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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
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## Abstract

This thesis investigates parameters influencing the concentration of aqueous tin in acidic sulphate solutions containing Fe(III/II) as they arise in the Reduction Releach process at Teck Cominco Trail Operations (TCML). This study documents the impact of initial sulphuric acid and As(V) concentrations, temperature, and lead concentrate reductant amount on tin solubility in acidic Fe(III/II) sulphate solutions as they arise in an intermediate leaching step at TCML. Supporting test work examined the speciation of commercial tin bearing residues involved in the processing of indium and germanium. Analysis of these residues determined the oxidation state of crystalline tin in ZnO fume, Ge Preconcentrate, and Releach residue to be primarily Sn(IV), and associated with zinc, lead, and iron oxides; in addition to lead, iron, and aluminum silicates, and minor amounts of Sn(II) as SnO or SnSO<sub>4</sub>.

Experimental validation of Sn(II) solubility values in 100 g/L H<sub>2</sub>SO<sub>4</sub>, between 30 to 90 °C, compared well with literature and theoretical tin solubility values. Measured tin solubility values ranged between 95 g/L Sn and 99 g/L Sn concentration. The aqueous tin concentration decreased slightly (4 g/L Sn) when the temperature was increased from 30 to 90 °C. Measured aqueous tin values for both thesis benchscale test work and commercial Reduction Releach process were all less than 1 g/L Sn. The oxidation rate of Sn(II) between 300 mg/L and 700 mg/L in 100 g/L H<sub>2</sub>SO<sub>4</sub> at 20 °C, was first order kinetics with a rate constant ranging between 0.0002 and 0.0003 mg Sn/L·s, and the REDOX potential (Eh) varied between 550 and 650 mV. The low rate constants may have been due to poor mass transfer. Iodometry could not be used for aqueous tin analysis with other divalent and trivalent cations present in solution and, therefore, inductive coupled plasma analysis was used.

Higher acidities promote tin solubility, as predicted by Pourbaix (1966). The terminal tin concentrations compare well with previously reported literature values for similar solutions (Brubaker, 1955). Acidity impacts tin precipitation kinetics. At starting acidities below 220 g/L H<sub>2</sub>SO<sub>4</sub>, tin precipitation was second order (rate constants ranged from 0.0004 to 0.0009 1/mg Sn/min·L). At 220 g/L H<sub>2</sub>SO<sub>4</sub>, tin precipitation was first

order (rate constants ranged from 0.0072 to 0.0146 min<sup>-1</sup>). The tin re-dissolution observed with the benchscale thesis tests at 220 g/L H<sub>2</sub>SO<sub>4</sub> initial acidity did not occur with the observed tin dissolution in the commercial Releach at similar initial acidity.

Adding As(V) to the leach increased the total acidity and tin solubility. The addition of 8 g/L As increased the terminal acidity by about 15 g/L H<sub>2</sub>SO<sub>4</sub>. Terminal aqueous tin concentrations increased for the highest arsenic acid addition compared to the baseline experiment (40 mg/L Sn with 10 g/L As added vs. 25 mg/L Sn for the baseline). Tin precipitation kinetics decreased with increasing arsenic concentration. Experiments with 10 g/L As added to the leach, resulted in a tin precipitation rate that was third order (with a rate constant of 0.00001(1/mg Sn/L·min)<sup>2</sup>). With arsenic additions of 5 g/L or less, the kinetics were second order kinetics (rate constants varying from 0.0009 to 0.0006 (1/mg Sn/L·min)). The ionic strength was determined to be related to acid strength which can affect aqueous tin concentration sharply. SnO<sub>2</sub> dissolution possibly varies with activity [H<sup>+</sup>]<sup>4</sup>, and small changes in acid concentration can significantly affect tin concentration.

Temperature (30 to 90 °C) also affects the final aqueous tin concentration. Calculated tin precipitation activation energies varied from 11 to 18 kJ/mol, depending on the time frame examined during the Releach cycle, and compared to previously reported values. The addition of lead concentrate (sulphide reductant) increases the rate of arsenate precipitation, precipitate stability, and final aqueous tin concentration. Higher lead concentrate addition ( $R_{PbCon/PreCon} = 1$ ) resulted in an unstable tin precipitate which underwent arsenic re-dissolution and led to higher terminal aqueous tin concentrations. Pure acidic sulphate solutions (110 to 220 g/L initial H<sub>2</sub>SO<sub>4</sub> @90 °C) containing As(V) in the absence of Fe(III) precipitate tin readily. Releach solutions with arsenic concentrations less than 1 g/L As resulted in the aqueous tin concentrations increasing dramatically. In all tests, the greatest rate of tin precipitation occurs during the Fe(III) reduction period. Tin precipitates as amorphous SnO<sub>2</sub> dispersed in a mixed lead, arsenic, and zinc oxide.

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## Nomenclature

Symbol	Description	Units
$\gamma_{\pm}$	Geometric mean activity coefficient	none
$\gamma^{-}$	Activity of anion coefficient	none
$\gamma^{+}$	Activity of cation coefficient	none
$\gamma^{\pm}$	Geometric mean ion activity coefficient	mol/L
$\rho_l$	Solution density	$\text{Kg} \cdot \text{m}^{-3}$
$\rho_s$	Solid Particle density	$\text{Kg} \cdot \text{m}^{-3}$
$\Phi$	The electrical potential near a leaching ZnO surface.	mV
$a_{+}$	Activity of cation	mol/L
$a_{-}$	Activity of anion	mol/L
A	Kielland ion-size parameter	Å
B	Adjustable parameter	$\approx 0.6$ for free settling conditions
$C_s^i$	Ion Concentration of element - surface	mol/L
$C_b^i$	Ion Concentration of element - bulk	mol/L
$C_i$	Concentration of every ion	mol/L
$D_i$	Diffusion coefficient of element	$\text{m}^2 \cdot \text{sec}^{-1}$
$E^{\circ}$	Electrical Potential	Volts - V
$E_a$	Arrhenius activation energy	Joules/mole
E	Dielectric Constant	mV
E	Fractional Porosity	
F	Faraday	96485 coulombs

Symbol	Description	Units
G	Gravitational constant	9.81 m.sec <sup>-2</sup>
H	Enthalpy	kJ
<i>I</i>	Ionic Strength	mol/L
J <sub>i</sub>	Mass transfer rate	mols/sec
k <sub>L</sub>	Heterogeneous Mass Transfer Coefficient	mol · m <sup>-2</sup> · s <sup>-1</sup>
K <sub>so</sub>	Concentration Solubility Product	mol/L
K <sub>Ti</sub>	Mass transfer coefficient	m · s <sup>-1</sup>
M	Solution viscosity	N · s · m <sup>-2</sup>
P <sub>T</sub>	Total pressure - Pascals	Pa
P <sub>i</sub>	Partial Pressure Pascals	Pa
R <sub>PbCon: Precon</sub>	Reductant mass ratio: t Pb Concentrate/ t Ge Preconcentrate	t · t <sup>-1</sup>
r	“Stokes” radius of the particle	M
R	Universal gas constant	8.3144 J.mole <sup>-1</sup> K <sup>-1</sup>
t	time	S
T	Absolute temperature - Kelvin	K
V	Solution Volume	m <sup>-3</sup>
W	Weight of unleached solid per m <sup>3</sup> solution	kg · m <sup>-3</sup>
x	The variable distance from the surface	m

## Acknowledgements

I wish to thank Dr. Jochen Petersen for his guidance throughout this work. I also wish to thank Dr. Juris Harlamovs, Dr. Suzanne Belanger, and Dr. Cash Mason for their constructive thoughts and insights on this thesis. It would not be possible to complete this work in any way without patience and understanding from John Higginson. The resources he provided for me made the research, studies and thesis work possible.

University of Cape Town

## Dedication

I dedicate this Thesis to my daughters, Felicity and Isabelle, who endured endless hours without Dad, and to my wife Jennifer, who is still enduring endless hours with her husband.

University of Cape Town



# 1 INTRODUCTION AND BACKGROUND

## 1.1 Background

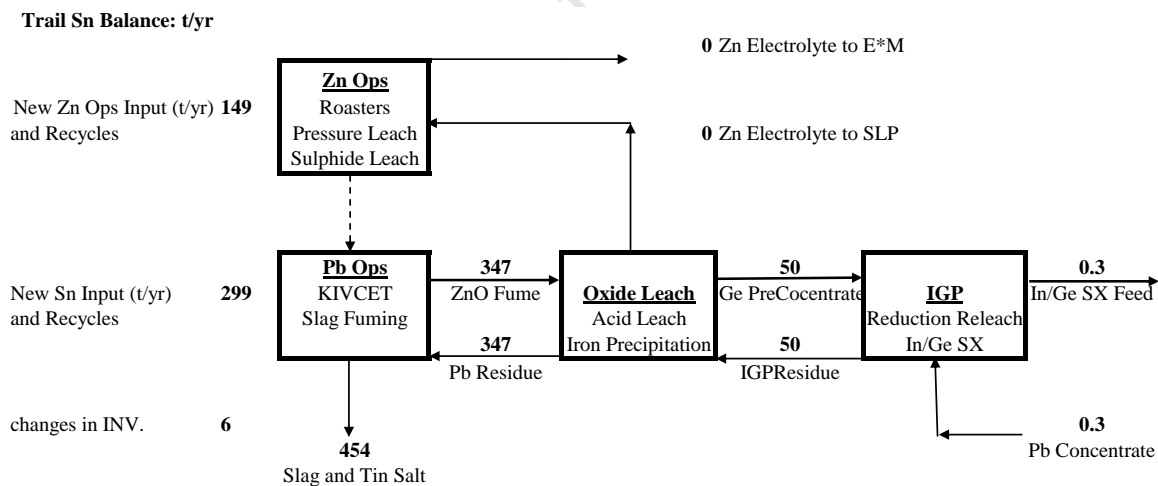
Zinc concentrates contain impurities which have negative effects on zinc metallurgy in the integrated metallurgical circuit at Teck Cominco Metals Limited (“TCML”) Trail Operations. With the increase in silver, indium and germanium prices over the last five years, there has been an increase in treating custom zinc and lead concentrates containing elevated concentrations of these metals. Unfortunately, these custom concentrates also contain high concentrations of undesirable impurities such as tin, antimony, and arsenic (Table 1.1).

**Table 1.1: Pb and Zn Concentrate Assays, TCML 2006**

	In	Ge	Ag	Sn	Sb	As
	%	%	%	%	%	%
Custom 1	0.11	0.004	4.1	4.2	8.0	0.7
Custom 2	0.09	0.001	2.1	1.8	4.5	1.0
Custom 3	0.04	0.000	1.6	1.3	6.0	1.1
Custom 4	0.04	0.000	1.3	1.3	6.0	1.1
Custom 5	0.04	0.000	1.1	0.7	4.5	0.8
Custom 6	0.15	0.001	0.1	0.7	0.5	0.4

The custom concentrates make up approximately 10 to 15 % of the total zinc and lead concentrates processed at TCML and contain 80 to 90 % of silver, indium and tin inputs, and about 50 % of arsenic inputs. These sulphide-based concentrates, as well other feed components, form the continuous feed charge for the KIVCET flash smelting furnace. The KIVCET flash smelting furnace converts sulphide concentrates, precipitated iron, and lead-based residues to oxides at 1450 °C, which then pass through a molten carbon layer of “coke” and are reduced to a mixture of oxides and metallics. This molten bullion and slag mixture is at a temperature of between 1300 and 1380 °C and proceeds to an electric furnace where the molten mixture separates into bullion and slag layers. Both the bullion and slag layers are discharged from the electric furnace on a batch basis. The slag proceeds to slag fuming furnace for further processing which

produces a ZnO fume and barren slag. The bullion advances to dressing and softening processes to remove copper, arsenic, and antimony impurities. The negative impact of tin on lead and zinc metallurgy is two-fold. Firstly, in lead pyrometallurgy, the high tin, arsenic, and antimony levels cause high viscosity slags, which do not flow well from the bullion softening furnace, ultimately restricting KIVCET throughput. To address this metallurgical issue, a bullion de-tinning plant was installed to treat high tin bullion in 2006. Secondly, and most importantly from an indium and germanium recovery perspective, some tin reports to the KIVCET electric furnace slag which then forwards to a slag fuming furnace, in which some tin reports to ZnO fume. The ZnO fume is treated hydrometallurgically to recover the zinc, indium and germanium, and the elevated tin inputs in ZnO fume precipitates in the Ge Preconcentrate, which is treated in the Reduction Releach process. The purpose of the Reduction Releach is to liberate indium and germanium from the Ge Preconcentrate for recovery in the indium and germanium solvent extraction processes. Elevated tin inputs into the Indium Germanium Process (IGP) circuit can cause a decrease in downstream indium recovery.



**Figure 1. 1: Trail Tin Block Flow Diagram**

Trail Operations indium, germanium, and tin inputs are concentrated into one process stream, the ZnO fume, which then proceeds to the Oxide Leach process for recovery of zinc, indium and germanium (Figure 1.1). Most of the tin entering the acid leach process (347 t/yr) leaves in the acid leach residues which return to the smelter (347 t/yr) for re-processing. However, some tin (50 t/yr) reports to the Ge

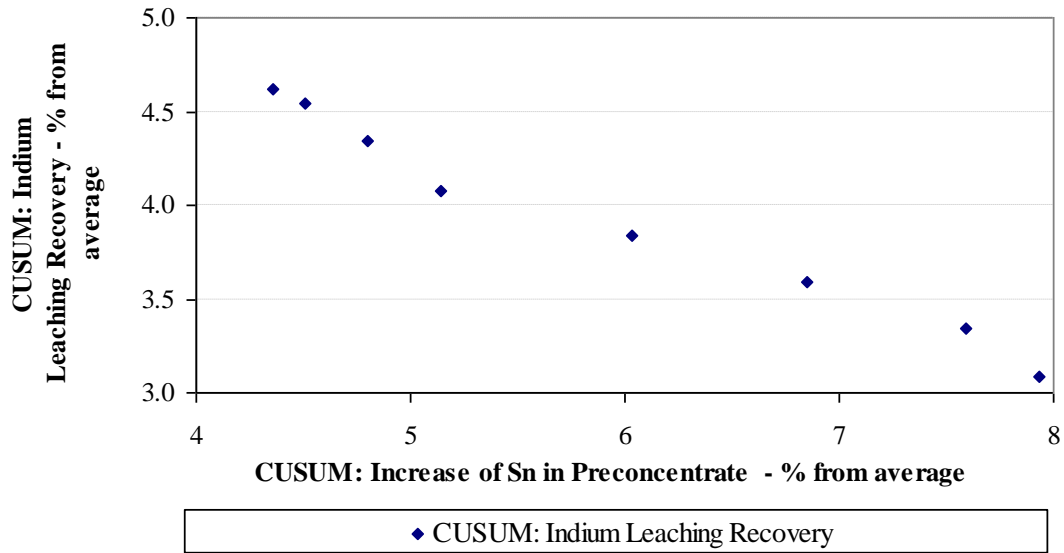
Preconcentrate residue which is formed in the oxidative iron precipitation step (pH 4, acidic sulphate media). The Reduction Releach is a batch reductive Releach with the sole purpose of producing an aqueous stream which contains desirable concentrations of both indium and germanium for further processing. Lead sulphide reductant (lead concentrate @ 50 % Pb) is added as a slurry to the Releach process for impurity precipitation during the Releach cycle.

