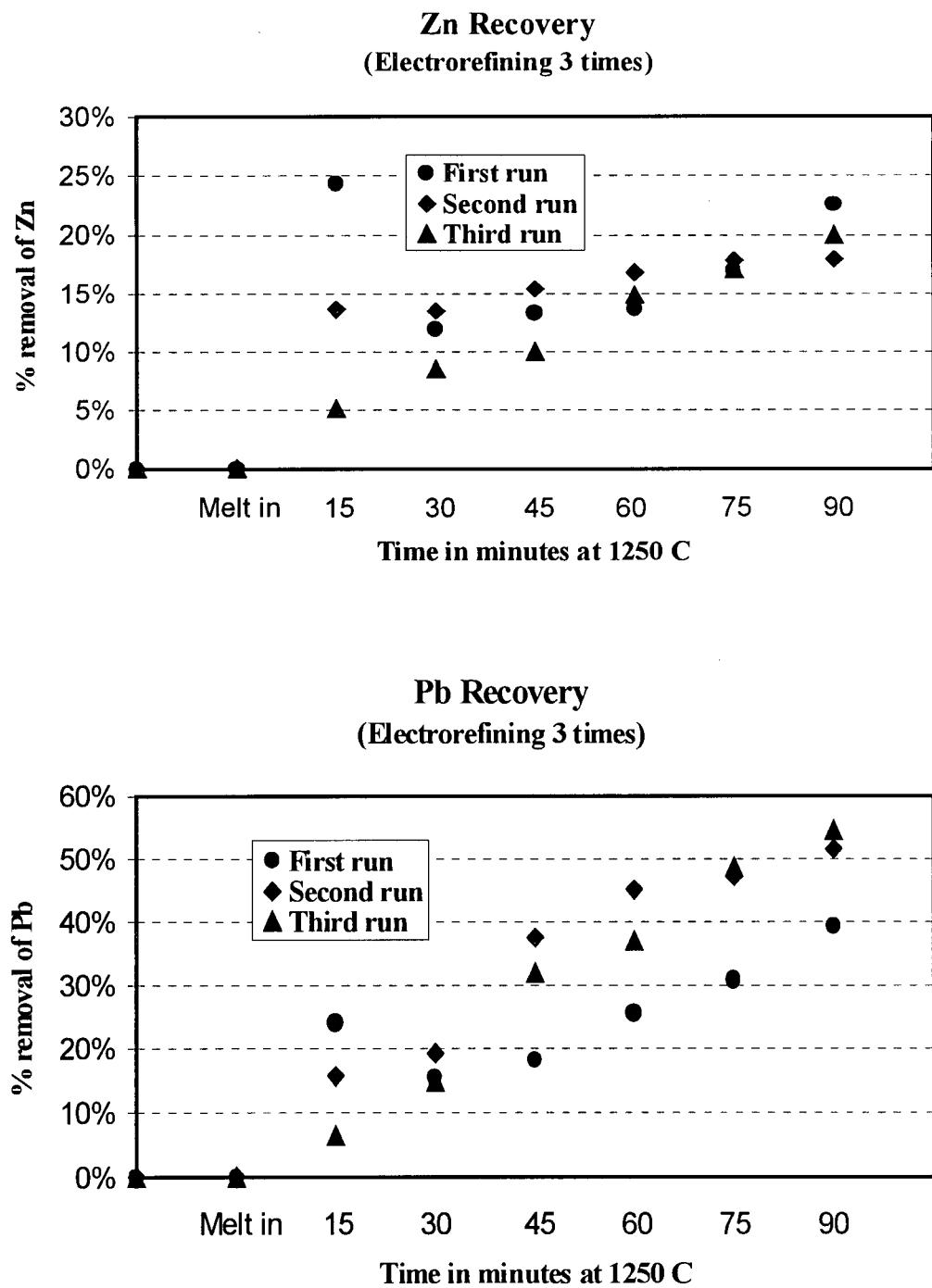
#### *Repeat Treatment of Kivcet Slag*

Kivcet slag was treated to remove some of the zinc and the lead. The slag produced contained 9.8% zinc and 2.3% lead. The slag basicity at 0.23 was similar to that of the final slags in Kivcet slag melting. After the treatment, there should be no metallic lead and carbon present in the slag produced.

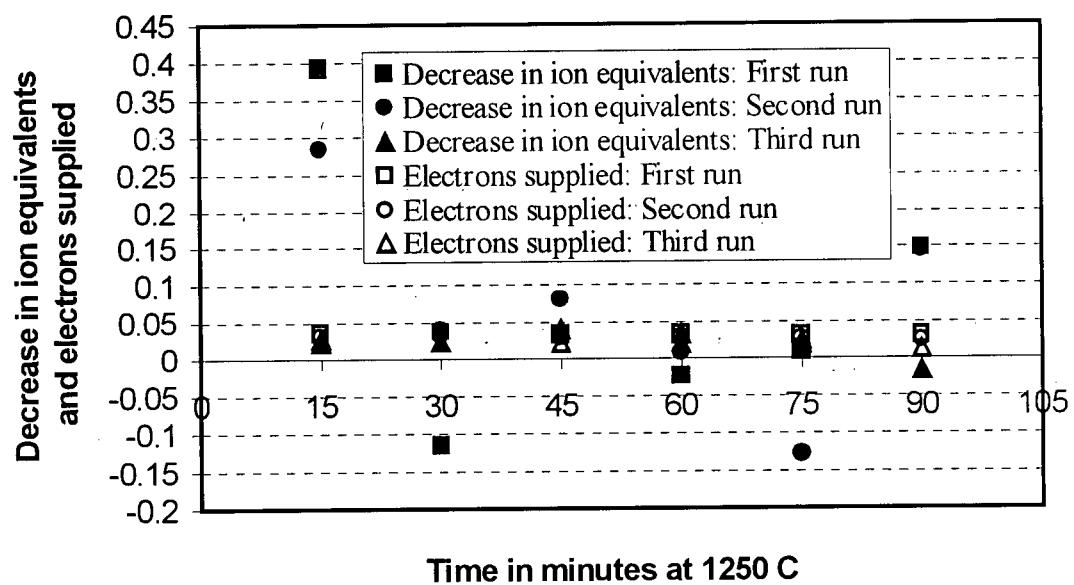
This produced slag was electro-refined with new copper and 5 volts three times (90 minutes each time). The increase in slag weight from crucible erosion was less than 5% in each run

and the effect of the newly dissolved crucible in each run was very small. After three treatments, although zinc and lead concentrations dropped to 5.9% and 0.3% respectively, metal recoveries in the third treatment were still high at about 20% of the zinc and 50% of the lead present after the second run (Fig. 36). Most of the lead in the slag was removed but the zinc content was still quite high. Further refining would still be required to recover the remaining zinc.

As shown in Fig. 37, the decrease in total ion equivalents was roughly equal to the moles of electrons supplied with some error particularly in the first sample taken. Total ion equivalents of the recovered metals (Zn, Pb and Fe) in the copper buttons in the first, second and third run were 0.22, 0.16 and 0.08 respectively, corresponding to 0.20, 0.17 and 0.12 moles of electrons supplied in the three runs respectively.



**Fig. 36: Metal recoveries from the slag during electrorefining 3 times**



**Fig. 37: Drop of ion equivalents and electrons (moles) supplied during electrorefining 3 times**

## 7.2. ELECTRICAL RESISTANCE MEASUREMENT

### *Slag Measurement*

At 1250 °C, two graphite rods were immersed into the liquid slag. The distance between the graphite rods was 2 cm or 4 cm. When a voltage was applied across the graphite rods, we can write following equations:

$$R_{\text{total-slag (2cm)}} = R_{\text{slag (2cm)}} + 2(R_{\text{contact-1}} + R_{\text{graphite}} + R_{\text{contact-2}}) \quad (\text{i})$$

$$R_{\text{total-slag (4cm)}} = R_{\text{slag (4cm)}} + 2(R_{\text{contact-1}} + R_{\text{graphite}} + R_{\text{contact-2}}) \quad (\text{ii})$$

$$R_{\text{slag (4cm)}} - R_{\text{slag (2cm)}} = R_{\text{total-slag (4cm)}} - R_{\text{total-slag (2cm)}} \quad (\text{iii})$$

where:  $R_{\text{total-slag (2cm)}}$  – the total resistance when the distance between the graphite electrodes was 2 cm

$R_{\text{total-slag (4cm)}}$  – the total resistance when the distance between the graphite electrodes was 4 cm

$R_{\text{slag (2cm)}}$  – the slag resistance when the distance between the electrodes was 2 cm

$R_{\text{slag (4cm)}}$  – the slag resistance when the distance between the electrodes was 4 cm