Table 1.2 shows solid and aqueous assays before and after the Reduction Releach batch process. An aqueous tin concentration of approximately 40 mg Sn/L (approximately 5 kg Sn/d) in the input stream to the indium recovery process is sufficient to significantly disrupt the indium recovery process.

**Table 1. 2: Assay Comparison Before and After Reduction Releach, TCML 2005**

Assay Comparison before and after Reduction Releach					
	Pb	Zn	Fe <sub>T</sub>	As	Sn <sub>T</sub>
	wt %	wt %	wt %	wt %	wt %
Ge Preconcentrate before Leach	29	4	11	2	1
Residue Solids after Leach	50	3	4	1	0.8
	Pb	Zn	Fe <sub>T</sub>	As	Sn <sub>T</sub>
	mg/L	mg/L	mg/L	mg/L	mg/L
Aqueous Feed to In/Ge Recovery	26	49000	24000	3100	12

Soluble tin is an indium extractant poison and not a new problem. However, the mechanisms that influence tin solubility in the Releach process have not been studied and are not understood. Figure 1.2 shows the relationship between change in overall indium Releach recovery and change in tin concentration in the Ge Preconcentrate.



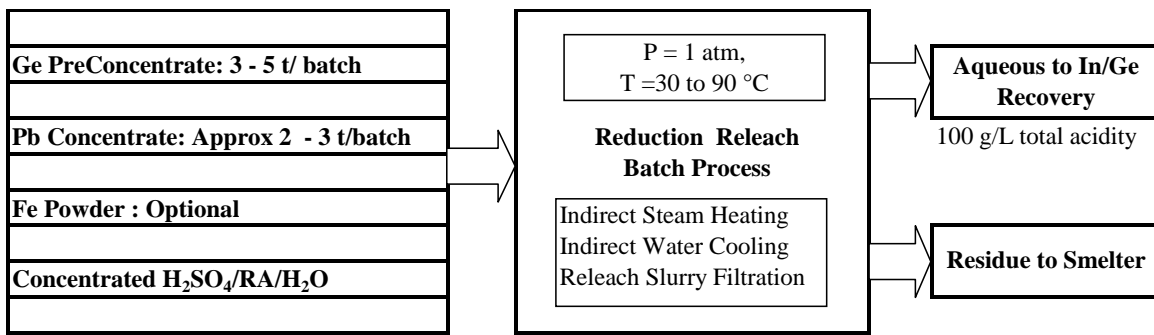
**Figure 1. 2: Indium Recovery vs. Tin in Ge Pre-Concentrate, TCML 2005**

The data presented in Figure 1.2 is taken from actual TCML 2005 Reduction Releach data. Very clearly, as the tin content in the Ge Preconcentrate increases, the indium leach recovery decreases. From this data set, a 4 % increase in Ge Preconcentrate contained tin translates to a 1.5 % decrease in indium recovery. Although not shown, as arsenic concentration increases in the Ge Preconcentrate, indium leach recovery decreases as well.

## 1.2 Reduction Releach Batch Process

### 1.2.1 Reduction Releach: General Information

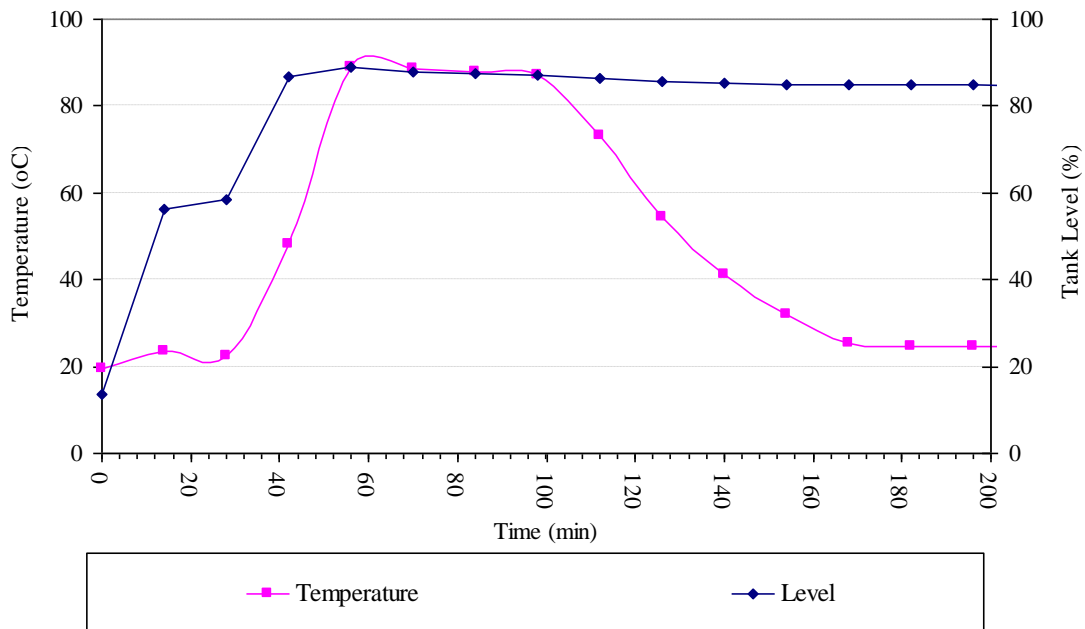
The reagents for the batch Reduction Releach Process are shown in Figure 1.3. In the batch Reduction Releach Process, indium and germanium are leached from Ge Preconcentrate using sulphuric acid (240 g/L  $H_2SO_4$  (conc.  $H_2SO_4$  + water)) in the presence of a sulphide reductant (lead concentrate).



**Figure 1. 3: Reduction Releach Process, Atmospheric Leach**

The Ge Preconcentrate contains Fe(III), As(V), In(III), Ge(IV), and Sn(IV), and small amounts of Sn(II). The lead concentrate contains the sulphide necessary for soluble iron reduction and impurity precipitation. The iron powder is used near the end of the leach as a reductant to convert any remaining ferric iron to ferrous iron, and to precipitate any remaining copper (a poison in germanium extraction). The diluted H<sub>2</sub>SO<sub>4</sub> solution is the aqueous leach medium. Typical initial H<sub>2</sub>SO<sub>4</sub> concentration is 220 g/L, and the target final total acidity is 100 g/L H<sub>2</sub>SO<sub>4</sub>.

The Reduction Releach Process is a batch process which is approximately 200 minutes in duration (Figure 1.4). There are three main stages to the leach process: filling/heating/filling; leaching; and cooling.



**Figure 1. 4: Reduction Releach Batch Cycle**

The leach temperature is 90 °C, however, reagents are added before this temperature is reached. The 90 °C temperature is required for iron reduction kinetics and impurity precipitation. The 100 g/L terminal H<sub>2</sub>SO<sub>4</sub> concentration is required to inhibit silica dissolution which can cause downstream solid/liquid separation problems, as well as adversely affect the indium and germanium recovery processes. The precipitation kinetics of silica (condensation) is strongly dependent upon pH, and salt content (Makrides, 1980; Iler, 1955). Independent test work conducted at TCML recommended that the terminal total acidity should be greater than 75 g/L H<sub>2</sub>SO<sub>4</sub> to inhibit soluble silica precipitation. As well, work has been done relating the effect of silicate on the adsorption of arsenate on co-precipitated ferrihydrite, and found that silica (as SiO<sub>3</sub><sup>-2</sup>) can complex arsenic leading to higher aqueous arsenic concentrations in acidic conditions (Singh et al., 2005). As well, extensive research work of zinc electrolyte in terms of silica and iron precipitation has been conducted with respect to precipitate filterability (Loan et al., 2006).

There are several key process steps in the batch Reduction Releach cycle. The steps follow reagent addition, heating to leach temperature, leaching, and then cooling the Releach solution prior to filtration.

Table 1.3 indicates the stepwise addition of the reagents, and the approximate duration of each step.

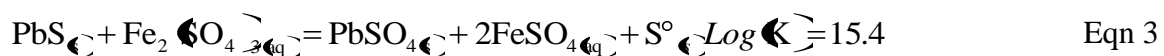
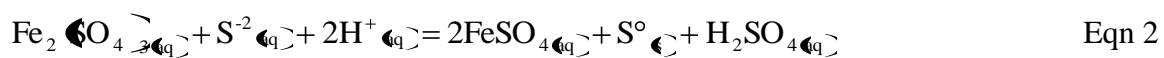
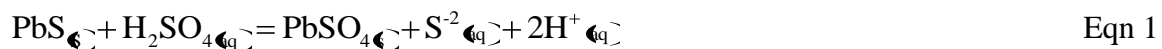
**Table 1.3: Reduction Releach Batch Cycle, 2005**

Reduction Releach Batch Cycle, TCML 2006	Tank Level	Interval
	%	min
1 Heel	15	0
2 Add Concentrated H <sub>2</sub> SO <sub>4</sub> and H <sub>2</sub> O	40	10
3 Start addition of Pre-Con Slurry (add 10 % of required)	50	5
4 Pre-Con Slurry (add balance - 90%) + PbConc. Slurry	84	30
5 Heat from 25 °C to 90 °C - start at 60 % level		30
6 Leach		45
7 Add 2 Bags Fe Powder (Optional)		
8 Cool to 25 °C		70
Total Cycle:		190

Note: Overlap Heating/Filling (Steps 3 to 5)

### 1.2.2 Reduction Releach: Chemistry

The sulphide reductant (PbS) is provided by lead concentrate (@50 % Pb). The Fe(III), as well as other impurities such copper, arsenic, tin, zinc, lead, indium, and germanium, originate from the Ge Preconcentrate. Fe(III) reduction and copper precipitation are the two key reactions which are analysed (qualitatively – colorimetric determination) during the leach to ensure the Releach impurity removal is complete, as these two are two key impurities in terms of SX operations. Fe(III) is an indium extractant poison, and Cu(II) is a germanium extractant poison. The generally accepted iron reduction chemistry by sulphide at 90 °C is as follows:



Copper is thought to be precipitated by lead concentrate (lead sulphide) through a metathesis reaction:



Iron Powder is also added as a trim at the end of the Releach to reduce any remaining Fe(III) to Fe(II) aqueous ion, and to cement Cu(II). The reactions and equilibrium constants at 90 °C are shown below.



The Eh for the commercial Releach varies by (+)200 mV to (+)800 mV, with an acidity change of 220 to 100 g/L H<sub>2</sub>SO<sub>4</sub> and temperature range of 25 to 90 °C.

#### Aqueous Sn and As Correlation at end of Releach Cycle

When Releach operation has experienced high aqueous tin concentrations (>10 mg/L) at the end of the Releach cycle, further analysis of the data has shown that aqueous arsenic is usually at a low concentration, and correlates well with aqueous tin. Aqueous arsenic may play a role in the final aqueous tin concentration, or may be an artifact of, or proxy for some other type of tin precipitation mechanism and warrants further investigation.



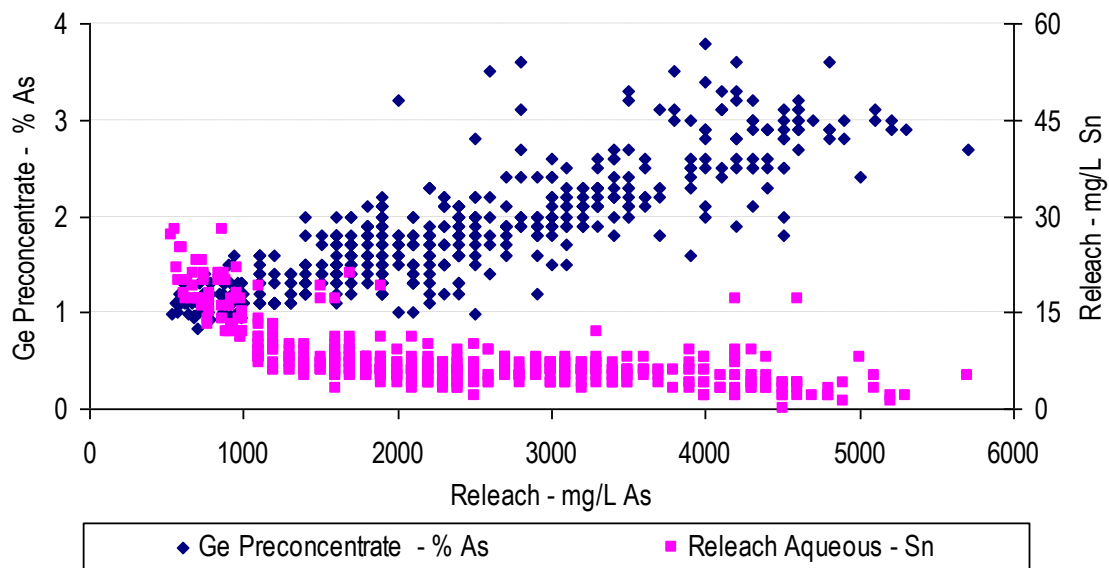


Figure 1. 5: Ge Precon % As versus Releach Aqueous Sn and As, TCML

### 1.3 Objectives of Investigation

The objectives of this investigation are to understand how aqueous tin concentration during the Releach process is influenced by key parameters such as total acidity, temperature, reductant amount, and arsenic concentration. Supporting test work will examine tin speciation/oxidation states in the Zinc Oxide Fume, Ge Preconcentrate, and Releach residue. Further supporting test work will validate tin solubility predicted by theoretical calculations, and a Sn(II/IV) aqueous measurement method will be evaluated for use in the bench scale experiments. The ultimate goal of this work is to advise on how to ensure acceptable levels of Sn in the Releach solution. The key parameters chosen for this testwork were selected with the purpose of proposing a Releach operation strategy to minimize Releach aqueous tin concentration.

## 2 LITERATURE REVIEW

### 2.1 Mineralogy

#### 2.1.1 Pb Concentrates, Fume, Ge Preconcentrate, and Releach Residue

##### Lead Concentrates:

Tin occurs in the Bolivian and Huari Huari Pb concentrates treated in Trail primarily as sulphide compounds, such as potosite ( $\text{Pb}_6\text{Sn}_2\text{FeSb}_2\text{S}_{14}$ ), stannite ( $\text{Cu}_2\text{S}\cdot\text{FeSSnS}_2$ ), stannoidite ( $\text{Cu}_8(\text{Fe,Zn})_3\text{Sn}_2\text{S}_{12}$ ), mawsonite ( $\text{Cu}_6\text{Fe}_2\text{SnSnS}_8$ ), kesterite ( $\text{Cu,Zn,Fe,Ag}_3\text{SnS}_4$ ), and theallite ( $\text{PbSnS}_2$ ). Furthermore, the dominant oxide form of tin is Cassiterite ( $\text{SnO}_2$ ) (Approx. 80 %) (Schwarz-Schampera and Herzig, 2002).

Within Teck Cominco's operation at Trail, BC, the lead concentrates and residues are smelted in a KIVCET flash smelting process. The slag generated by the KIVCET smelting process is further processed in a slag fuming furnace to produce a ZnO rich fume. The ZnO fume contains tin, indium and germanium, which are subsequently acid-leached and then precipitated at pH 4.0 in an oxidizing acidic sulphate iron purification process. The precipitated iron solids also contain tin, which leaches and re-precipitates during the Reduction Releach Process. Aqueous tin is detrimental to the Releach indium leaching efficiency, as well as to the downstream indium recovery process.

**Table 2. 1: Results of LSQ Fitting on SN Bearing Mill Samples (Kotzer, 2005)**

Sample Description	$\text{SnO}_2$	$\text{SnSO}_4$	$\text{SnO}$	$\text{SnCl}_2$
	%	%	%	%
"Normal" Preconcentrate	100	0	0	0
"Normal" Releach residue	100	0	0	0
"Abnormal" Releach residue1	90	10	0	0
"Abnormal" Releach residue2	88	0	8	4

Speciation of tin in Ge Preconcentrate was carried out using X-Ray Absorption Near Edge Structure Spectroscopic Analyses (XANES), combined with a linear least-squares (LSQ) fitting procedure and a set of well-characterized reference compounds (Table 2.1, Kotzer, 2005). This technique is frequently used to quantify cations and their

oxidation states. The analysis shows a Sn(IV)-bearing complex similar to SnO<sub>2</sub> (>80 %) (Table 2.1), suggesting the dominant formal oxidation state of tin in these samples is Sn(IV), with minor amounts of Sn(II) present. Further, the Releach residue showed Sn(IV) compounds similar to SnO<sub>2</sub>, and Sn(II)-bearing complexes in the “abnormal” Releach sample, similar to SnSO<sub>4</sub>, SnO and SnCl<sub>2</sub> (Table 2.1).

The Ge Pre-concentrate precipitation step is conducted at pH 4, where tetravalent tin undergoes rapid hydrolysis to produce an amorphous SnO<sub>2</sub>·nH<sub>2</sub>O. This solid form of tetravalent tin is in agreement with data shown in Table 2.1. However, from thermodynamic considerations, other Sn(II/IV) solid phases could be present such as SnSO<sub>4</sub> O<sub>2(s)</sub>, SnS<sub>(s)</sub> (as suggested by the HSC v5.0 software), SnO<sub>2</sub>, SnOSO<sub>4</sub> or Sn(SO<sub>4</sub>)<sub>2</sub> (Mellor, 1924). Although thermodynamically possible, there is little kinetic or other published data to support existence of the SnSO<sub>4</sub>O<sub>2</sub> species, and some form of hydrous SnO<sub>2</sub> is thought to occur. At higher acidities, a greater concentration of sulphate and bisulphate ions in solution are available for Sn(II/IV) complexation. Other tin solubility work found that tin dissolution increased with increasing acidity and temperature between 0.1 and 1.5 molar maleic acid (1 mol/L maleic acid ~pH 0.9) at temperatures between 10 to 70 °C (El Rehim et al., 2004). From Table 2.1, Sn(II) was only detected in Releach Residue during the abnormal operation periods. There has been speculation that tin fluorides, oxy fluorides, or bromides may be soluble as well, although the present analysis did not examine these structures. An exception appears to be the “Abnormal Releach” residue sample, which indicated that the sample still contains predominantly a Sn(IV) bearing complex similar to SnO<sub>2</sub> (≥88 % SnO<sub>2</sub>), but also minor amounts of SnSO<sub>4</sub>, SnO and SnCl<sub>2</sub>. Statistical results from this study suggest a slight bias (~ 3% better) towards a SnO<sub>2</sub>-SnSO<sub>4</sub> mixture (Kotzer, 2005). Also, Sn(II), as SnSO<sub>4</sub> in the presence of dilute H<sub>2</sub>SO<sub>4</sub> at temperatures between 54 to 93°C, may form Sn(SO<sub>4</sub>)<sub>2</sub> (s), Sn(SO<sub>4</sub>)<sub>2</sub> 2H<sub>2</sub>O<sub>(s)</sub>, or SnOSO<sub>4</sub>, and if lead or calcium are present, then (Ca, Pb) · Sn(SO<sub>4</sub>)<sub>3</sub> · 3H<sub>2</sub>O<sub>(s)</sub> may form.

In summary, the starting tin valency in the Ge Preconcentrate precipitated solid is likely tetravalent Sn (solid phase) as hydrous  $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ ,  $\text{Sn}(\text{SO}_4)_2 \cdot n\text{H}_2\text{O}$ ,  $\text{Sn}(\text{SO}_4)_2$ ,  $\text{SnSO}_4$  and bivalent tin (solid phase) as  $\text{SnSO}_4$ ,  $\text{SnS}$ , or  $\text{SnO}$ .

With respect to arsenic, speciation of arsenic has been studied in systems pH 4 to 8, where co-precipitation of As(V) with Fe(III) in sulphate media occurs (Jia et al., 2005). This arsenic speciation study identified several different iron phases where arsenic was present: a crystalline scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ), and amorphous scorodite ( $\text{FeAsO}_4 \cdot 2.39\text{H}_2\text{O}$ ) adsorbed on goethite ( $\text{FeOOH}$ ). This could apply to TCML Ge Preconcentrate arsenic speciation. In terms of speciation, lead arsenates have a superior capacity for adsorption of hydrated amorphous hydroxides (Al, Mn, Fe) when compared to crystalline compounds. The formation of iron arsenates is very pH dependent, and ferric arsenates are more soluble than calcium arsenates (Magalhães, 2002).

## 2.2 Acidic Tin Solution Chemistry

Most literature reviewed for the chemistry of tin in acidic media came from the lead or tin electro-refining and electrowinning industries. A significant amount of work has been done around arsenate precipitation from acidic sulphate media for impurity removal from zinc electrolytes, as well as environmental applications for removing arsenic from wastewater effluents. Information regarding the chemistry of the sulphide reductants in acidic media was referenced from other studies investigating ferric leaching of sulphide minerals in sulphate/chloride media. The literature reviewed for the arsenic and iron systems in sulphate media came from a plethora of information available regarding iron precipitation for purification of zinc electrolytes.

### 2.2.1 Equilibria: Pure Tin System: Sn-S-O-H

#### 2.2.1.1 Pure System: Eh-pH for Sn-S-O-H

Figure 2.1 shows the Eh-pH diagram for the Sn-S- $\text{H}_2\text{O}$  system at 90 °C. The acidity for the Reduction Releach Process ranges between 60 and 160 g/L free  $\text{H}_2\text{SO}_4$

(pH < 1). In that acidity range, the possible oxidation states are Sn(0), Sn(II), and Sn(IV) (Pourbaix, 1966).

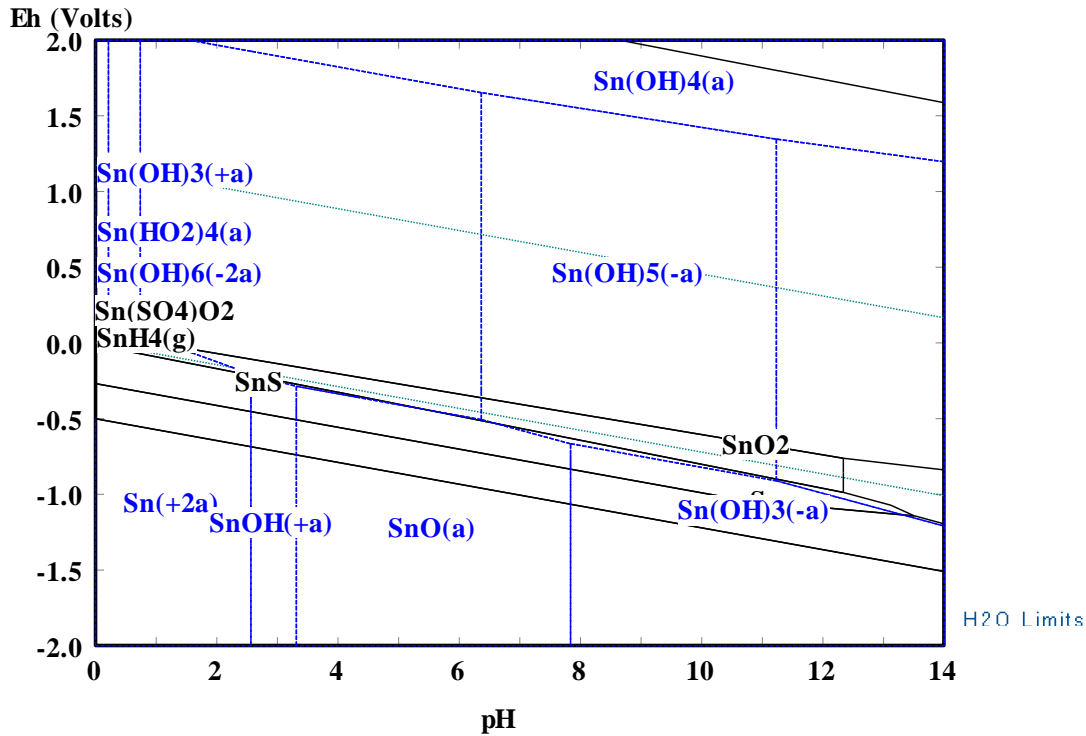
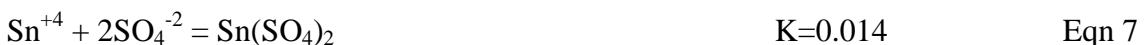


Figure 2. 1: Eh-pH Diagram for Sn-S-H<sub>2</sub>O System at 90 °C (HSC v5.0)

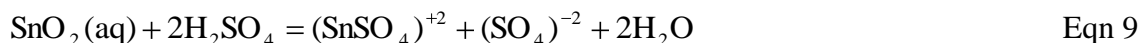
With respect to the Pourbaix diagram for tin (Figure 2.1), as the leach solution becomes more reducing, stannous sulphide precipitates (Eh < 100 mV), and eventually stannic hydride gas. Both Sn(II) and Sn(IV) oxidation states are thermodynamically stable and can exist as an aqueous or solid species at pH < 1. However, Sn(II) ions are generally not as stable and act as strong reducing agents. Sn(IV) ion therefore predominates as the stable aqueous ion between Eh values of +200 mV and 800 mV. Some authors have suggested the existence of intermediate Sn(I/III) aqueous ions, although this is not well documented (Laitinen et al., 1992, Stirrup and Hampson, 1977). In the presence of an oxidant such as dissolved and/or entrained oxygen, Sn(II) is oxidized to the Sn(IV) state. Spectrophotometric and electromagnetic studies (Stirrup and Hampson, 1977) have shown that Sn(IV) in low concentration of H<sub>2</sub>SO<sub>4</sub> behaves similarly as in perchloric acid and can precipitate as stannic sulphate:



For higher concentrations in sulphuric acid, tin may follow the reaction:



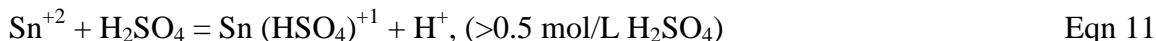
The hydrolysis of Sn(IV) was also reviewed by Brubaker (1955) and it was postulated that Sn(IV) would form sulphate salts:



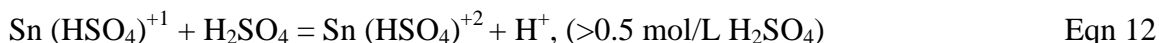
$K = 5 \times 10^{-2}$  @30 °C, and  $K = 2.8 \times 10^{-2}$  @18 °C

Addition electrochemical and thermodynamic data for Sn(II/IV) can be found in *Standard Potentials in Aqueous Solutions* (Bard et al., 1985).