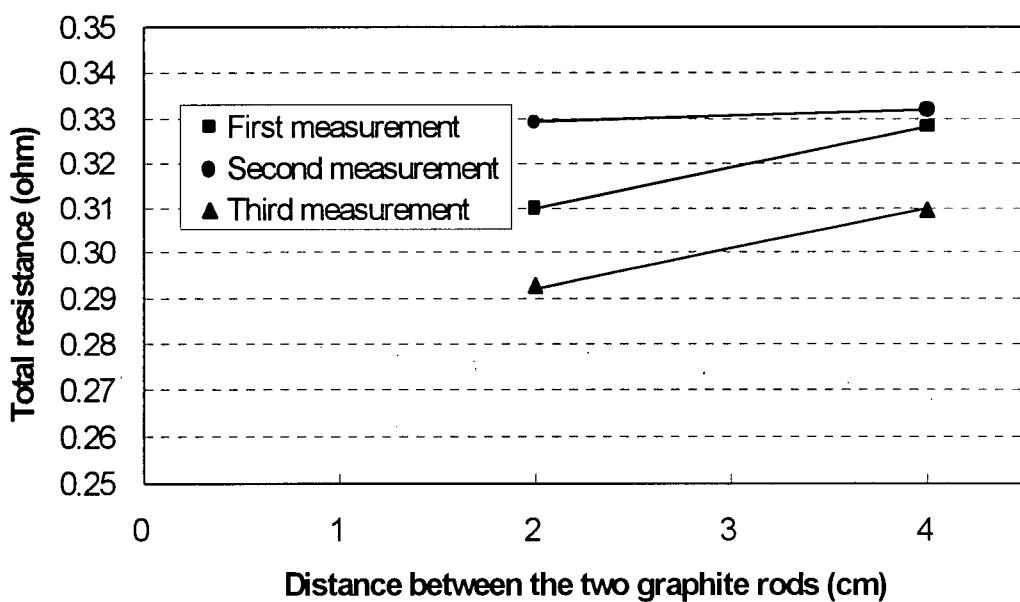
$R_{\text{graphite}}$  – the resistance of a graphite electrode

$R_{\text{contact-1}}$  – the contact resistance between a graphite electrode and a wire from the power supply

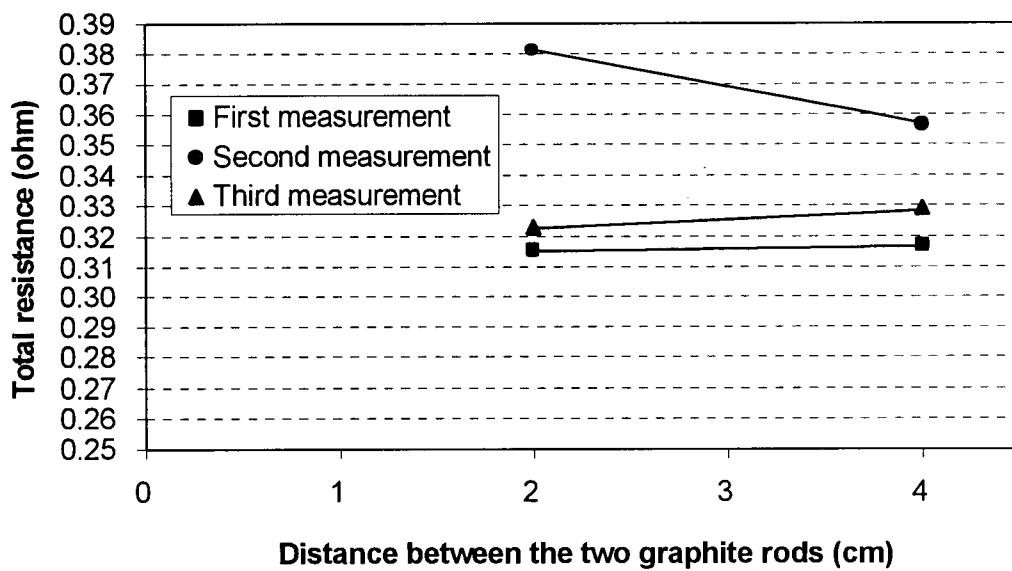
$R_{\text{contact-2}}$  – the contact resistance between a graphite electrode and the liquid slag

The total resistances,  $R_{\text{total-slag (2cm)}}$  and  $R_{\text{total-slag (4cm)}}$ , can be calculated using the voltage and the current readings. The results, shown in Fig.38, Fig.39 and Fig.40 indicated that, when the

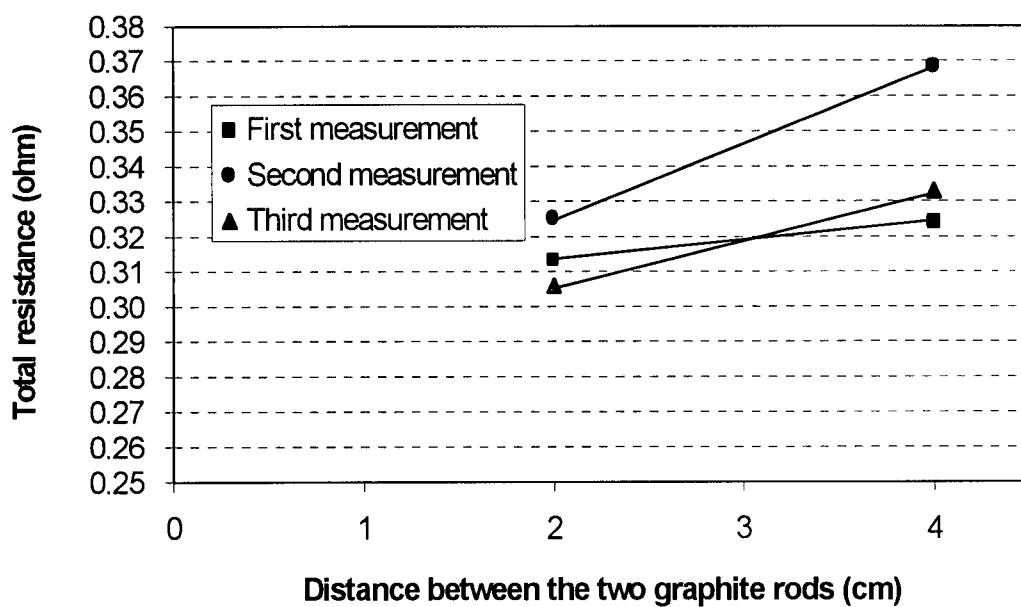
distance between the electrodes was increased from 2 cm to 4 cm, the total resistance increased by only 0.012 ohm (average) for the high residual fumer slag, 0.004 ohm for the low residual fumer slag, and 0.027 ohm for the Kivcet slag. In a measurement for the low residual fumer slag, the total resistance decreased with increasing the distance between the electrodes (see Fig.39). This group of data was not used in the above calculation. The increase in the total resistance was assumed to be equal to  $R_{\text{slag}(2\text{cm})}$ . When the distance between the electrodes was 2 cm, the ratio of the distance to the section area was similar to that of the slag zone in electrorefining. Therefore,  $R_{\text{slag}(2\text{cm})}$  was also assumed to be the slag resistance in electroreduction.



**Fig.38: Total electrical resistance in slag measurement – High residual fumer slag**



**Fig.39:** Total electrical resistance in slag measurement – Low residual fumer slag



**Fig.40:** Total electrical resistance in slag measurement – Kivcet slag

According to Equation (i), we have

$$R_{\text{contact-1}} + R_{\text{graphite}} + R_{\text{contact-2}} = \frac{1}{2}(R_{\text{total-slag (2cm)}} - R_{\text{slag (2cm)}}) \quad (\text{iv})$$

The left side of Equation (iv) was named anode resistance ( $R_{\text{anode}}$ ) in electrorefining. The calculation result indicated that  $R_{\text{anode}}$  was 0.150 ohm (average). This result can be confirmed by a measurement. When the two electrodes were lifted out of the liquid slag and their tips contacted each other with the voltage applying, the total resistance of the circuit was 0.264 ohm. In other words, the following equation is true:

$$R_{\text{contact-1}} + R_{\text{graphite}} + \frac{1}{2} R_{\text{contact-3}} = 0.132 \text{ ohm} \quad (\text{v})$$

where:  $R_{\text{contact-3}}$  – contact resistance between the two electrodes

The result in Equation (v) is a little smaller than that calculated using Equation (iv). A possible reason is that the value of  $\frac{1}{2}R_{\text{contact-3}}$  is smaller than that of  $R_{\text{contact-2}}$ .