One study examined the anodic behaviour of tin at acid concentrations less than 9 mol/L H<sub>2</sub>SO<sub>4</sub>, and suggested that above 0.5 mol/L H<sub>2</sub>SO<sub>4</sub>, Sn(II) exists as Sn(HSO<sub>4</sub>)<sup>-1</sup> and Sn(HSO<sub>4</sub>)<sub>2</sub> (Stirrup and Hampson, 1977). Absorption spectroscopy and column chromatography solution studies (Stirrup and Hampson, 1977) of Sn(II) in the aqueous state (0 to 9 mol/L H<sub>2</sub>SO<sub>4</sub>, room temperature) determined that stannous hydroxide hydrolyses to non-hydrated Sn(II) below 0.5 M sulphuric acid concentration, and proposed the following reactions:



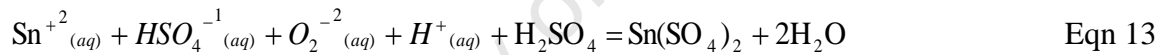
and



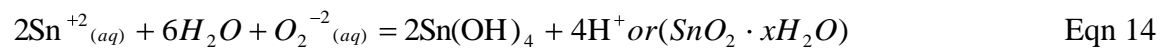
Sn(IV) in acidic media is thought to be present as free ions or partially hydrolyzed species such as Sn<sup>+4</sup>, Sn(OH)<sup>+3</sup>, Sn(OH)<sub>2</sub><sup>+2</sup>, and Sn(OH)<sub>3</sub><sup>+1</sup>. Alternatively, with sulphate ions, stannic sulphates such as SnSO<sub>4</sub><sup>+2</sup> and Sn(SO<sub>4</sub>)<sub>2</sub> are formed. Sn(II) can form complexes in acidic media such as Sn[Sn(SO<sub>4</sub>)<sub>2</sub>], H<sub>2</sub>Sn<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Sn(OH)<sub>4</sub><sup>-2</sup>,

$\text{Sn}^{+2}$ ,  $\text{Sn}(\text{OH})^{+1}$ ,  $[\text{Sn}(\text{OH})\text{SO}_4]^{-1}$  (Tunold and Broli, 1973). From anodic dissolution tests of tin, it was postulated that the bisulphate ion was actively involved in tin dissolution and functioned as a complexing agent for tin. Sn(II) was present as  $\text{Sn}^{+2}$ ,  $\text{Sn}(\text{HSO}_4)^{+1}$ , and  $\text{Sn}(\text{HSO}_4)_2$  in solutions of between 0.5 and 1 mol/L  $\text{H}_2\text{SO}_4$ . Above 1 mol/L  $\text{H}_2\text{SO}_4$ , Sn(IV) was present as  $\text{Sn}^{+4}$  and  $\text{Sn}(\text{SO}_4)_2$ . Above 3 mol/L  $\text{H}_2\text{SO}_4$ , Sn(IV) was present as  $\text{H}_2\text{Sn}(\text{SO}_4)_3$  (Laitinen et al., 1992). Furthermore, the Sn(IV) solubility increases rapidly as the acidity increases (Stirrup and Hampson, 1977).

A thermodynamically possible precipitated tin species in the oxidizing region at  $\text{pH} < 1$  is Sn(IV) peroxide sulphate  $(\text{SnSO}_4)_2\text{O}_2$ , which is thermodynamically very stable in an oxidizing leaching regime. The peroxytannic acids  $\text{H}_2\text{Sn}_2\text{O}_7$ , and  $\text{HSnO}_4$  can produce Sn(IV) salts by the presence of peroxides (Latimer and Hildebrand, 1956). The presence of dissolved oxygen and the role of peroxide anion ( $\text{HO}_2^{-1}$ ) have also been studied in the context of Sn(IV) precipitation in acidic media (Martyak and Seedfeldt, 2005). This study postulated the following reaction mechanism ( $\Delta\text{Grx} = 98.49$  kcal/mol) between the peroxide ion and Sn(II) and subsequent Sn(IV) precipitation:



This paper also reported that as the total sulphate concentration increases, the rate of Sn(II) oxidation decreases, and subsequent precipitation of Sn(IV) decreases. Other authors (Mori et al., 2002), have postulated the role of peroxides in weakly acidic media as:



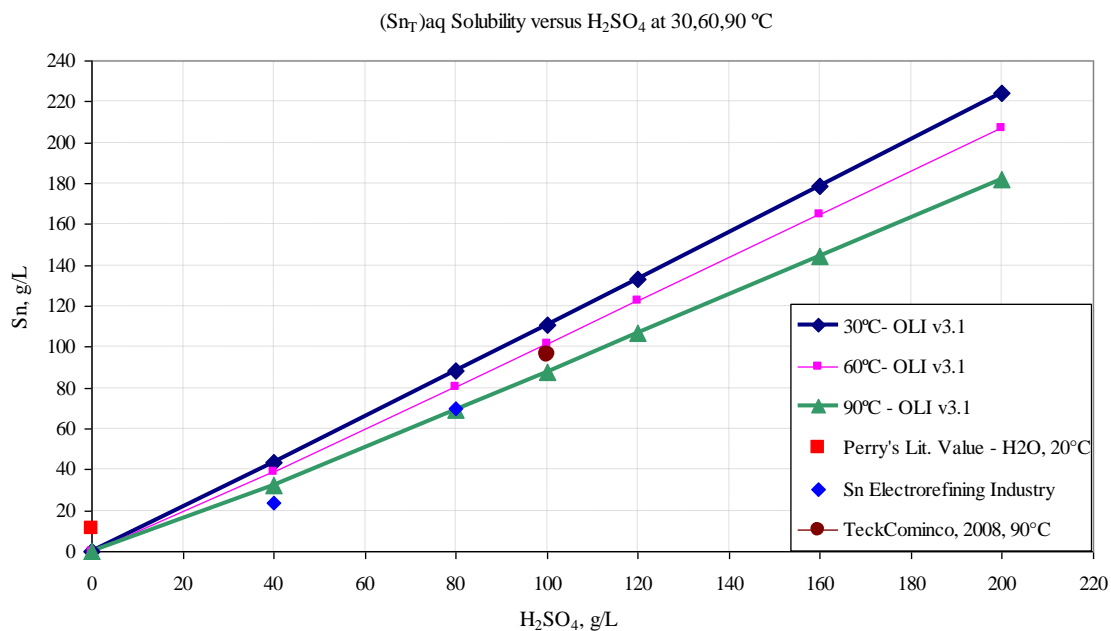
Literature reports Sn(IV) precipitating as a sulphate, oxide, or hydrous oxide (Weiser, 1926). Predominantly, SnO and  $\text{SnO}_2$  form intermediate oxides, such as  $\text{Sn}_2\text{O}_3$  during acidic or basic leaching processes. Sn(II) oxides are amphoteric, dissolving both in acidic and alkali media. SnO dissolves in acids to give Sn(II) ion, or Sn(II) complexes. In alkali solutions, the predominant ion is  $\text{Sn}(\text{OH})_3^{-1}$ . The hydrolysis of Sn(II) salt solutions indicates the presence of  $\text{Sn}(\text{OH})^{+1}$ , and  $\text{Sn}_2(\text{OH})_2^{+2}$  ions. Hydrous  $\text{SnO}_2$  is

formed by the hydrolysis of Sn(IV) salt solutions. These Sn(IV) ions are amphoteric as well, and dissolve in both acid and basic solutions. The solubility of Sn(II) sulphate in water and acid decreases steadily with the rise in temperature (35.2 g/L at 20 °C to 22 g/L at 100 °C). Sn(IV) sulphate dihydrate is formed from hydrous Sn(IV) oxide in hot dilute sulphuric acid. Sn(IV) sulphate hydrolyses completely in water with precipitation of hydrous SnO<sub>2</sub>, and is freely soluble in dilute sulphuric acid. If any halides are present, the solubility of SnF<sub>2</sub> is substantially lower than that of SnCl<sub>2</sub>. The dissociation constants of the various Sn(II) complexes can be found in Appendix N.

## 2.2.2 Total Acidity

### 2.2.2.1 Proton Condition: Sn-S-O-H Systems

The predominance of the Sn(II) ion increases as both the temperature and acidity are increased (Figure 2.2).



**Figure 2. 2: Sn (II) solubility: Acidity and Temperature Effects**

With respect to electrochemical studies of tin in acidic sulphate media, Salmi et al. (1992) found that tin dissolution rate is independent of acid concentration, and that the oxidation of Sn(II) to Sn(IV) seemed to occur at high anodic potentials. The above



finding of tin dissolution versus acidity contradicts tests completed earlier by TCML, which dealt with tin removal in an acidic sulphate media. These tests found that tin dissolution increased with increasing acidity (Harlamovs, 1989).

For complex ionic systems containing several different cations and anions, the apparent pH (total acidity) of the solution is affected not only by the sulphate/bisulphate equilibrium, but also the affinity of each cation for sulphate, thus affecting the second proton dissociation of H<sub>2</sub>SO<sub>4</sub> (Hogfeldt, 1982, Potter, 1989).



For the above system, zinc and sulphuric acid versus sodium and sulphuric acid, the calculated and observed acidities are quite different. For a 1 mol/L solution of H<sub>2</sub>SO<sub>4</sub>, containing 1 mol/L zinc or 1 mol/L sodium the pH's are 1.5, and 1.2, respectively. An in-depth evaluation of proton activities in mixed sulphate systems was undertaken for application to zinc sulphate-ferric/ferrous sulphate-sulphuric acid systems to estimate the activity of H<sup>+1</sup> from 298 to 473 K in this multi-component system (Filippou, 1993). The addition of divalent and trivalent metal sulphate salts decreased the activity of the proton with zinc having the most suppressing effect on hydrogen activity, followed by ferric ion, and ferrous iron.

**Table 2. 2: Activity of H<sup>+</sup>; ZnSO<sub>4</sub> (Filippou, 1993)**

[SO <sub>4</sub> <sup>2-</sup> ] <sub>tot</sub>	[Zn <sup>2+</sup> ] <sub>tot</sub>	Solute Composition (mol/L)			Calculated - a <sub>H<sup>+</sup></sub>				
		[Fe <sup>2+</sup> ] <sub>tot</sub>	[Fe <sup>3+</sup> ] <sub>tot</sub>	[H <sub>2</sub> SO <sub>4</sub> ] <sub>free</sub>	298 K	323 K	373 K	423 K	473 K
0.25	0.00	0.00	0.00	0.25	0.211	0.208	0.196	0.194	0.195
0.50	0.00	0.00	0.00	0.50	0.426	0.405	0.384	0.381	0.382
1.00	0.00	0.00	0.00	1.00	0.87	0.834	0.799	0.792	0.797
1.50	0.00	0.00	0.00	1.50	1.386	1.335	1.287	1.282	1.297
2.00	0.00	0.00	0.00	2.00	1.996	1.932	1.872	1.875	1.913
0.50	0.25	0.00	0.00	0.25	0.165	0.137	0.092	0.069	0.061
1.00	0.50	0.00	0.00	0.50	0.338	0.292	0.219	0.187	0.186
2.00	1.00	0.00	0.00	1.00	0.815	0.747	0.655	0.64	0.684
0.50	0.00	0.25	0.00	0.25	0.104	0.068	0.028	0.013	0.007
1.00	0.00	0.00	0.25	0.13	0.079	0.061	0.024	0.008	0.01
1.00	0.50	0.10	0.00	0.40	0.217	0.169	0.102	0.072	0.064
2.00	1.00	0.25	0.00	0.75	0.415	0.34	0.242	0.209	0.224
3.00	2.00	0.50	0.00	0.50	0.144	0.083	0.026	0.01	0.004
1.00	0.50	0.00	0.10	0.35	0.209	0.166	0.091	0.048	0.036
2.00	1.00	0.00	0.25	0.63	0.402	0.332	0.195	0.114	0.107
3.00	2.00	0.00	0.50	0.25	0.113	0.079	0.03	0.012	0.014
3.00	2.00	0.10	0.50	0.15	0.049	0.029	0.01	0.007	0.011

Similar research (Wang and Dreisinger, 1998) investigated the effect of acidity in multi-ion systems. The authors described the effects of free acid and acid salts and metal ions on pH behaviour in terms of metal ion activities, hydrolysis, stability quotients, and sulphate/bisulphate activities. The majority of the analysis addressed solution thermodynamic for zinc sulphate electrolytes. The bisulphate/sulphate equilibrium and the stability quotient have been modeled as a function of ionic strength and temperature using the Pitzer form of the extended Debye-Hückel equation. These models were developed for zinc sulphate electrolytes, which operate in an acidity range between pH 1.8 and 6, and are discussed in the paper. In theory, zinc hydrolysis, as well as sulphate/bisulphate equilibrium, could play a role in tin chemistry.

The activity of Sn(II) in a pure Sn(II) – H<sub>2</sub>SO<sub>4</sub> system was studied by Tunold (1973). The increase in tin dissolution rate has been determined as second order in hydrogen ion concentration, and the activity coefficient of Sn(II) has been determined to vary between  $1.6 \times 10^{-2}$  and  $6.4 \times 10^{-2}$ .

**Table 2. 3: Activity of Sn(II) in Acidic Sulphate Media (Tunold, 1973)**

Activity mol/L (20 °C)	pH = 0.5	pH = 1.0	pH = 1.5	pH = 2
$a_{\text{Sn}^{2+}}$	$1 \times 10^{-3.25}$	$1 \times 10^{-3.5}$	$1 \times 10^{-3.75}$	$1 \times 10^{-4.0}$

Note:  $[\text{SnSO}_4]$ : 0.1 to 0.001 mol/L, 0.3 to 2.2 pH, and  $[\text{SO}_4]_{\text{T}} = 0.09$  to 1.55 mol/L

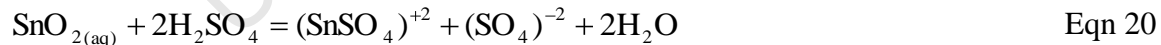
The values were determined electrochemically by varying the stannous concentration and measuring the change in cell voltage, and then applying the Nernst equation:

$$E_{(\text{Sn}/\text{Sn}^{2+})} = E^{\circ}_{(\text{Sn}/\text{Sn}^{2+})} + (RT/2F) \times \ln (a_{\text{Sn}^{2+}}) \quad \text{Eqn 19}$$

This same paper also determined that the activity of Sn(II) increases with acidity, although some Sn(II) may have been complexed at the higher acidity conditions.

Although the form of tin that Tunold tested (solid versus precipitated) is different from the tin species in the Releach tests, the principle of the tin dissolution mechanism may be the similar.

Tin equilibrium studies have also estimated Sn(IV) activities as a function of  $\text{H}_2\text{SO}_4$  concentration and temperature of Sn(IV) compounds in acidic sulphate media (18 and 30 °C , 0 to 0.96 mol  $\text{H}_2\text{SO}_4/\text{L}$ ) (Brubaker, 1955). The reaction for Sn(IV) hydrolysis and subsequent activities of Sn(IV) and sulphuric acid are indicated in the equations below:



$$K = \frac{a_{(\text{SnSO}_4)(\text{SO}_4)} a^2_{\text{H}_2\text{O}}}{a^2_{\text{H}_2\text{SO}_4}} = \frac{(\text{SnSO}_4^{+2})(\text{SO}_4^{-2}) \gamma^2_{\text{SnSO}_4\text{SO}_4} a^2_{\text{H}_2\text{O}}}{16(\text{H}_2\text{SO}_4)^6 \gamma^6_{\text{H}_2\text{SO}_4}} \quad \text{Eqn 21}$$

$$\frac{1}{16} a^2_{\text{H}_2\text{SO}_4} = (\text{H}_2\text{SO}_4)^6 \gamma^6_{\text{H}_2\text{SO}_4} \quad \text{Eqn 22}$$

The experimentally determined equilibrium K value at 30 °C was  $5 \times 10^{-2}$  compared to the 18 °C value of  $2.8 \times 10^{-2}$ , due to the existence of partially complexed

species ( $\text{SnSO}_4^{+2}$ ) being formed at the higher temperature. As a side note, the hydrolysis of Sn(IV) in perchloric acid was also tested but discontinued in this work due to formation of precipitates ( $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ ) that were colloidal, prohibiting the separation of phases.

The effect of sulphuric acid concentration on tin-bearing sludge production from a tin mill tailings pond was investigated (USX Engineers and Consultants, Inc., 1998). The sulphuric acid concentration ranged from 0 to 234 g/L, Sn(II) from 30 to 80 g/L, Fe(III) from 0 to 5 g/L, and temperature between 41 to 55 °C. The findings suggest that above 100 g/L sulphuric acid, tin sludge production increases, and substantially increases above 180 g/L  $\text{H}_2\text{SO}_4$ . No explanation was offered as to why the tin sludge precipitation rate increased.

The mechanism proposed to explain the increase in tin solubility was the formation of soluble Sn(II) complexes utilizing the greater availability of sulphate and bisulphate ions at the higher acid concentrations. Previous research showed for Sn(0)/Sn(II) dissolution in acidic sulphate media, that above 0.5 mol/L  $\text{H}_2\text{SO}_4$ , aqueous tin exists as Sn(II), as well as complexes  $\text{Sn}(\text{HSO}_4)^{+1}$ , and  $\text{Sn}(\text{HSO}_4)_2$ . For acid concentrations exceeding 1 mol/L  $\text{H}_2\text{SO}_4$ , tin dissolves as  $\text{Sn}(\text{SO}_4)_2$ ; for concentrations exceeding 3 mol/L  $\text{H}_2\text{SO}_4$  as  $\text{H}_2\text{Sn}(\text{SO}_4)_3$  (Stirrup and Hampson, 1977).

Kinetic studies between 20 to 50 °C in sulphuric acid media determined that the reaction rate of Sn(IV)/ Sn(II) decreased as acidity increased following first order kinetics, and increased with increasing sulphate concentration (Gordon and Brubaker, 1960). Similarly, the hydrolysis of Sn(IV) follows fourth order in sulphuric acid concentration (Brubaker, 1955). Research involving the oxidation of Sn(II) in sulphuric acid solutions found that the rate of Sn(II) oxidation to Sn(IV) increased with an increase in acidity (Rozovskii et al., 1996).

The leaching of galena (PbS) in ferric sulphate media at sulphuric concentration ranging from 20 to 300 g/L, Fe(III) concentration from 10 to 110 g/L Fe(III), and temperatures between 60 to 90 °C was investigated (Dutrizac and Chen, 1995). The leaching rate was diffusion controlled and increased by direct acid attack on the sulphide mineral. Initial acidity and Fe(III/II) concentration can affect the concentration of arsenic in solution.

#### 2.2.2.2 Proton Condition: Sn-As-S-O-H Systems

Arsenic exists as As(V) and As(III) oxidation states below pH=1 as shown in Figure 2.3. Although lead arsenate is shown on the stability diagram, ferric arsenate precipitation has been well studied and shown to form below pH 2 (Robins, Nishimura et al., 2005). The removal of arsenic from sulphate solutions has been well studied (Singhania et al., 2005; Jia and Demopoulos, 2005; Robins, Nishimura et al., 2005). If tin is co-precipitated with iron and arsenic solids, the final level of tin in solution may be related to arsenic concentration in the Reduction Releach Process. Initial acidity, As(V), and Fe(III/II) can affect the concentration of arsenic in solution. As(V) may be complexed with Fe(III) and exist as metastable phase in which initial acidity or Fe(III/II) concentrations are important with respect to the stability of the precipitated amorphous ferric arsenate, or crystalline scorodite phase (Singhania et al., 2006; Dove and Rimstidt, 1985). Also not shown on the Eh diagram are iron arsenates (scorodites) which have been thoroughly investigated and proven to exist (Figure 2.3).

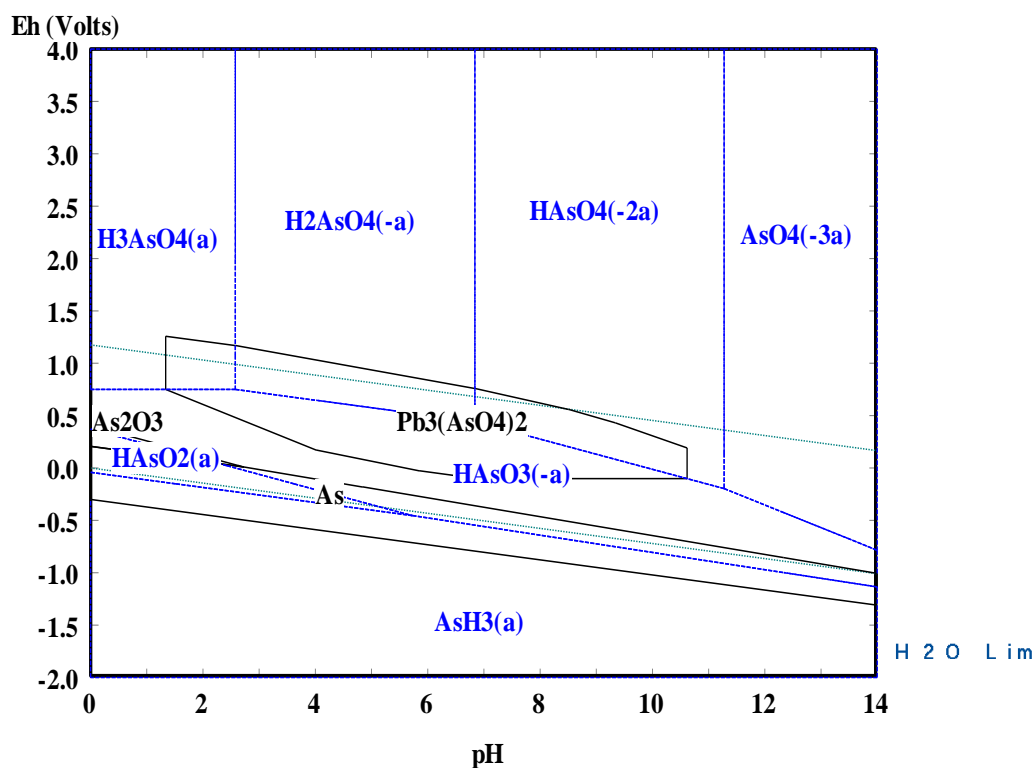
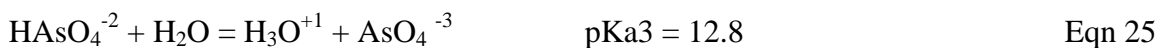
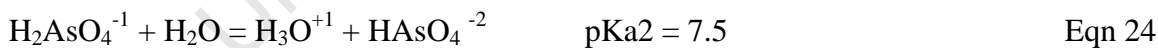
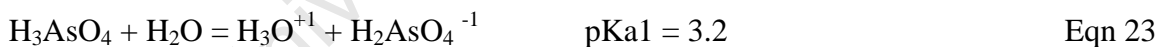


Figure 2. 3: Eh-pH Diagram for Pb-As-Sn (HSC v5.0)

Additional arsenic speciation work in ferric sulphate /sulphuric acid media and the resulting stability of As(III/IV) precipitates have been analysed by Tan and Dutrizac (1985). This paper discusses the arsenic acids and As(III/V) stability and metastability versus pH and Fe(III/II) concentrations in sulphuric acid solutions.



Aqueous As(V) ions can react with tin to form insoluble Sn(II) and Sn(IV) species in either oxidizing or reduction conditions (Table 2.4; HSC v5.0). The presence of iron and oxygen increase the thermodynamic possibility of these tin and arsenic reactions occurring. Furthermore, the amount of ferric iron in solution relative to aqueous arsenic (lower arsenic cases) has been shown to decrease both the precipitation rate and amount

of arsenic precipitated (scorodite), and produce a more unstable precipitate which can release (Singhania et al., 2006).

Aqueous phase reactions between Sn(II/IV) species and As(V) have been determined from a thermodynamic perspective (Table 2.4), however they may not be kinetically practical (Table 2.4, reactions 1 to 9). Some reactions (Table 2.4) may be feasible by bacterial catalysis (Table 2.4, reactions 2, 3, 7-9).

**Table 2. 4: Tin and Arsenic Reactions at 90 °C**

Tin and Arsenic Reactions at 90°C		$\Delta G_{R_x}$	mol Sn	$\Delta G_{R_x}$
		kcal		kcal/mol Sn
1	$\text{Sn} + 10\text{H}^+(\text{a}) + 2\text{HSO}_4^-(\text{a}) + 4\text{AsO}_4^{3-}(\text{a}) + \text{Sn}^{+4}(\text{a}) = 2\text{Sn}(\text{SO}_4)\text{O}_2 + 4\text{H}_3\text{AsO}_3(\text{a})$	-358	1	-358
2	$\text{Sn}(\text{HSO}_4)_4(\text{a}) + 2\text{H}_3\text{AsO}_4(\text{a}) + 19\text{H}_2(\text{g}) = \text{SnS}(\text{s}) + \text{As}_2\text{S}_3(\text{s}) + 24\text{H}_2\text{O}$	-319	1	-319
3	$\text{Sn}(\text{HSO}_4)_4(\text{a}) + 2\text{H}_3\text{AsO}_4(\text{a}) + 13\text{H}_2(\text{g}) = \text{Sn}(\text{SO}_4)\text{O}_2(\text{s}) + \text{As}_2\text{S}_3(\text{s}) + 18\text{H}_2\text{O}$	-310	1	-310
4	$5\text{H}^+(\text{a}) + \text{HSO}_4^-(\text{a}) + 2\text{AsO}_4^{3-}(\text{a}) + \text{Sn}^{+2}(\text{a}) = \text{Sn}(\text{SO}_4)\text{O}_2 + \text{As}_2\text{O}_3 + 3\text{H}_2\text{O}$	-174	1	-174
5	$5\text{H}^+(\text{a}) + \text{HSO}_4^-(\text{a}) + 2\text{AsO}_4^{3-}(\text{a}) + \text{Sn}^{+2}(\text{a}) = \text{Sn}(\text{SO}_4)\text{O}_2 + 2\text{H}_3\text{AsO}_3(\text{a})$	-172	1	-172
6	$\text{H}^+(\text{a}) + \text{HSO}_4^-(\text{a}) + 2\text{Sn}^{+2}(\text{a}) + \text{O}_2(\text{g}) = \text{Sn}(\text{SO}_4)\text{O}_2 + \text{Sn}^{+4}(\text{a}) + \text{H}_2(\text{g})$	-154	1	-154
7	$3\text{Sn}(\text{HSO}_4)_2(\text{a}) + 2\text{H}_3\text{AsO}_4(\text{a}) + 26\text{H}_2(\text{g}) = 3\text{SnS}(\text{s}) + \text{As}_2\text{S}_3(\text{s}) + 32\text{H}_2\text{O}$	-443	3	-148
8	$2\text{H}^+(\text{a}) + 10\text{HSO}_4^-(\text{a}) + 2\text{AsO}_4^{3-}(\text{a}) + 7\text{Sn}^{+2}(\text{a}) = 7\text{Sn}(\text{SO}_4)\text{O}_2 + \text{As}_2\text{S}_3 + 6\text{H}_2\text{O}$	-667	7	-95
9	$4\text{As} + \text{SnSO}_4(\text{a}) + 2\text{H}_3\text{AsO}_4(\text{a}) = 6\text{HAsO}_2(\text{a}) + \text{SnS}(\text{s})$	-57	1	-57
10	$\text{SnSO}_4(\text{a}) + \text{H}_3\text{AsO}_4(\text{a}) + \text{H}_2\text{SO}_4 = \text{Sn}(\text{SO}_4)_2(\text{a}) + \text{HAsO}_2(\text{a}) + 2\text{H}_2\text{O}$	-29	1	-29
11	$\text{Sn}^{+2}(\text{a}) + \text{H}_3\text{AsO}_4(\text{a}) + 2\text{H}^+(\text{a}) = \text{Sn}^{+4}(\text{a}) + \text{HAsO}_2(\text{a}) + 2\text{H}_2\text{O}$	-20	1	-20
12	$\text{Sn}(\text{HSO}_4)_2(\text{a}) + \text{H}_3\text{AsO}_4(\text{a}) = \text{Sn}(\text{SO}_4)_2(\text{a}) + \text{HAsO}_2(\text{a}) + 2\text{H}_2\text{O}$	-18	1	-18
13	$6\text{O}_2(\text{g}) + 3\text{PbS} + 2\text{H}_3\text{AsO}_4(\text{a}) = \text{Pb}_3(\text{AsO}_4)_2 + 3\text{H}_2\text{SO}_4$	-413	0	n/a

### 2.2.2.3 Ligand Substitution: Sulphate and Arsenate Anions

Precipitates of Fe(III) and As(V) can be formed by direct or co-precipitation: the phases can be crystalline, amorphous, or a combination of both. Anions or cations can be adsorbed or incorporated into either crystalline or amorphous matrix. The adsorption of an ion onto the surface of a solid particle follows the four factors of the “Paneth – Fajans – Hahn Law” (Fischer, 1961). When two or more ions are available for adsorption, the ions which form the lowest solubility compound with one of the lattice ions in the precipitated solid will adsorb on the surface of the solid. The concentration effect states the ion in greater concentration will adsorb preferentially. The ionic charge effect states that multivalent ions adsorb preferentially over those with a single charge. The size of

the ion factor states that an ion of similar size and charge to one of the lattice ions will adsorb preferentially.