### ***Copper Measurement***

In the copper measurement using two molybdenum electrodes, we can write the following equation:

$$R_{\text{total-Cu (2cm)}} = R_{\text{Cu (2cm)}} + 2(R_{\text{contact-4}} + R_{\text{Mo}} + R_{\text{contact-5}}) \quad (\text{vi})$$

$$R_{\text{total-Cu (4cm)}} = R_{\text{Cu (4cm)}} + 2(R_{\text{contact-4}} + R_{\text{Mo}} + R_{\text{contact-5}}) \quad (\text{vii})$$

$$R_{Cu(4cm)} - R_{Cu(2cm)} = R_{total-Cu(4cm)} - R_{total-Cu(2cm)} \quad (viii)$$

where:  $R_{total-Cu(2cm)}$  – the total resistance when the distance between the molybdenum electrodes was 2 cm

$R_{total-Cu(4cm)}$  – the total resistance when the distance between the molybdenum electrodes was 4 cm

$R_{Cu(2cm)}$  – the copper resistance when the distance between the molybdenum electrodes was 2 cm

$R_{Cu(4cm)}$  – the copper resistance when the distance between the molybdenum electrodes was 4 cm

$R_{Mo}$  – the resistance of a Mo electrode

$R_{contact-4}$  – the contact resistance between a molybdenum electrode and a wire from the power supply

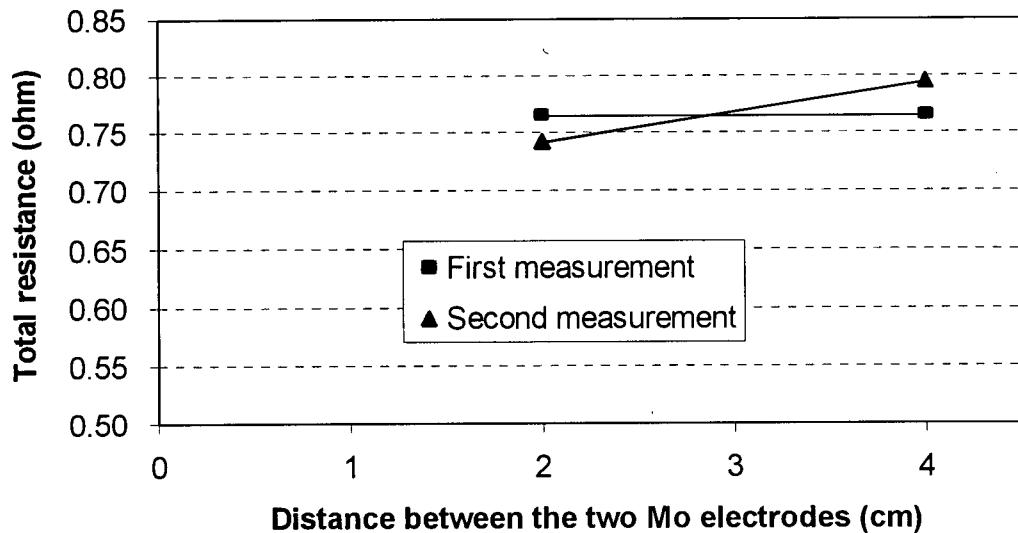
$R_{contact-5}$  – the contact resistance between a Mo electrode and the liquid copper

Again, the total resistances were calculated using the voltage and the current readings. The results shown in Fig. 41 indicated that, when the distance between the Mo electrodes was increased from 2 cm to 4 cm, the total resistance increased by 0 ohm in one measurement and 0.053 ohm in another measurement. The resistivity of copper at 1250 °C (about  $24 \times 10^{-8}$  ohm-m)<sup>33</sup> and the ratio of the distance to the section area in case of “2 cm copper zone” (about 25 m<sup>-1</sup>) suggest that  $R_{Cu(2cm)}$  is approximately  $6 \times 10^{-6}$  ohm.

Using Equation (vi), we have

$$R_{contact-4} + R_{Mo} + R_{contact-5} = \frac{1}{2}(R_{total-Cu(2cm)} - R_{Cu(2cm)}) \quad (ix)$$

The left side of Equation (ix) was called cathode resistance ( $R_{cathode}$ ) in electrorefining. The calculation result indicates that  $R_{cathode}$  is about 0.377 ohm.



**Fig.41: Total electrical resistance in copper measurement**

### ***Electrorefining Measurement***

In electrorefining, we can write

$$R_{total\_electro} = R_{anode} + R_{slag(electro)} + R_{interface} + R_{Cu(electro)} + R_{cathode} \quad (x)$$

where:  $R_{total\_electro}$  – the total resistance in electrorefining

$R_{slag(electro)}$  – the slag resistance in electrorefining

$R_{\text{interface}}$  – the resistance of the slag-copper interface

$R_{\text{Cu(electro)}}$  – the copper resistance in electrorefining

The total resistance,  $R_{\text{total -electro}}$ , can be calculated using the voltage and the current readings.

$R_{\text{anode}}$  and  $R_{\text{cathode}}$  have been defined in the slag and copper measurements.  $R_{\text{slag(electro)}}$  is equal to  $R_{\text{slag(2cm)}}$  as mentioned above. In electrorefining, the ratio of the distance to the section area in the copper zone is about  $10 \text{ m}^{-1}$  and the copper resistance,  $R_{\text{Cu(electro)}}$ , is almost zero. Having the above data, we can calculate the resistance of the slag-copper interface and determine voltage distribution in electrorefining. The results shown in Table 14 indicated that the resistances of the slags in electrorefining were very low. Most of the total voltage focused on the anode (about 15%), the slag-copper interface (40~50%) and the cathode (30~40%).

**Table 14: Voltage distribution in electrorefining**

<b>High Residual Fumer Slag</b>				
<b>Item</b>	<b>Resistance</b>		<b>Voltage</b>	
	<b>Ohm</b>	<b>%</b>	<b>Volts</b>	<b>%</b>
Total	1.107	100	5.000	100
Anode	0.150	14	0.678	14
Slag	0.013	1	0.059	1
Slag-copper interface	0.567	51	2.561	51
Copper	0.000	0	0.000	0
Cathode	0.377	34	1.703	34
<b>Low Residual Fumer Slag</b>				
<b>Item</b>	<b>Resistance</b>		<b>Voltage</b>	
	<b>Ohm</b>	<b>%</b>	<b>Volts</b>	<b>%</b>
Total	1.001	100	5.000	100
Anode	0.150	15	0.749	15
Slag	0.004	0	0.020	0
Slag-copper interface	0.470	47	2.348	47
Copper	0.000	0	0.000	0
Cathode	0.377	38	1.883	38
<b>Kivcet Slag</b>				
<b>Item</b>	<b>Resistance</b>		<b>Voltage</b>	
	<b>Ohm</b>	<b>%</b>	<b>Volts</b>	<b>%</b>
Total	0.975	100	5.000	100
Anode	0.150	15	0.771	15
Slag	0.027	3	0.138	3
Slag-copper interface	0.421	43	2.157	43
Copper	0.000	0	0.000	0
Cathode	0.377	39	1.933	39

## 8. CONCLUSIONS

Metal recovery from COMINCO's fumer slags and Kivcet slag under different conditions was tested in this study. Voltage distribution in electrorefining was also roughly defined. The following conclusions have been drawn.

### *Metal Recovery from the Fumer Slags*

- Even heating without copper, some zinc, lead and trace elements indium and germanium could be removed from the fumer slags. The main contents in the fume were zinc and lead oxides. Some trace elements (In, Ge) were also found.
- When copper was used as a “getter”, a higher lead recovery was obtained from high residual fumer slag. However, zinc recovery from both fumer slags was not improved. Some zinc and lead were recovered from the slags to the copper melt.
- In electrorefining, zinc and lead recoveries from high residual fumer slag were enhanced by the voltage applied. But the effect of current on metal recovery from low residual fumer slag was not noticeable. About 50% of the zinc and most of the lead were removed from the fumer slags by 90 minute of electroreduction. The zinc in the fumer slag could not be removed when its content was lower than about 0.5wt%.

### *Metal Recovery from the Kivcet Slag*

- FACT calculation indicated that the Kivcet slag has a significant self-reduction

potential. Metal recovery from the Kivcet slag will be influenced dramatically by the dissolution of the fireclay crucible.

- Simple holding of the charge-mixture (Kivcet slag was mixed with the crucible powder at a crucible/slag weight ratio of 1/10) at 1250 °C permits some zinc, lead and trace elements such as Sb, As, In, Ge to be recovered. The main content of the fume was zinc and lead oxides.
- When copper was used as a “getter”, zinc and lead recoveries were a little higher than those in holding without copper. About half of the recovered lead entered the copper, while most of the reduced zinc vaporized to fume.
- Lead recovery using electrorefining was improved over equilibration with copper. However, zinc recovery was not noticeably enhanced.
- Kivcet slag was treated to remove some of the zinc and the lead and then was electro-refined 3 times. Most of the lead was recovered. However, zinc concentration was still as high as 6%. Further treatment would be required.
- The experimental results were biased by the dissolution of the acidic crucible. Kivcet slag is very corrosive. A significant amount of the fireclay crucible dissolved into the slag at high temperature. Slag weight generally increased by 30%. Recoveries in an industrial system, where the activities of the principal metal oxides would be higher, would be expected to be better than those reported.

### ***Voltage Distribution in Electrorefining***

The resistances of the slags in electrorefining were very low. Most of the total voltage focused on the anode (about 15%), the slag-copper interface (40~50%) and the cathode (30~40%).