The precipitation of scorodite under atmospheric pressure at 95 °C was investigated (Singhania et al., 2006). This paper also documents the effects of substitution of important anions ( $\text{SO}_4^{-2}$ ,  $\text{PO}_4^{-3}$ ) on precipitate leach ability. The sulphate and phosphate anions produced an unstable precipitate which leached more readily than the arsenic (arsenate) anion scorodites. Further studies regarding the effect of aqueous sulphate concentration and ferric arsenate precipitate stability have been completed.

The acidity level in the mother liquor affects the extent of adsorption of sulphate on ferrihydrite precipitates between pH 2.5 and 4.5, and, with respect to Sn(IV) precipitation, and this may be applicable to the Reduction Release conditions (Dutrizac, 1989). This study determined that as the acidity increases, the precipitate is more amorphous. A similar paper investigated the adsorption of arsenate onto ferrihydrite or iron arsenate precipitate from aqueous solution in acidic sulphate conditions (Jia and Demopoulos, 2005). This paper proposed the ligand exchange mechanism, where sulphate and arsenate anions are easily interchangeable and sulphate displaces adsorbed arsenate ions on the ferrihydrite iron surface. More sulphate anions displace adsorbed arsenate anions at higher acidity and higher Fe/As molar ratios, which can result in the production of a more unstable precipitate. The same authors investigated surface precipitation of arsenate on ferrihydrite, and the impact of initial acidity on the type of ferrihydrite phase precipitated. The findings indicated that more acidic conditions produce more amorphous than crystalline ferrihydrite solids which are not stable (Jia et al., 2006). Zinc can also complex Fe(III), and that either zinc or sulphate can be adsorbed onto the surface of the ferrihydrite precipitate matrix. Furthermore, both cations and anions can be incorporated into crystalline ferric arsenate precipitated below pH 4, and above 90 °C. Cations such as Al, Mn, Fe, Zn, Cu, Pb, Ni, Cd, and Co, and anions such as  $\text{PO}_4^{-3}$ ,  $\text{SO}_4^{-2}$ , and  $\text{Cl}^-$  can be incorporated in the iron precipitate matrix (goethite, ferric-arsenates, ferric hydroxides) by adsorption or co-precipitation (Singhania et al. 2006; Robins, Singh et al., 2005).



#### 2.2.2.4 Ionic Equilibrium and Sulphate

The total aqueous sulphate concentration is composed of sulphate contributions from free acid  $\text{H}_2\text{SO}_4$  such as ( $[\text{HSO}_4^{-1}]$ ), unprotonated ionic salts, and complexes in solution ( $[\text{SO}_4^{-2}]$  ionic) such as  $\text{ZnSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$ . The presence of bisulphate ion with dissolved oxygen has been mentioned previously with respect to precipitation of Sn(IV) in acidic media (Martyak and Seedfeldt, 2005). This investigation also found that as the total sulphate concentration increased, the rate of Sn(II) oxidation decreased, and subsequent precipitation of Sn(IV) decreased. Further research investigating sulphate concentration and rate of Sn(II) oxidation in acidic sulphate media found that the rate of Sn(II) oxidation decreased with an increase in total sulphate ions, possibly due to complex formation with Sn(II) oxidizing agents (Fe(III), Cu(II) and oxygen) which would result in a reduced Sn(IV) precipitation rate (Rozovskii et al., 1996). Further kinetic studies in acidic sulphate media found that the exchange reaction rate of Sn(II) to Sn(IV) increased as the sulphate concentration increased (Gordon and Brubaker, 1960).

### 2.2.3 Temperature

#### 2.2.3.1 Tin Precipitation Rate and Fe(III) Reduction/Activity

Kinetic studies using Fe(III) to precipitate Sn(IV) below 80 °C have shown that the rate of Sn(IV) precipitation increases with increasing temperature in the presence of Fe(III) by reducing the activation energy (Danilov and Tsygankov, 1975). Ferric iron readily oxidizes Sn(II) to Sn(IV) and has a large equilibrium value ( $K = 21$ , @ 25 °C), and Sn(IV) can precipitate in oxidizing regimes such as hydrous Sn(IV) sulphate or oxide type compound (Table 2.6).

Temperature effects on the precipitation of scorodite from mixed sulphate solutions under atmospheric pressure conditions have been studied for Fe(III) – As(V) co-precipitate systems (usually Fe:As > 4 molar ratio), and for temperatures between 85 and 100 °C (Singhania et al., 2005). Fe(III)-As(V) solids formation increases with

increasing temperature due to higher thermodynamic effects from supersaturation, or kinetic effects of Fe/As precipitation rates of secondary nuclei growth and crystal growth. This may assist with co-precipitation of tin. Furthermore, temperature effects were evaluated for the leaching of galena in ferric sulphate media and results show that the lead sulphide kinetics between 65 to 90 °C increased significantly with increasing temperature, and follow a diffusion-controlled mass transport (Dutrizac and Chen, 1995). Zink and Dutrizac (1998) also studied Sn(IV) precipitation in zinc sulphate and ferric sulphate solutions, and found that Sn(II) oxidation by Fe(III) and subsequent precipitation was affected by acidity and Fe(III) concentration. As the Sn(II) concentration increased, the precipitate Fe(II) and sulphate contents decreased and tin content in the precipitate increased. As the tin is oxidized to Sn(IV) by Fe(III) the tin is precipitated with the ferrihydrite. The tin precipitate was determined to be amorphous  $\text{SnO}_2 \cdot n\text{H}_2\text{O}$  dispersed to two-line ferrihydrite. There was less mass of precipitate formed from Sn(II) addition than from Sn(IV) addition, as some of the Fe(III) required for iron precipitation was still soluble as Fe(II) from oxidation or Sn(II) to Sn(IV). Theoretical Sn(II) solubility does exceed 1 g/L, and total tin levels measured during the Reduction Releach Process during the dissolution phase do not exceed 1 g Sn /L concentration, which is far below solubility limits for both Sn(II) and Sn(IV) compounds. Therefore, complexation (discussed in the iron section) and kinetics may influence final tin levels in solution.

#### 2.2.3.2 Tin Precipitation Rate and Polymerization

Tin forms soluble  $\alpha$ -stannic acid or  $\alpha$ -oxides ( $\text{H}_2\text{SnO}_3$  or  $\text{SnO}(\text{OH})_2$ ), and insoluble  $\beta$ -stannic acid or  $\beta$ -oxides ( $\text{H}_2\text{SnO}_3$ )<sub>5</sub> in various mineral acids such as  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{H}_2\text{SO}_4$ . These oxides are sometimes referred to as stannic and perstannic acids. These  $\alpha$ -stannic acids are easily soluble in  $\text{H}_2\text{SO}_4$ , and the metastannic acid ( $\beta$ -oxide) form is insoluble. The first experimental indication of tin polymerization was with acidic solutions of stannic chloride which showed that acidity slows the polymerization of Sn(IV), and temperature increases the degree of polymerization (Vignon, 1890). The  $\alpha$ -oxide is always the first product of hydrolysis, and converts to the  $\beta$ -oxide which polymerizes rapidly as the temperature is increased and precipitates as the insoluble  $\beta$ -oxide (Weiser, 1926). This polymerization of tin or “colloidal theory” is also described by transformation of the soluble  $\alpha$ -stannic acid to the insoluble  $\beta$ -form of stannic acid

with an increase in temperature (Mellor, 1924). The “colloidal” theory was used to explain the polymerization process of Sn(IV) in acidic media, and was explained further by Kleinschmidt (Mellor, 1924).

Kleinschmidt proposed that the polymerization of Sn(IV) was due to the amphoteric nature of aqueous tin and subsequent condensation and loss of water molecules upon heating in three defined steps:

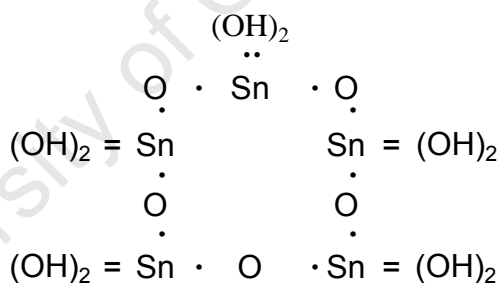
1. Heating
2. Conversion of Sn(IV) hydroxide to  $\alpha$ -stannic acid.  $\text{SnO}(\text{OH})_2$

A-stannic acid:  $\text{H}_2\text{SnO}_3$ ,



3. Loss of  $\text{H}_2\text{O}$  and polymerization of Sn(IV) to  $(\text{H}_2\text{SnO}_3)_5$

B-stannic acid:  $(\text{H}_2\text{SnO}_3)_5$ :



In addition to polymerization of tin in mineral acids, basic tin salts ( $\text{Sn}_5\text{O}_8\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Sn}_5\text{O}_9\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ) can react with mineral acids and peptize to form colloidal suspensions in the form of ortho, meta, and parastannic acids (Weiser, 1926). Fe(III) – Sn(IV) research has found that mixtures were not salt solutions but either hydrous ferric oxides peptized by hydrous stannic oxides, or hydrous or colloidal Sn(IV) oxide peptized by Fe(III) or hydrogen ions.

Temperature was investigated for the tin dissolution and hydrolysis of Sn(IV) in acidic media, and the following reactions were determined (El Rehim et al., 2004).



The temperature was varied between 10 to 70 °C, and 0.5 to 1.5 mol/L maleic acid. The findings indicated that tin dissolution increases with increasing acidity and increasing temperature. The oxidation of Sn(II) to Sn(IV) was very rapid, and the experimentally determined apparent activation energy was estimated to be 18 kJ/mol.

The temperature affects the activities of the metal ions in solution as suggested by Wang and Dreisinger (1998). This paper describes the effects of free acid salts and metal ions on pH behaviour in terms of metal ion activities, hydrolysis, stability quotients, and sulphate/bisulphate activities in terms of solution thermodynamic models.

#### 2.2.4 Dissolved and Entrained Oxygen

If any oxidant is present, such as dissolved and/or entrained oxygen, the Sn(II) ion is oxidized to a Sn(IV) state. This is the case with electrodeposition of tin during tin plating and electrowinning processes using stannous sulphate. Stannous sulphate baths (30 to 40 g/L Sn(II), 40 to 70 g/L H<sub>2</sub>SO<sub>4</sub>) are protected against atmospheric oxidation by several different oxygen scavengers. Typical oxygen scavengers such as creosulphonic acid (70 to 120 g/L), tartaric acid, diphenyl-amine-sulfamic acid, and potassium sodium tartrate are used to inhibit the oxidation of Sn(II) to Sn(IV). Sn(IV) compounds may undergo hydrolysis to form insoluble Sn(OH)<sub>4</sub> or SnO<sub>2</sub> solids (Wright, 1982; USX Engineers and Consultants, Inc., 1998).

The oxidation of Sn(II) by oxygen (dissolved and entrained) is shown in Table 2.5 (Salmi et al., 1992). Sn(II) oxidation is thermodynamically very favourable, with both aqueous and solid Sn(IV) compounds forming. Aqueous Sn(II) ions are unstable and oxidize rapidly, and also act as reducing agents for other dissolved ionic species such as aqueous Fe(III) ion. The log K values are favourable for Sn(II) oxidation reactions

involving either sulphate or bisulphate ions at 90 °C. The Eh-pH diagram for tin (Figure 2.1) indicates the tin species below pH=1 are predominantly Sn(IV) species. During the Reduction Releach Process, the measured concentration of dissolved and entrained oxygen does not exceed 5 mg/L. This lower than theoretical oxygen concentration may be due to poor mass transfer (inefficient mixing), or by Sn(II) oxidation. Sn(II) oxidation in acidic sulphate or sulphonate media by oxygen has been documented both in experimental papers as well as the stannous sulphate electrowinning industry (USX Engineers and Consultants, Inc., 1998; Martyak and Seedfeldt, 2005; Dennis, 1961).

**Table 2. 5: Tin and Oxygen Reactions**

<b>Tin and Oxygen Reactions at 90 °C</b>		$\Delta G_{Rx}$	mol Sn	$\Delta G_{Rx}$
		kcal		kcal/mol Sn
1	$\text{Sn}(\text{HSO}_4)_4(\text{a}) + 3\text{Fe} + 2\text{O}_2(\text{g}) = \text{Sn}(\text{SO}_4)_2(\text{s}) + 2\text{H}_2\text{O} + 3\text{FeSO}_4$	-348	1	-348
2	$\text{Sn}(\text{HSO}_4)_2(\text{a}) + \text{Fe} + 1.5\text{O}_2(\text{g}) = \text{Sn}(\text{SO}_4)_2(\text{s}) + \text{H}_2\text{O} + \text{FeSO}_4$	-241	1	-241
3	$\text{SnSO}_4(\text{a}) + \text{O}_2(\text{g}) = \text{Sn}(\text{SO}_4)_2(\text{s})$	-165	1	-165
4	$\text{Sn}(\text{HSO}_4)_2(\text{a}) + \text{O}_2(\text{g}) = \text{Sn}(\text{SO}_4)_2(\text{s}) + \text{H}_2\text{SO}_4$	-154	1	-154
5	$2\text{SnSO}_4(\text{a}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{SO}_4 = 2\text{Sn}(\text{SO}_4)_2(\text{a}) + 2\text{H}_2\text{O}$	-114	2	-57
6	$2\text{Sn}^{+2}(\text{a}) + \text{O}_2(\text{g}) + 4\text{H}^+(\text{a}) = 2\text{Sn}^{+4}(\text{a}) + 2\text{H}_2\text{O}$	-96	2	-48
7	$2\text{SnSO}_4(\text{a}) + \text{O}_2(\text{g}) + 2\text{H}_2\text{SO}_4 = 2\text{Sn}(\text{SO}_4)_2(\text{s}) + 2\text{H}_2\text{O}$	-89	2	-45

Figure 2.4 shows oxygen solubility in sulphuric acid and water at different temperatures. Literature values for dissolved oxygen concentration reported at atmospheric pressure, do not exceed 15 mg/L O<sub>2</sub> (g) in sulphuric acid for the Reduction Releach conditions. Again, poor mass transfer due to inefficient mixing, or another oxygen consuming reaction (Sn(II)) may contribute to the lower measured oxygen values. The TCML measured dissolved oxygen values are lower than the values reported in the literature which could be due to measurement error and instrument type. The oxygen solubility system for zinc sulphate and sulphuric acid systems has been well researched (Kaskiala and Salminen, 2003).

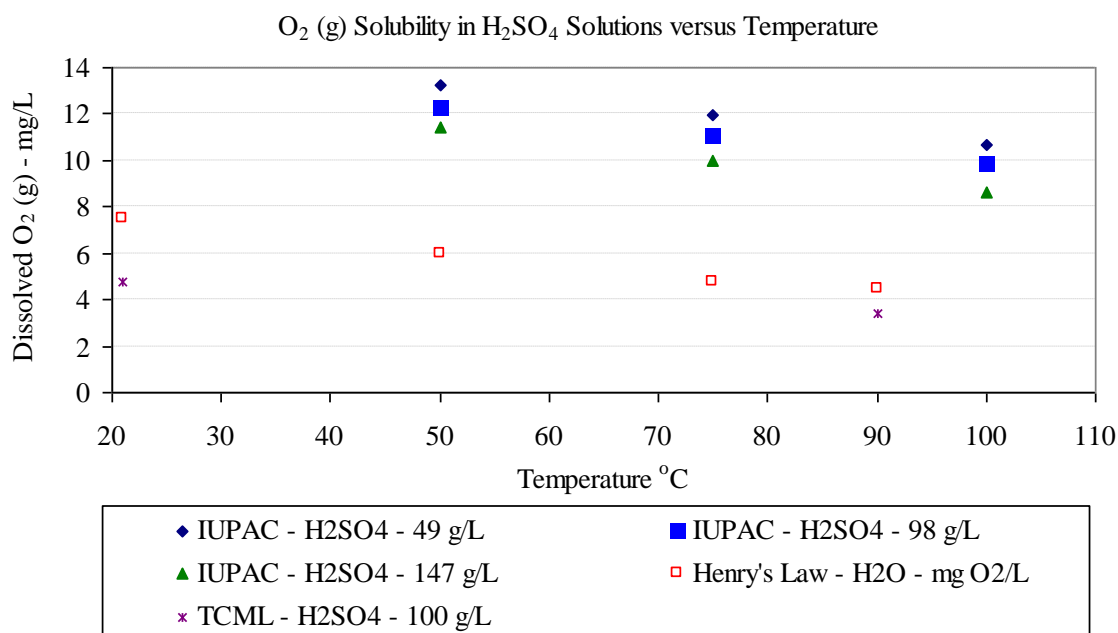


Figure 2. 4: Oxygen Solubility in water and sulphuric acid.

### 2.2.5 Iron

Ferric ion is the dominant aqueous iron species present at the lower pH range as shown in Eh-pH diagram (Figure 2.5). Previous work has shown that the Fe(III) aqueous ion can oxidize Sn(II) to Sn(IV), which then precipitates as an insoluble tin hydroxide. This work showed that as the Fe(III) concentration increases, the rate of tin residue precipitation increases (USX Engineers and Consultants, Inc., 1998). On the other hand, addition of iron powder to an acidic sulphate media at 100 g/L H<sub>2</sub>SO<sub>4</sub> (pH <1) acts as a very strong reducing agent.

At reducing REDOX conditions, iron is stable at the bottom of the Eh-pH diagram giving way to magnetite and then hematite at higher Eh. On the acidic side, Fe(II) and Fe(III) will form (Figure 2.5).

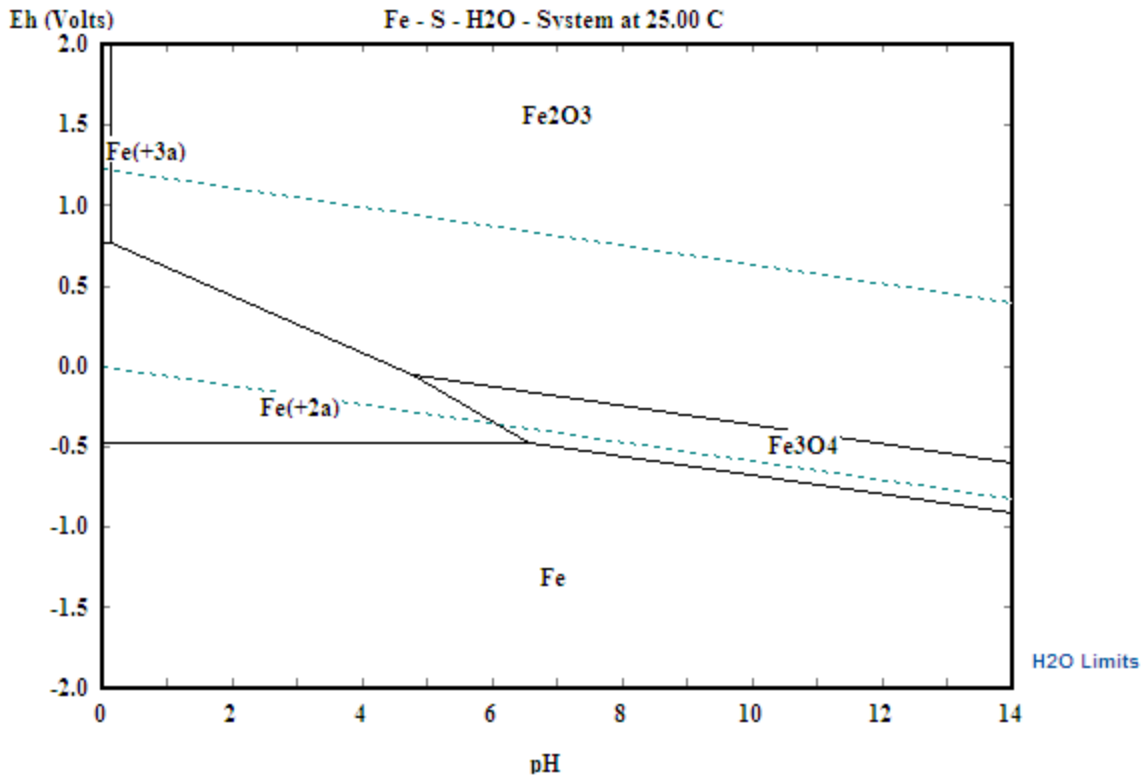


Figure 2. 5: Eh-pH Diagram for Fe –S – H<sub>2</sub>O (HSC v5.0)

Fe(0) in acidic sulphate media (pH<1) can react thermodynamically with either Sn(II) or Sn(IV) and produce Fe(II) aqueous species. In the absence of dissolved or entrained oxygen, hydrogen gas may be generated (Table 2.6). The iron powder assists with Fe(III) reduction, however, dissolved or entrained oxygen will convert Fe(II) to Fe(III) aqueous ion. As well, Fe(III) will readily oxidize Sn(II). Iron powder will preferentially react with Sn(II), Sn(IV), and oxygen to precipitate tin and oxidize iron to ferrous (Table 2.6) (Salmi et al., 1992). The intended use for iron powder in the Reduction Releach Process is to reduce the final amounts of Fe(III) to Fe(II), and precipitate aqueous Cu(II). The use of ferric iron has been proposed to rapidly oxidize Sn(II) to insoluble Sn(IV) species in both stannous sulphate and chloride from iron precipitation and electrowinning solutions (Zink and Dutrizac, 1998; USX Engineers and Consultants, Inc., 1998).

Several thermodynamically possible reactions between tin and iron are listed in Table 2.6. However, reactions 1 and 2 are most likely kinetically irrelevant due to the low solubility of dissolved oxygen at 90 °C.

**Table 2. 6: Tin and Iron Reactions at 90 °C**

Tin and Iron Reactions at 90 °C		$\Delta G_{RX}$	mol Sn	$\Delta G_{RX}$
		kcal		kcal/mol Sn
1	$\text{Sn}(\text{HSO}_4)_4(\text{a}) + 3\text{Fe} + 2\text{O}_2(\text{g}) = \text{Sn}(\text{SO}_4)_2(\text{s}) + 2\text{H}_2\text{O} + 3\text{FeSO}_4$	-348	1	-348
2	$\text{Sn}(\text{HSO}_4)_2(\text{a}) + \text{Fe} + 1.5\text{O}_2(\text{g}) = \text{Sn}(\text{SO}_4)_2(\text{s}) + \text{H}_2\text{O} + \text{FeSO}_4$	-241	1	-241
3	$\text{Sn}(\text{HSO}_4)_4(\text{a}) + 3\text{Fe} = \text{SnSO}_4 + 2\text{H}_2(\text{g}) + 3\text{FeSO}_4$	-110	1	-110
4	$\text{Sn}^{+2}(\text{a}) + 2\text{Fe}^{+3}(\text{a}) + 2\text{H}_2\text{O} = \text{SnO}_2 + 2\text{Fe}^{+2}(\text{a}) + 4\text{H}^+(\text{a})$	-43	1	-43
5	$3\text{Sn}(\text{HSO}_4)_2(\text{a}) + 2\text{Fe} = 3\text{SnSO}_4 + 3\text{H}_2(\text{g}) + \text{Fe}_2(\text{SO}_4)_3$	-121	3	-40
6	$\text{Fe} + \text{Sn}^{+4}(\text{a}) = \text{Sn}^{+2}(\text{a}) + \text{Fe}^{+2}(\text{a})$	-28	1	-28
7	$\text{Fe} + \text{Sn}(\text{SO}_4)_2(\text{a}) = \text{SnSO}_4(\text{a}) + \text{FeSO}_4(\text{a})$	-26	1	-26
8	$\text{SnSO}_4(\text{a}) + \text{Fe}_2(\text{SO}_4)_3(\text{a}) + 2\text{H}_2\text{O} = \text{SnO}_2(\text{s}) + 2\text{FeSO}_4(\text{a}) + 2\text{H}_2\text{SO}_4$	-22	1	-22
9	$\text{Fe} + \text{SnO}_2 + 2\text{H}_2\text{SO}_4(\text{a}) = \text{SnSO}_4(\text{a}) + \text{FeSO}_4(\text{a}) + 2\text{H}_2\text{O}$	-15	1	-15
10	$\text{Fe} + \text{Fe}_2(\text{SO}_4)_3(\text{a}) = 3\text{FeSO}_4(\text{a})$	-57	n/a	n/a
11	$\text{Fe}_2(\text{SO}_4)_3 + \text{PbS} = \text{PbSO}_4 + 2\text{FeSO}_4 + \text{S}$	-26	n/a	n/a



## 2.2.6 Sulphur (Sulphide Reductant)

### 2.2.6.1 Redox and the Role of Sulphur in PbS Reductants

Shown is the Eh-ph diagram for tin, sulphur (Figure 2.6).

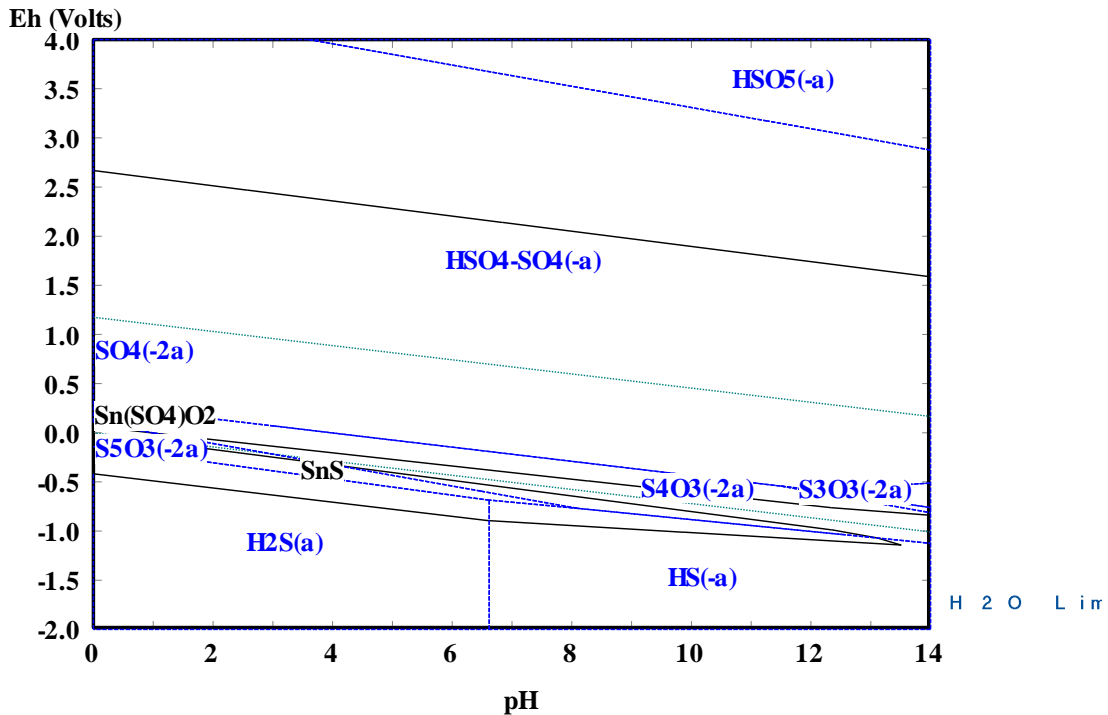


Figure 2. 6: Eh-pH Diagram for S and Sn (HSC v5.0)

The predominant aqueous phase sulphur species are sulphate and bisulphate ions below pH 1 and in an oxidizing environment, as shown on the Eh-pH diagram for sulphur and tin (Figure 2.6). Several studies have been carried out examining ferric leaching of galena (PbS) in sulphate media, and subsequent lead sulphate and elemental sulphur formation (Dutrizac and Chen, 1995; Chen and Dutrizac, 1991). These papers report that the leaching rate of PbS increased by temperature as well as acidity.