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**APPENDIX-1: ANALYSIS OF THE SLAG SAMPLES AND THE CRUCIBLE**





**CERTIFICATE OF ANALYSIS**  
**iPL 02H0885**

INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
Project: P.O.# 900354-0S

5 Samples  
5=CoarsePulp

[088508:44:12:20082902]

Sample Name	Pb ppm	Mg ppm	Mn ppm	Hg ppm	Mo ppm	Ni ppm	P ppm	K ppm	Sc ppm	Ag ppm	Na ppm	Sr ppm	Tl ppm	Ti ppm	W ppm	V ppm	Zn ppm	Zr ppm
OKIV	10%	3413	5097	<3	87	3	282	2252	2	41.6	2112	910	<10	623	<5	50	15%	58
NKIV	5.8%	4576	5036	<3	98	2	164	3482	2	3.0	3051	795	<10	798	<5	93	17%	58
OF	10952	4170	6570	<3	102	29	492	2248	3	7.3	2689	975	<10	968	<5	70	4.5%	79
NF	376	7382	9064	<3	150	25	501	4076	3	10.2	4747	1378	<10	1289	<5	96	2.9%	90
BRN	325	5907	7262	<3	124	<1	336	3995	3	5.9	3817	1167	<10	1252	<5	130	15326	84

Out: Aug 28, 2002  
In : Aug 14, 2002

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Minimum Detection  
Maximum Detection  
Method  
Ins=Insufficient Sample Del=Delay Max=No Estimate Rec=ReCheck m=1000 %Estimate % NS=No Sample  
No Test



**CERTIFICATE OF ANALYSIS**  
**iPL 03A0038**

INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
Project: CBMR 11R 81526

**2 Samples**  
**2=CoarsePulp**

Sample Name	Type	Fe+2 %	Fe+3 %	SiO2 %	Ge ppm	In ppm	Al ppm	Sb ppm	As ppm	Ba ppm	Bi ppm	Cd ppm	Ca ppm	Cr ppm	Co ppm	Cu ppm	La ppm	Fe ppm	La ppm
Barren : 1	CoarsePulp	30.65	0.76	30.28	24	<5	17283	571	282	5719	<2	<0.1	14*	352	117	3978	30%	17	
Barren : 2	CoarsePulp	30.96	0.51	29.75	44	<5	18413	634	267	6656	<2	<0.1	14*	369	123	4095	31%	17	

[003815:44:01:30011503]

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FM 64220	Page 1 of 1
Out: Jan 15, 2003	Section 1 of 2
In : Jan 13, 2003	

Minimum Detection  
 Maximum Detection  
 Method  
 ---=No Test Ins=Insufficient Sample Del=Delete Max=No Estimate Rec=ReCheck m=x 1000 %=Estimate % NS=No Sample



**CERTIFICATE OF ANALYSIS**  
**iPL 03A0038**

INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
Project: CBMR 11R 81526

**2 Samples**  
**2=CoarseSep1p**

Sample Name	Pb ppm	Mg ppm	Mn ppm	Hg ppm	Mo ppm	Ni ppm	P ppm	K ppm	Sc ppm	Ag ppm	Na ppm	Sr ppm	Tl ppm	Ti ppm	W ppm	V ppm	Zn ppm	Zr ppm
Barren : 1	206	5503	6994	<3	112	9	374	3846	3	5.2	3478	1073	<10	1135	<5	130	15421	71
Barren : 2	186	5799	7143	<3	120	8	410	3882	3	5.0	3640	1139	<10	1216	<5	138	15128	79

[003815:44:01:30011503]

Out: Jan 15, 2003

In : Jan 13, 2003

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Minimum Detection	2	100	1	3	1	100	100	1	0.1	100	1	10	100	5	2	1	1
Maximum Detection	20000	100000	100000	100000	10000	100000	100000	100000	1000.0	50000	100000	10000	10000	10000	10000	10000	10000
Method	IPL	IPL	IPL	IPL	IPL	IPL	IPL	IPL	IPL	IPL	IPL	IPL	IPL	IPL	IPL	IPL	IPL
No Test	InS=Insufficient Sample	Max=No Estimate	Det=Delay	Max=No Estimate	Det=Delay	ReC=ReCheck	n=n	m=m	%=%	Estimate %	n=n	m=m	1000	10000	100000	1000000	10000000

InS=Insufficient Sample Max=No Estimate Det=Delay ReC=ReCheck n=n m=m %=% Estimat % n=n m=m 1000 10000 100000 1000000 10000000 NS=No Sample



**CERTIFICATE OF ANALYSIS**  
**iPL 02L1341**

INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
Project: P.O.# 900334-0S

2 Samples  
2=Slag

Sample Name	Type	C (T) %	C (Org) %	C (Inorg) %	C Graphite %	Pb %	0x.Pb %
Kivcet Slag	Slag	0.02	0.01	<0.01	<0.01	10.320	9.52
Old Fumer Slag	Slag	0.05	0.01	0.03	<0.01	1.180	0.80



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Out: Dec 16, 2002

In: Dec 11, 2002

[13416:21:00:20121602]

Section 1 of 1

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Minimum Detection  
Maximum Detection  
Method  
—=No Test Ins=Insufficient Sample Del=Delay Max=No Estimate Rec=ReCheck m=x1000 %e=Estimate % NS=No Sample







**CERTIFICATE OF ANALYSIS**  
**iPL 02G0685**

INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
Project : B928F06 CBWR 713000

**60 Samples**  
**60=CoarsePulp**

Sample Name	Type	Fe+2 %	Fe+3 %	Si02 %	Ge ppm	In ppm	Al ppm	Sb ppm	As ppm	Ba ppm	Bi ppm	Cd ppm	Ca ppm	Co ppm	Cu ppm	Cr ppm	Fe ppm	La ppm
S 8-7	CoarsePulp	20.62	15.71	39.88	16	<5	5.2%	568	<5	3598	<2	<0.1	99375	413	76	1534	22%	35
S 8-8	CoarsePulp	20.50	7.36	39.09	25	<5	5.3%	536	<5	3664	<2	<0.1	10%	420	76	1440	22%	36
S 8-9	CoarsePulp	20.23	5.31	40.70	<5	<5	5.5%	536	<5	3703	<2	<0.1	10%	417	76	1442	22%	38
S 9-1	CoarsePulp	19.08	9.15	22.41	146	233	10079	0.3%	2855	4060	<2	45.0	91387	425	100	3205	22%	17
S 9-2	CoarsePulp	17.83	10.35	25.39	73	210	22451	0.3%	2416	3822	<2	2.0	88895	399	98	3018	21%	22
S 9-3	CoarsePulp	17.65	8.65	28.48	110	205	29979	0.3%	1898	3539	<2	<0.1	80074	92	73	2824	19%	26
S 9-4	CoarsePulp	17.45	4.52	30.33	89	164	34060	0.3%	1557	3523	<2	<0.1	79378	79	73	4212	19%	29
S 9-5	CoarsePulp	17.31	4.80	31.38	97	168	37714	0.3%	1309	3509	<2	<0.1	80434	87	73	2873	20%	30
S 9-6	CoarsePulp	16.99	5.61	32.91	49	157	42238	0.2%	1002	3557	<2	<0.1	79212	77	72	2795	19%	31
S 9-7	CoarsePulp	16.42	3.05	33.83	73	144	43328	0.3%	1140	3503	<2	<0.1	78493	81	70	3409	19%	31
S 9-8	CoarsePulp	16.25	6.88	32.37	58	173	38921	0.3%	1541	3483	<2	<0.1	79228	68	71	3102	19%	29
S 9-9	CoarsePulp	16.15	15.50	32.05	94	186	37476	0.3%	1615	3596	<2	<0.1	80120	68	73	3065	20%	29
S 10-1	CoarsePulp	18.17	14.39	23.07	144	230	10014	0.3%	2828	4270	<2	<0.1	9097	434	83	3351	23%	18
S 10-2	CoarsePulp	17.75	11.60	26.46	91	192	24487	0.3%	2310	3887	<2	<0.1	87409	360	97	360	21%	24
S 10-3	CoarsePulp	17.38	11.82	29.35	105	200	33921	0.2%	1920	3639	<2	<0.1	83279	102	75	2920	20%	28
S 10-4	CoarsePulp	16.45	4.72	39.24	74	166	44106	0.2%	1520	3495	<2	<0.1	77639	75	71	2728	19%	31
S 10-5	CoarsePulp	16.12	8.95	33.19	41	134	47527	0.2%	1083	3449	<2	<0.1	76645	69	68	2574	18%	33
S 10-6	CoarsePulp	14.25	9.43	34.16	35	125	5.0%	0.2%	995	3259	<2	<0.1	70669	65	65	4027	17%	33
S 10-7	CoarsePulp	14.43	5.39	34.93	76	182	5.2%	0.2%	1175	3052	<2	<0.1	67769	76	63	2350	16%	35
S 10-8	CoarsePulp	13.89	5.76	35.40	57	136	5.7%	0.2%	1130	2975	<2	<0.1	66373	84	65	2332	16%	37
S 10-9	CoarsePulp	13.60	5.32	37.12	22	131	6.0%	0.2%	1090	2917	<2	<0.1	66152	85	63	2270	16%	38

Out: Jul 11, 2002  
In : Jul 03, 2002

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Minimum Detection  
 Maximum Detection  
 Method  
 No Test Ins=Insufficient Sample Det=Detectable Rec=ReCheck  
 AsyMet AsyFus ICP-AQR ICP-HF ICP ICP NS=No Sample m=x 1000 % Estimate % ReCheck



INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
Project: BD28F06 CBNR 713000

# CERTIFICATE OF ANALYSIS

iPL 02G0685

## 60 Samples 60=coarsePulp

[068513:26:18:20071102]

Out: Jul 11, 2002  
In : Jul 03, 2002

Sample Name	Pb ppm	Mg ppm	Mn ppm	Hg ppm	Mo ppm	Ni ppm	P ppm	K ppm	Sc ppm	Ag ppm	Na ppm	Sr ppm	Tl ppm	Ti ppm	W ppm	V ppm	Zn ppm	Zr ppm
S 8-7	3466	3576	4763	<3	59	11	509	4066	11	0.7	2594	819	<10	3312	<5	108	2.2%	93
S 8-8	4086	3554	4879	<3	66	22	551	4083	11	<0.1	2617	825	<10	3509	<5	110	2.6%	94
S 8-9	4235	3688	4937	<3	63	14	532	4056	11	<0.1	2520	826	<10	3605	<5	111	2.7%	91
S 9-1	9.6%	3292	5037	<3	32	21	1134	2265	2	39.2	2523	926	<10	762	<5	42	16%	50
S 9-2	7.7%	3223	4758	<3	26	11	1064	2755	5	30.9	2484	916	<10	1451	<5	56	15%	64
S 9-3	7.1%	3108	4394	<3	46	24	425	3106	6	27.2	2376	865	<10	1915	101	76	13%	65
S 9-4	5.6%	3153	4367	<3	46	29	394	3245	8	0.2m	2273	868	<10	2356	68	82	13%	72
S 9-5	5.5%	3135	4413	<3	47	18	380	3337	8	21.6	2175	865	<10	2597	<5	85	13%	79
S 9-6	4.6%	3212	4299	<3	45	28	408	3594	9	1.1	2266	869	<10	2776	<5	89	11%	76
S 9-7	4.7%	3155	4225	<3	44	18	367	3594	9	0.2m	2296	868	<10	2877	<5	90	11%	80
S 9-8	5.7%	3085	4309	<3	45	28	421	3453	8	23.4	2178	863	<10	2617	<5	85	12%	66
S 9-9	5.9%	3205	4434	<3	46	20	398	3252	8	22.6	2165	853	<10	2576	<5	85	13%	58
S 10-1	9.1%	3450	5183	<3	56	19	424	2336	2	37.7	2549	968	<10	761	<5	56	16%	47
S 10-2	7.1%	3250	4792	<3	15	28	1099	2990	5	24.9	2433	911	<10	1546	<5	58	15%	59
S 10-3	6.7%	3218	4559	<3	50	29	418	3402	7	24.7	2384	900	<10	2342	<5	82	14%	59
S 10-4	5.7%	3152	4259	<3	39	25	409	3729	9	21.2	2209	854	<10	2952	<5	91	12%	68
S 10-5	4.8%	3159	4120	<3	42	18	381	3979	10	18.0	2948	845	<10	3101	<5	93	11%	70
S 10-6	4.3%	2982	3810	<3	39	47	354	4176	10	85.1	3353	800	<10	3324	<5	93	9.5%	89
S 10-7	4.9%	2962	3697	<3	37	13	299	3974	11	18.6	2024	764	<10	3479	<5	96	10%	93
S 10-8	4.6%	2876	3645	<3	38	27	362	4470	12	17.4	4380	764	<10	3739	<5	102	10%	89
S 10-9	4.7%	3004	3608	<3	36	28	392	4403	12	17.5	2106	769	<10	3878	<5	107	10%	58

Minimum Detection    2    100    1    1    100    100    1    0.1    100    1    10    100    5    2    1    1  
 Maximum Detection    20000    100000    10000    10000    10000    10000    10000    10000    10000    10000    10000    10000    10000    10000    10000    10000  
 Method    ICP    ICP  
 Ins=Insufficient Sample    Max=No Estimate    Del=Delay    Rec=ReCheck    m=x1000    %Estimate %    NS=No Sample

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**CERTIFICATE OF ANALYSIS**  
**iPL 02G0796**

Client : Metals & Materials Eng UBC  
Project: P.O. # 900354-0S

**128 Samples**  
**128=CoarsePulp**

Out: Aug 20, 2002  
In : Jul 29, 2002  
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Sample Name	Type	Fe+2 %	Fe+3 %	S+2 %	Ge ppm	In ppm	Al ppm	Sb ppm	As ppm	Ba ppm	Bi ppm	Cd ppm	Ca ppm	Cr ppm	Cu ppm	Co ppm	Fe ppm	La ppm
S 25-4	CoarsePulp	17.53	12.93	38.41	<5	<5	43682	134	<5	4754	<2	<0.1	10*	460	81	7098	24%	26
S 25-5	CoarsePulp	17.12	14.28	38.99	<5	<5	45286	252	<5	4638	<2	<0.1	10*	404	81	5712	23%	29
S 25-6	CoarsePulp	16.95	9.96	40.00	<5	<5	49443	87	<5	4628	<2	<0.1	10*	456	79	5044	23%	29
S 25-7	CoarsePulp	17.34	9.75	39.17	<5	<5	5.0%	103	<5	4475	<2	<0.1	99502	387	78	4802	22%	33
S 26-1	CoarsePulp	17.21	15.29	31.60	<5	<5	22744	0.3*	1203	5289	<2	<0.1	12*	457	167	13308	27%	21
S 26-2	CoarsePulp	17.15	13.23	35.23	<5	<5	34028	0.3*	720	5259	<2	<0.1	12*	412	119	13313	26%	24
S 26-3	CoarsePulp	17.11	14.59	34.93	<5	<5	36878	539	<5	5153	<2	<0.1	11*	419	86	4944	25%	26
S 26-4	CoarsePulp	16.11	12.60	36.39	<5	<5	42324	270	<5	4996	<2	<0.1	11*	455	76	3932	24%	26
S 26-5	CoarsePulp	18.94	8.65	35.96	<5	<5	45539	470	<5	4955	<2	<0.1	11*	441	73	5636	24%	30
S 26-6	CoarsePulp	18.72	8.24	36.83	<5	<5	47715	69	<5	4826	<2	<0.1	11*	462	69	3607	24%	30
S 26-7	CoarsePulp	19.00	6.82	37.45	<5	<5	49801	111	<5	4525	<2	<0.1	10*	404	66	4438	23%	29

Minimum Detection  
Maximum Detection  
Method  
---No Test Ins=Insufficient Sample Del=Delay Max=No Estimate AsyNet AsyFus ICPAQR ICPHF m=x1000 %=Estimate % Rec=ReCheck NS=No Sample

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**CERTIFICATE OF ANALYSIS**  
**iPL 02G0796**

INTERNATIONAL PLASMA LABORATORY LTD.  
Client : Metals & Materials Eng UBC  
Project: P.O.# 900354-05

**128 Samples**  
**128=coarsegrain**

Out: Aug 20, 2002  
In : Jul 29, 2002  
[079618:24:57:200082002]  
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Section 2 of 2

Sample Name	Pb ppm	Mg ppm	Mn ppm	Hg ppm	Mo ppm	Ni ppm	P ppm	K ppm	Sc ppm	Ag ppm	Na ppm	Sr ppm	Tl ppm	Ti ppm	W ppm	V ppm	Zn ppm	Zr ppm
S 25-4	121	4454	5136	<3	101	<1	249	4520	7	<0.1	3242	1094	<10	2446	<5	136	6790	101
S 25-5	101	4443	5058	<3	96	<1	297	4701	7	<0.5	3221	1080	<10	2571	<5	137	7124	102
S 25-6	123	4451	5032	<3	98	11	337	4690	8	<0.1	3316	1090	<10	2764	10	140	6781	107
S 25-7	96	4333	4849	<3	92	<1	339	5073	8	<0.1	3191	1054	<10	2814	<5	139	6750	110
S 26-1	212	4917	5964	<3	119	86	231	3890	3	18.0	3569	1197	<10	1423	<5	127	11202	84
S 26-2	120	4798	5669	<3	107	67	216	4385	5	17.6	3501	1181	<10	1994	7	132	5687	96
S 26-3	93	4714	5515	<3	106	9	317	4694	6	1.9	3521	1156	<10	2140	<5	135	5288	100
S 26-4	74	4563	5314	<3	103	<1	326	4644	7	<0.1	3419	1132	<10	2393	10	138	4471	103
S 26-5	77	4635	5344	<3	101	6	314	4778	7	<0.1	3426	1129	<10	2586	17	144	4924	109
S 26-6	96	4578	5252	<3	102	<1	301	4887	8	<0.1	3278	1114	<10	2703	13	145	5126	112
S 26-7	137	4356	4944	<3	96	<1	298	4685	8	<0.1	3202	1053	<10	2776	16	142	4995	113

Minimum Detection  
Maximum Detection  
Method  
Ins=Insufficient Sample Del=Delete Rec=ReCheck Max=No Estimate Min=Yes Estimate % m=1000 n=No Sample

113



**CERTIFICATE OF ANALYSIS**  
**iPL 02H0871**

INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
Project: P.O # 900354-0S

**27 Samples**  
**27=CoarsePulp**

[08/11/13:19:23:20082802]

Out: Aug 28, 2002  
In : Aug 14, 2002

Sample Name	Type	Fe+2 %	Fe+3 %	SiO2 %	Ge ppm	In ppm	Al ppm	Sb ppm	As ppm	Ba ppm	Bi ppm	Cd ppm	Ca ppm	Co ppm	Cu ppm	Cr ppm	La ppm
S 27-1	CoarsePulp	25.89	3.57	35.01	<5	<5	28084	273	<5	5429	<2	<0.1	12%	665	82	4182	26%
S 27-2	CoarsePulp	24.86	4.58	36.46	<5	<5	37418	444	<5	5372	<2	<0.1	12%	761	74	5628	24%
S 27-3	CoarsePulp	24.40	3.19	37.91	<5	<5	43602	181	<5	5386	<2	<0.1	12%	470	73	5142	24%
S 27-4	CoarsePulp	24.37	2.24	38.33	<5	<5	42562	113	<5	5018	<2	<0.1	11%	433	59	4858	22%
S 27-5	CoarsePulp	23.68	2.59	39.61	<5	<5	49890	217	<5	5196	<2	<0.1	11%	495	60	6666	23%
S 27-6	CoarsePulp	24.36	0.70	40.19	<5	<5	5.0%	88	<5	5030	<2	<0.1	11%	471	55	4730	22%
S 27-7	CoarsePulp	22.58	2.41	40.51	<5	<5	5.3%	22	<5	5060	<2	<0.1	11%	468	50	3504	22%
S 28-1	CoarsePulp	24.50	4.01	36.54	<5	<5	37226	227	<5	5639	<2	<0.1	12%	470	86	5186	25%
S 28-2	CoarsePulp	22.86	5.48	39.01	<5	<5	47292	193	<5	5379	<2	<0.1	12%	464	78	7575	23%
S 28-3	CoarsePulp	23.47	2.02	39.49	<5	<5	5.1%	169	<5	5013	<2	<0.1	11%	441	69	2.5%	22%
S 28-4	CoarsePulp	22.23	4.91	39.45	<5	<5	5.2%	56	<5	4801	<2	<0.1	11%	443	65	5592	22%
S 28-5	CoarsePulp	21.91	3.61	40.27	<5	<5	5.4%	24	<5	4716	<2	<0.1	10%	453	63	5530	21%
S 28-6	CoarsePulp	22.21	0.57	40.13	<5	<5	5.6%	18	<5	4711	<2	<0.1	11%	455	60	5090	22%
S 28-7	CoarsePulp	21.69	2.05	40.69	<5	<5	5.8%	10	<5	4713	<2	<0.1	11%	448	61	5484	21%
S 29- 1	CoarsePulp	24.84	1.89	36.67	<5	<5	42568	0.3%	<5	764	<2	<0.1	11%	469	106	2.2%	23%
S 29- 2	CoarsePulp	21.13	4.68	39.35	<5	<5	5.1%	215	<5	4807	<2	<0.1	11%	477	80	8585	22%
S 29- 3	CoarsePulp	21.26	2.10	39.55	<5	<5	5.4%	121	<5	4564	<2	<0.1	10%	405	76	8484	21%
S 29- 4	CoarsePulp	20.91	4.89	40.53	<5	<5	5.7%	59	<5	4490	<2	<0.1	10%	1106	78	7618	21%
S 29- 5	CoarsePulp	20.40	3.86	41.58	<5	<5	5.9%	32	<5	4397	<2	<0.1	98281	530	77	7929	20%
S 29- 6	CoarsePulp	20.17	4.31	41.07	<5	<5	6.1%	9	<5	4226	<2	<0.1	94468	435	75	8204	20%
S 29- 7	CoarsePulp	20.26	1.07	43.43	<5	<5	6.4%	18	<5	4225	<2	<0.1	93654	581	76	8526	19%
S 29- 8	CoarsePulp	20.38	4.52	44.71	<5	<5	6.4%	16	<5	4248	<2	<0.1	94446	554	76	8586	20%
S 29- 9	CoarsePulp	20.14	2.30	44.31	<5	<5	6.5%	7	<5	4151	<2	<0.1	92424	422	69	7918	19%
S 29-10	CoarsePulp	19.72	2.85	44.14	<5	<5	6.8%	11	<5	4100	<2	<0.1	91225	557	68	7553	19%
S 29-11	CoarsePulp	18.64	3.10	45.27	<5	<5	7.2%	18	<5	4006	<2	<0.1	88339	630	60	8916	18%
S 29-12	CoarsePulp	19.62	4.01	44.06	<5	<5	6.6%	33	<5	4141	<2	<0.1	92560	633	53	5506	18%
S 29-13	CoarsePulp	16.04	6.97	46.88	<5	<5	7.3%	19	<5	4228	<2	<0.1	94217	451	47	11380	16%

Minimum Detection  
Maximum Detection  
Method  
Ins=Insufficient Sample Del=Delay Max=No Estimate Rec=ReCheck m=x1000 n=NS=No Sample

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**CERTIFICATE OF ANALYSIS**  
**iPL 02L1340**

Client : Metals & Materials Eng UBC  
Project: P.O.# 900354-05

**18 Samples**

18=Slag

INTERNATIONAL PLASMA LABORATORY LTD.

[134016:55:03:20121802]

Sample Name	Type	Fe+2 %	Fe+3 %	Si02 %	Ge ppm	In ppm	Al ppm	Sb ppm	As ppm	Ba ppm	Bi ppm	Cd ppm	Ca ppm	Cr ppm	Cu ppm	Co ppm	Fe ppm	La ppm
S 38-1	Slag	16.90	11.96	22.91	145	246	12933	0.2%	2550	4054	<2	56.7	91597	442	80	3216	21%	19
S 38-2	Slag	18.07	11.41	25.24	163	251	21210	0.2%	2128	3889	<2	<0.1	87585	306	80	3072	21%	22
S 38-3	Slag	19.80	5.62	27.87	143	229	25565	0.1%	1465	3887	<2	<0.1	87576	268	78	2821	20%	23
S 38-4	Slag	19.88	5.39	29.58	140	223	29348	0.1%	1024	3722	<2	<0.1	84096	287	77	2633	20%	24
S 38-5	Slag	20.01	5.49	30.96	61	189	34089	0.2%	861	3744	<2	<0.1	84179	262	78	3637	20%	28
S 38-6	Slag	19.75	5.85	32.07	95	173	36004	0.1%	673	3642	<2	<0.1	81667	293	76	2713	19%	28
S 38-7	Slag	18.80	4.47	33.84	96	155	40638	0.1%	535	3629	<2	<0.1	80866	241	75	2781	18%	30
S 38-8	Slag	19.04	4.03	34.01	57	163	42444	0.1%	545	3589	<2	<0.1	80444	278	75	2841	18%	29
S 38-9	Slag	18.61	3.19	35.67	82	152	43854	0.1%	434	3530	<2	<0.1	78999	220	73	2761	18%	33
S 39-1	Slag	16.32	7.69	22.84	116	271	10654	0.2%	3064	4108	2	98.4	90784	444	82	3338	21%	17
S 39-2	Slag	17.89	5.64	27.30	141	235	26116	0.2%	240	3674	<2	<0.1	81438	292	77	6239	19%	23
S 39-3	Slag	17.22	5.38	30.23	134	235	34171	0.1%	1897	3579	<2	<0.1	79559	206	75	2923	18%	27
S 39-4	Slag	16.97	4.71	31.66	118	194	39867	0.1%	1812	3412	<2	<0.1	75843	150	71	2648	18%	29
S 39-5	Slag	15.42	4.99	32.81	73	170	43993	0.2%	1842	3115	<2	<0.1	70251	267	66	2357	16%	30
S 39-6	Slag	16.30	3.40	34.21	94	168	45255	0.1%	1359	3180	<2	<0.1	70520	174	68	2322	16%	30
S 39-7	Slag	16.84	2.49	36.27	71	136	5.2%	0.1%	816	3108	<2	<0.1	69705	314	83	1895	16%	36
S 39-8	Slag	16.78	1.42	37.79	64	118	5.6%	0.1%	715	3108	<2	<0.1	69752	275	81	1664	16%	36
S 39-9	Slag	17.14	1.20	38.69	56	102	5.7%	580	329	3119	<2	<0.1	69328	310	64	1427	16%	37

Minimum Detection	0.01	0.01	0.01	5	5	100	5	5	2	0.1	100	1	1	100	1	1	100	2
Maximum Detection	100.00	100.00	100.00	100000	100000	500000	10000	10000	2	100.0	100000	100.0	100000	10000	10000	100000	100000	2
Method	AsyNet	AsyNet	AsyNet	ICPAQR	ICPAQR	ICPAQR	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP
=No Test	Insufficient Sample	Del=Delay	Max=No Estimate	Rec=ReCheck	m=x1000	%=Estimate %	n=x1000	NS=No Sample										

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ISO 9002:1994  
FM 64220  
Out: Dec 18, 2002  
In : Dec 11, 2002  
Page 1 of 2  
Section 2 of 2

# CERTIFICATE OF ANALYSIS

## iPL 02L1340

Client : Metals & Materials Eng UBC  
Project: P.O. # 900354-0S

### 18 Samples

INTERNATIONAL PLASMA LABORATORY LTD.

Sample Name	Pb ppm	Mg ppm	Mn ppm	Hg ppm	Mo ppm	Ni ppm	P ppm	K ppm	Sc ppm	Ag ppm	Na ppm	Sr ppm	Tl ppm	Ti ppm	W ppm	V ppm	Zn ppm	Zr ppm
S 38-1	9.1%	3344	5061	<3	72	29	356	2378	3	40.9	2140	890	<10	847	<5	56	15%	40
S 38-2	7.6%	3298	4851	<3	72	18	372	2698	5	26.6	2029	871	<10	1319	<5	67	15%	38
S 38-3	6.1%	3302	4847	<3	71	18	360	2796	5	18.1	1997	857	<10	1551	<5	71	14%	41
S 38-4	5.2%	3294	4656	<3	71	19	371	2902	6	11.4	1964	851	<10	1815	<5	77	13%	38
S 38-5	5.1%	3250	4635	<3	71	36	351	3219	7	39.4	2018	865	<10	2056	<5	84	12%	17
S 38-6	4.3%	3233	4502	<3	65	18	385	3847	8	8.9	2344	841	<10	2184	<5	85	12%	90
S 38-7	3.8%	3184	4408	<3	63	5	377	3619	8	11.8	2027	838	<10	2425	<5	90	11%	40
S 38-8	4.1%	3350	4392	<3	70	25	333	3509	9	12.6	2006	850	<10	2551	<5	94	11%	25
S 38-9	3.6%	3190	4242	<3	61	12	296	3817	9	25.5	1947	819	<10	2608	<5	93	10%	34
S 39-1	10.0%	3270	5088	<3	82	27	389	2272	3	47.3	2180	899	<10	719	<5	54	16%	41
S 39-2	7.2%	3195	4510	<3	71	31	369	2669	6	0.3m	1938	831	<10	1617	<5	73	14%	38
S 39-3	6.5%	3130	4382	<3	80	20	322	3077	7	28.6	1908	833	<10	2062	<5	82	13%	38
S 39-4	6.2%	2987	4185	<3	66	12	298	3365	8	26.8	1889	793	<10	2407	<5	88	12%	53
S 39-5	5.6%	2808	3728	<3	72	17	349	3791	9	21.6	1943	764	<10	2695	<5	89	11%	67
S 39-6	5.2%	2922	3870	<3	62	22	283	3445	9	18.3	1913	768	<10	2759	<5	95	11%	91
S 39-7	4.0%	3010	3852	<3	<1	19	841	3890	11	13.2	1985	769	<10	3190	<5	98	9.7%	110
S 39-8	3.5%	3100	3839	<3	7	50	852	4081	12	11.8	2070	773	<10	3378	<5	101	9.0%	117
S 39-9	2.7%	3044	3837	<3	6	50	295	4081	12	8.2	1860	769	<10	3423	<5	114	8.3%	92

Method	Insufficient Sample	Max=No Estimate	Min=No Estimate	Del=Delay	ReCheck	n=1000	%=Estimate %	ICP										
=No Test																		





**iPL**

INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
Project: BD28F06 CBR 7130000

**44 Samples**  
*44=CoarsePulp*

Sample Name	Type	Fe+2 %	Fe+3 %	S102 %	Ge ppm	In ppm	Al ppm	Sb ppm	As ppm	Ba ppm	Bi ppm	Cd ppm	Ca ppm	Cr ppm	Co ppm	Cu ppm	Fe ppm	La ppm
S 45-3	CoarsePulp	17.00	4.35	29.27	102	564	35143	1963	1981	3391	<2	5.5	81524	195	63	2659	18x	22
S 45-4	CoarsePulp	16.53	5.48	31.37	99	540	40352	0.2x	1778	3368	<2	<0.2	79523	223	61	4277	18x	23
S 45-5	CoarsePulp	15.65	6.67	33.10	58	472	43732	1753	1366	3122	<2	<0.2	75181	207	58	2560	17x	24
S 45-6	CoarsePulp	15.34	4.70	34.73	62	459	46403	1752	1356	2931	<2	<0.2	71539	201	57	2318	16x	26
S 45-7	CoarsePulp	15.01	5.38	37.56	31	427	5.3x	1647	1246	2841	<2	<0.2	68445	165	55	2251	15x	27

**CERTIFICATE OF ANALYSIS**  
**iPL 03C0357**

[035709:50:30:30041003]																			
Out: Apr 10, 2003 In : Mar 26, 2003																			
FM 84220 ISO 9002:1994																			
Method	Max=Detection	Min=Detection	AsyNet	AsyFus	ICPAQR	ICPHF	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP
=No Test	In=Insufficient Sample	Del=Delay	Max=No Estimate	Min=Estimate %	m=x1000	%=ReCheck	m=x1000	%=ReCheck	m=x1000	%=No Sample									
0.01	0.01	0.01	5	5	100	5	2	2	0.2	100	1	1	100	1	100	1	100	2	
100.00	100.00	100.00	100.00	100.00	50000	20000	20000	20000	20000	100000	100000	100000	100000	100000	100000	100000	100000	100000	

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Minimum Detection  
Maximum Detection  
Method  
=No Test In=Insufficient Sample Del=Delay Max=No Estimate Min=Estimate % m=x1000 %=ReCheck m=x1000 %=No Sample

**iPL**

INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
Project: BD28F06 CBWR 713000

**CERTIFICATE OF ANALYSIS**  
**iPL 03C0357**

**44 Samples**  
**44-Coarseulp**

Sample Name	Pb ppm	Mg ppm	Mn ppm	Hg ppm	Mo ppm	Ni ppm	P ppm	K ppm	Sc ppm	Ag ppm	Na ppm	Sr ppm	Tl ppm	Ti ppm	W ppm	V ppm	Zn ppm	Zr ppm
S 45-3	7.2*	2944	4154	<3	45	20	396	3042	7	25.8	1482	743	<10	2282	<5	78	12*	66
S 45-4	6.5*	2964	4087	<3	43	14	334	3245	8	73.8	1469	728	<10	2602	<5	83	12*	74
S 45-5	5.6*	2827	3808	<3	39	19	322	3412	8	20.6	1437	700	<10	2765	<5	85	11*	74
S 45-6	5.6*	2744	3636	<3	36	18	304	3559	9	20.2	1479	678	<10	2957	<5	88	11*	89
S 45-7	5.4*	2715	3497	<3	35	19	298	3882	10	17.7	1361	662	<10	3334	<5	93	10*	91

Ins=Insufficient Sample Del=Delay Max=No Estimate Rec=RecCheck m=x(000) %Estimate % NS=No Sample

Method ICP ICP

No Test

ISO 9002:1994 FM 84220 Out: Apr 10, 2003 In : Mar 26, 2003

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Page 2 of 2

Section 2 of 2



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Page 2 of 2

Section 2 of 2

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INTERNATIONAL PLASMA LABORATORY LTD.  
Metals & Materials Eng UBC  
Object : P0# 900354.0S

# CERTIFICATE OF ANALYSIS

## iPL 02H0886

### 1 Samples

1-Crucible

ISO 2002  
Vancouver, B.C.  
Canada V5Y 3E1  
Phone (604) 879-7878  
Fax (604) 879-7898  
Email ipl@direct.ca

Out: Aug 29, 2002  
In: Aug 15, 2002

[088617:46:01:20082902]

sample Name	Type	A1203	BaO	CaO	Fe2O3	K2O	MgO	MnO	Na2O	P2O5	S1O2	TiO2	LOI	Total
RU	Crucible	35.78	0.01	0.23	1.24	0.99	0.38	0.01	1.34	0.09	56.96	1.98	0.40	99.41

minimum Detection	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	
maximum Detection	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
Method	WRock	WRock	WRock	WRock	WRock	WRock	WRock	WRock	WRock	WRock	WRock	WRock	WRock	WRock	
—No Test	In=Insufficient Sample	Del=Delay	Max=No Estimate	Rec=ReCheck	NS=No Sample	m=x1000	%=Estimate %								

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**APPENDIX-2: ANALYSIS OF THE FUME SAMPLES**









**CERTIFICATE OF ANALYSIS**  
**iPL 02G0797**

INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
 Project: P.O.# 900354-0S

**8 Samples**  
**8-Pulp**

Sample Name	Mg ppm	Mn ppm	Hg ppm	Mo ppm	Ni ppm	P ppm	K ppm	Sc ppm	Ag ppm	Na ppm	Sr ppm	Tl ppm	Ti ppm	W ppm	V ppm	Zn ppm	Zr ppm
F 19-1	218	8	<3	36	<1	<100	628	4	38.5	178.9	53	192	<100	<5	<2	21*	<1
F 19-2	<100	8	<3	6	4	505	<100	2	18.3	952	226	<10	730	<5	19	37*	15
F 20-1	<100	1	<3	7	<1	798	<100	<1	6.0	750	<1	87	<100	<5	<2	42*	<1
F 20-2	<100	11	<3	<1	5	662	304	2	21.0	987	355	<10	1235	<5	22	29*	25
F 23-1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
F 24-1	<100	2	<3	61	9	<100	<100	<1	0.1m	1669	3	177	<100	70	<2	31*	<1
F 25-1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
F 26-1	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

[079717:07:37:20082002] Out: Aug 20, 2002 In : Jul 29, 2002

Page 1 of 2  
 Section 2 of 2



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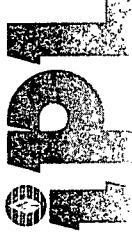
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Method	Detection	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP
Maximum Detection	100	1	3	1	100	1	100	1	0.1	100	1	10	100	5	2	1	1
Insufficient Sample	100000	10000	10000	10000	50000	100000	100000	10000	500000	100000	10000	10000	100000	10000	20000	100000	100000
Del=Delay	Max=No Estimate	Rec=ReCheck	m=1000	%=Estimate %	NS=No Sample												

\* = No Test    Ihs = Insufficient Sample

**APPENDIX-3: ANALYSIS OF THE COPPER BUTTONS**





INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
Project: B028F06 CBWR 7130007 Samples  
7=Drilling

**CERTIFICATE OF ANALYSIS**  
**IPL 02G0687**

2036 Columbia Street  
Vancouver, B.C.  
Canada V5Y 3E1  
Phone (604) 879-7878  
Fax (604) 879-7898  
Email ipl@direct.caOut: Jul 11, 2002  
In : Jul 03, 2002

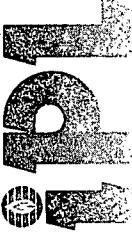
[068713:27:41:2007/102]

Sample Name	Mg ppm	Mn ppm	Hg ppm	Mo ppm	Ni ppm	P ppm	K ppm	Sc ppm	Ag ppm	Na ppm	Sr ppm	Tl ppm	Ti ppm	W ppm	V ppm	Zn ppm	Zr ppm
CB-1	<100	3	<3	2	42	<100	213	9	30.7	308	<1	<10	<100	235	4	16879	<1
CB-2	<100	1	<3	2	35	<100	103	9	31.0	539	<1	<10	<100	267	4	16970	5
CB-3	<100	3	<3	4	38	<100	100	9	35.1	218	<1	<10	<100	263	4	19323	9
CB-5	<100	1	<3	3	13	<100	100	9	58.8	237	<1	<10	<100	271	4	11204	3
CB-11	<100	2	<3	5	65	<100	<100	8	0.1m	229	<1	<10	<100	276	3	4053	5
CB-12	<100	<1	<3	2	20	<100	<100	9	31.3	369	<1	<10	<100	303	4	11213	29
CB-13	<100	1	<3	4	7	<100	<100	10	30.0	266	<1	<10	<100	298	3	6151	8

Minimum Detection	100	1	3	1	100	100	1	0.1	100	100	1	10	100	5	2	1	1
Maximum Detection	100000	10000	10000	1000	100000	100000	100000	100.0	500000	100000	100000	10000	10000	10000	20000	100000	100000
Method	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP
=No Test	Insufficient Sample	Def=Delay	Max=No Estimate	Min=No Estimate	RecCheck	m=x1000	%=Estimate %	NS=No Sample									

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INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
 Project: P.O.# 900354-0S

# CERTIFICATE OF ANALYSIS

## IPL 02G0798



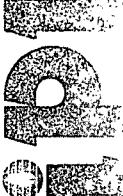
### 11 Samples 11=Drilling

Out: Aug 20, 2002  
 In : Jul 29, 2002  
 [079817:07:29:2008002]  
 Page 1 of 1  
 Section 2 of 2

Sample Name	Mo ppm	Ni ppm	P ppm	K ppm	Sc ppm	Ag ppm	Na ppm	Sr ppm	Tl ppm	Ti ppm	W ppm	V ppm	Zn ppm	Zr ppm
CB-14	19	<1	<100	13	3.2	240	<1	11	<100	340	7	<1	<1	<1
CB-15	18	52	<100	12	85.6	257	<1	50	<100	328	5	8328	<1	<1
CB-16	17	31	<100	12	10.8	259	<1	29	<100	194	7	3.2*	<1	<1
CB-17	17	11	<100	217	14	3.8	285	<1	40	<100	295	7	2.5*	<1
CB-18	23	5	<100	13	2.7	295	1	52	<100	331	7	14337	<1	<1
CB-19	20	50	<100	202	14	12.4	296	<1	50	<100	390	8	3382	<1
CB-20	19	35	<100	13	11.6	259	3	33	<100	363	7	2697	<1	<1
CB-21	18	21	<100	12	38.9	355	1	62	<100	318	6	12745	<1	<1
CB-22	17	27	<100	358	12	39.9	302	<1	57	<100	307	6	13233	<1
CB-25	22	44	<100	13	9.9	296	4	38	<100	347	9	3331	<1	<1
CB-26	19	41	<100	13	8.8	262	<1	<10	<100	327	8	5316	<1	<1

Minimum Detection 1 1000 10000 50000 100000 100000 100.0 100000 100000 1000 10000 10000 10000 10000 10000 10000  
 Maximum Detection ICP  
 Method Max=No Estimate Rec=RecCheck Del=Delay Max=x1000 %Estimate % NS=No Sample  
 ---=No Test Ins=Insufficient Sample

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INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
Project: P.O.# 900354-JS3 Samples  
3=Metal Bar

Sample Name	Type	Ge ppm	In ppm	Al ppm	Sb ppm	As ppm	Ba ppm	Bi ppm	Cd ppm	Ca ppm	Cr ppm	Co ppm	Cu ppm	Fe ppm	La ppm	Pb ppm	Mg ppm	Mn ppm	Hg ppm
CB-27	Metal Bar	78	<5	246	0.1%	511	24	<2	<0.1	833	3	125	96%	25455	<2	324	<100	38	<3
CB-28	Metal Bar	92	<5	273	0.1%	540	21	<2	<0.1	822	9	112	97%	16602	<2	336	<100	37	<3
CB-29	Metal Bar	41	<5	<100	0.1%	429	<2	<2	<0.1	264	6	73	97%	42937	<2	386	<100	12	<3

## CERTIFICATE OF ANALYSIS

iPL 02H0888

3 Samples 3=Metal Bar		[088813:18:45:20082802]	Out: Aug 28, 2002	In : Aug 14, 2002	Page 1 of 1	Section 1 of 2													
CB-27	Metal Bar	78	<5	246	0.1%	511	24	<2	<0.1	833	3	125	96%	25455	<2	324	<100	38	<3
CB-28	Metal Bar	92	<5	273	0.1%	540	21	<2	<0.1	822	9	112	97%	16602	<2	336	<100	37	<3
CB-29	Metal Bar	41	<5	<100	0.1%	429	<2	<2	<0.1	264	6	73	97%	42937	<2	386	<100	12	<3

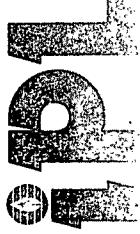
2036 Columbia Street  
Vancouver, B.C.  
Canada V5Y 3E1  
Phone (604) 879-7878  
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Email ipl@direct.ca

Minimum Detection	5	5	100	5	5	2	0.1	100	1	100	2	100	1	100	2	100	1	3
Maximum Detection	10000	10000	50000	1000	100000	100000	10000	100000	100000	100000	100000	500000	100000	200000	100000	100000	100000	100000
Method	ICPAQR	ICPAQR	ICPF	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP	ICP

Ins=Insufficient Sample Det=Delay Max=No Estimate Rec=ReCheck m=x1000 %Estimate % NS=No Sample

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=====  
 No Test Ins=Insufficient Sample Det=Delay Max=No Estimate Rec=ReCheck m=x1000 %Estimate % NS=No Sample



INTERNATIONAL PLASMA LABORATORY LTD.

Client : Metals & Materials Eng UBC  
Project: P.O.# 900354-0S

# CERTIFICATE OF ANALYSIS

## iPL 02H0888



### 3 Samples 3=Metal Bar

Sample Name	Mo ppm	Ni ppm	P ppm	K ppm	Sc ppm	Ag ppm	Na ppm	Sr ppm	Tl ppm	Ti ppm	W ppm	V ppm	Zn ppm	Zr ppm
CB-27	23	51	<100	113	13	8.6	473	7	<10	<100	<5	9	8386	<1
CB-28	24	60	<100	259	14	10.2	519	7	<10	<100	<5	11	7240	2
CB-29	39	60	<100	<100	13	9.7	502	2	<10	<100	<5	8	5714	3

Out: Aug 28, 2002  
In : Aug 14, 2002

[088813:18:45:20082802]

Page 1 of 1  
Section 2 of 22036 Columbia Street  
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Minimum Detection	Detection	1	1	100	100	0.1	100	1	10	100	5	2	1	1
Maximum Detection	Method	1000	10000	50000	100000	100000	50000	100000	10000	100000	1000	10000	20000	10000
=No Test	Insufficient Sample	Del=Delay	Max=No Estimate	Max=Estimate	Rec=ReCheck	m=>1000	%=Estimate %	NS=No Sample						