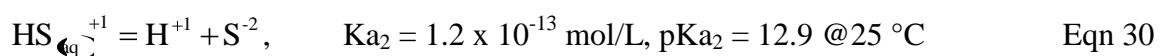
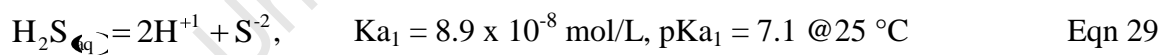
Sn (II/IV) compounds and lead sulphide have thermodynamically favourable reactions which are shown in the table below (Table 2.7) (HSC v5.0). However, formation of sulphate directly from sulphide ion oxidation is not likely at 90 °C at

atmospheric pressure conditions. Although reactions 7, 8, and 9 contain oxygen, they are considered impractical due to temperature and solubility limitations; it is thought the formation of elemental sulphur is preferential to sulphate in the aqueous phase.

**Table 2. 7: Tin and Sulphur Reactions at 90 °C**

Tin and Sulphur Reactions at 90 °C		$\Delta G_{Rx}$	mol Sn	$\Delta G_{Rx}$
		kcal		kcal/mol Sn
1	$6Pb(s) + 2Sn(HSO_4)_4(a) + PbS(s) = 2SnS(s) + 7PbSO_4(s) + 4H_2O$	-218	1	-218
2	$1.333Pb(s) + 1.333Sn(HSO_4)_2(a) + PbS = 1.333SnS + 2.333PbSO_4 + 1.333H_2O$	-64	1	-64
3	$SnSO_4(a) + PbS(s) = SnS(s) + PbSO_4$	-15	1	-15
4	$SnO_2(s) + 1.25PbS(s) + H_2SO_4 = SnS(s) + 1.25PbSO_4(s) + H_2O$	-9	1	-9
5	$SnCl_2 + PbS(s) = PbCl_2 + SnS(s)$	-8	1	-8
6	$Sn(SO_4)_2 + 2H_2O = SnO_2(s) + 2H_2SO_4$	-3	1	-3
7	$6O_2(g) + 3PbS + 2H_3AsO_4(a) = Pb_3(AsO_4)_2 + 3H_2SO_4$	-413	n/a	n/a
8	$O_2(g) + 1.25PbS + H_2SO_4 = 1.25PbSO_4 + H_2O + S$	-103	n/a	n/a
9	$1.5O_2(g) + 3PbS + 2H_3AsO_4(a) = Pb_3(AsO_4)_2 + 3H_2O + 3S$	-100	n/a	n/a

Lead and sulphur (sulphide) contents of lead concentrate are 49 % and 27 %, respectively. The lead and sulphur contents of pure reagent PbS are 87 % lead, and 13 % sulphide sulphur. From equilibrium theory, sulphide ions would precipitate Sn(IV) as SnS<sub>2</sub> or SnS, and not reduce Sn(IV) to Sn(II). On the basis of solubility products, impurities such as Sb(III), In(III), Cu(II) and Cd(II) would precipitate before tin. Furthermore, H<sub>2</sub>S (aq) is thought to undergo the following reaction (Harrison, 1972):

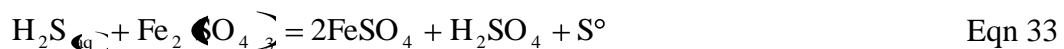
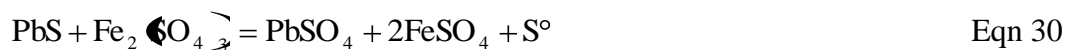


Lead concentrates used for Reduction Releach reduction of Fe(III) contain approximately 50 % Pb as PbS. Generally, sulphides have very low solubilities in the following order:

Sb>In>Cu>Cd>Sn>Pb>Zn Stannous sulphide has a K<sub>sp</sub> of  $3.25 \times 10^{-28}$ .

The leaching of galena (PbS) in ferric sulphate media in the sulphuric acid concentration ranging from 20 to 300 g/L H<sub>2</sub>SO<sub>4</sub>, and (III) concentration ranging from 10 to 110 g/L Fe(III), at temperatures between 60 to 90 °C, was investigated by Dutrizac and Chen (1995). The leaching rate was diffusion-controlled and increased by direct acid attack on the sulphide mineral. Furthermore, initial acidity and Fe(III/II) concentration can affect the concentration of arsenic in solution. Additional research has been carried out examining ferric leaching of sulphide minerals in sulphate media, and subsequent lead sulphate and elemental sulphur formation (Chen and Dutrizac, 1991, Dutrizac and Chen, 1995). These reports found that the leaching rate of PbS increased by temperature as well as acidity. Other investigations have shown that as acidity increased, elemental sulphur generation decreased and H<sub>2</sub>S generation increased for a given REDOX (Lotens and Wesker, 1987). Mulak and Wawrzak (1993) subsequently found that H<sub>2</sub>S generation rate and PbS dissolution rate increased with increasing Fe(III) concentration, and that PbSO<sub>4</sub> formation coated the PbS and reduced PbS dissolution. Reduced PbS dissolution may lead to Fe(III) reduction which in turn may reduce Sn(IV) precipitation reactions in the Releach process. Alternative tin precipitation studies in acidic media have concluded that tin precipitation increased as temperature and lead concentration in solution increased (Davis, 1980).

Dissolution of lead sulphide was researched in ferric sulphate leaching media, where Fe(III) is reduced and the sulphide mineral oxidized and leached. The sulphur was converted to a sulphate hydrogen sulphide, or elemental sulphur depending on the REDOX of the system. Furthermore, the sulphide reductant (PbS) in lead concentrate is thought to undergo the following reactions in acidified ferric sulphate media (Chen and Dutrizac, 1991, Dutrizac and Chen, 1995).



Results from the above investigation showed that lead sulphide dissolution increases with increasing temperature and Fe(III) concentration, and that PbSO<sub>4</sub> formation reduces lead sulphide dissolution. As well, if impurities such as Ag and Zn are present, they will precipitate as a sulphide (Chen and Dutrizac, 1991). The same authors found that the activation energy required for lead sulphide in a sulphate based system to be higher (E<sub>a</sub> = 61.2 kJ/mol) than an acidic chloride based system (E<sub>a</sub> = 43.5 kJ/mol) due to the generation of lead sulphate and elemental sulphur (Dutrizac, 1993). Further analysis of general thermodynamic and kinetic data for sulphide mineral dissolution in acidic ferric sulphate media examined sulphate and sulphur formation and the impact on dissolution behaviour of sulphide minerals (Crundwell, 1987; Holmes & Crundwell, 1995, 2000).

#### 2.2.6.2 Pb Solubility

In general, lead compounds are generally very insoluble compared to sulphides and sulphates in acidic sulphate leach solutions. Important oxidation states of arsenic are 3/0/+3/+5, with As(V) being best for precipitation because metal arsenates (H<sub>3</sub>AsO<sub>4</sub>) have a lower solubility than arsenites (H<sub>3</sub>AsO<sub>3</sub>). Furthermore, crystalline arsenates have a solubility two times less than equivalent amorphous solids (Robins, Nishimura et al., 2005). For reference, the following lead compounds are arranged in terms of increasing solubilities in water at 25 °C (Harrison, 1972): the lead arsenate has the least solubility, the sulphate has the largest solubility.



Lead can be removed from the leach solution by solubility limitations or direct cation substitution in the ferric arsenate precipitate matrix. There have been several studies investigating cation and anion substitution into the ferric arsenate matrix (Robins, Singh et al., 2005; Singhanian et al., 2006; Jia et al., 2006). This research has found that

cations such as Al, Mn, Fe, Zn, Cu, Pb, Ni, Cd, and Co can substitute Fe(III) in the arsenate matrix, and do not affect the precipitation rate or precipitate stability.

### 2.2.6.3 Pb and Fe Arsenate Rate of Precipitation

Investigations by Singhania et al. (2005) included temperature and seeding effects on the precipitation of scorodite in mixed sulphate systems at atmospheric pressure conditions. They found that the rate of scorodite precipitation rate increased dramatically during a temperature increase from 85 to 100 °C. The increase in arsenate precipitation rate was attributed to two main causes: firstly, a decrease in thermodynamic supersaturation, and resulting change in solubility; and, secondly, activation energy kinetic effects due to secondary scorodite nucleation, ultimately leading to increased crystal growth and a more stable precipitate, which does not re-lease (Claassen and Sandenbergh, 2004). Seeding with magnesium and calcium oxides also increased scorodite precipitation rate. Initial acidity and the type of arsenate phase precipitated as a result were also investigated in surface precipitation and adsorption of arsenate on ferrihydrite (Jia et al., 2006). The effects of acidity, valency, and third ion effects on the precipitation of scorodite at atmospheric pressure conditions for acidic mixed sulphate systems at 95 °C (Singhania et al., 2006) were evaluated. Initial acidity (induction pH) and As(V) concentration were found to be very important with respect to the amorphous or crystalline formation of precipitated solids. Key findings included: high acidity increases the scorodite precipitation rate, producing more amorphous precipitated solids that could re-lease. This study also found that solution with increasing aqueous ratios of Fe(III)/As(V) ratios reduced the rate of precipitation, but produced a more stable crystalline precipitate, less subject to re-leaching.

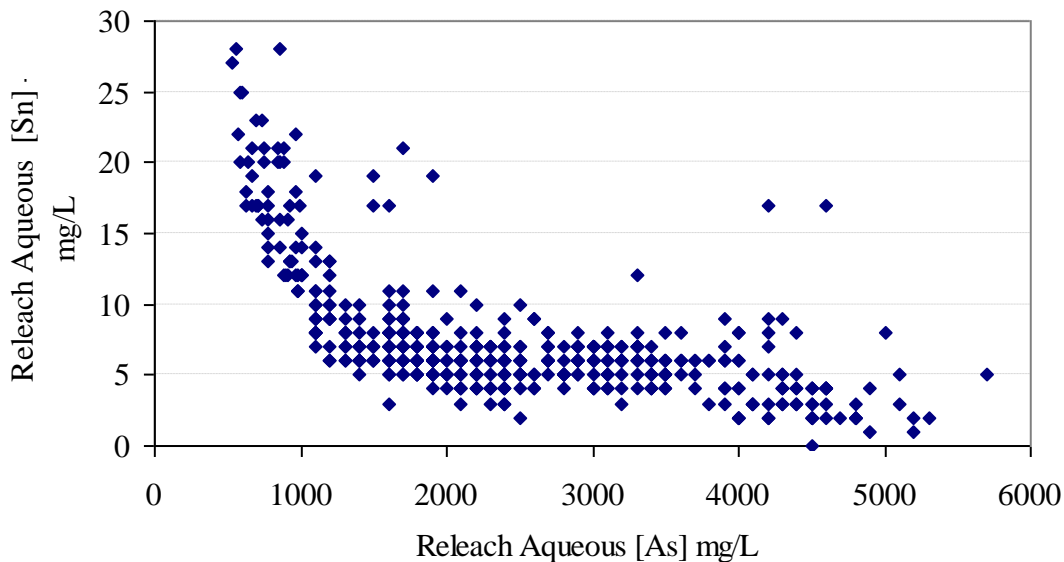
An investigation was conducted with regard to precipitation and impurity removal for treating complex tin dusts containing high arsenic and antimony (Tang and Zhao, 1992). This paper discusses using continuous impurity precipitation reactors versus batch to improve impurity removal. This study also reported that increased acidity does not mean more lead precipitation and removal. A sulphide reductant is used at the ratio of

0.122 g metal sulphide / g tin dust with subsequent H<sub>2</sub>S being generated. The TCML Reduction Releach Process uses a reductant ratio of  $R_{PbCon/PreCon} = 0.6$ .

#### 2.2.6.4 Arsenic Concentration

##### 2.2.6.4.1 As(V) versus Fe(III) Complexation

Shown below are actual Reduction Releach tin and arsenic trends for 2005/6. There is a general correlation between final aqueous tin and arsenic concentrations in solution at the end of the Reduction Releach cycle. It is not clear why this is the case, or if this trend reflects some other unknown relationship between tin and arsenic. When the final aqueous arsenic concentration is low, the final aqueous tin concentration is high. The TCML Plant data shows that as aqueous arsenic concentration increases above 1 g/L in the final Releach solution, tin concentration decreases (Figure 2.7).



**Figure 2.7: Release Aqueous Sn and As Trends, (TCML 2006 Process Data)**

Possibly, this is arsenic that is complexed by Fe(III) (excess in leach) and there is not enough arsenic remaining in solution to react with tin, and precipitate tin. Arsenic speciation studies in ferric sulphate /sulphuric acid media and the resulting stability of As(III/IV) precipitates have been investigated by Tan and Dutrizac (1985). This paper discusses the arsenic acids and As(III/V) stability, metastability, and the effect of pH

(0.3 mol/L H<sub>2</sub>SO<sub>4</sub>, 1 – 10 g/L As(V), 0.2 M FeSO<sub>4</sub>), and Fe(III) and Fe(III) on As(III/IV) stability and metastability in sulphuric acid solutions. The effect of solution speciation for Fe-S-As-Cl systems at 298 K was studied in Fe(III) systems and it was found that the degree of complexation was a function of the concentration of anions initially present in the solution (Welham et al., 2000). This research found that both arsenate anions and sulphate anions readily complex Fe(III) in mixed sulphate systems. Furthermore, arsenate anions complex Fe(III) better than sulphate anions in mixed sulphate systems. Further work examining the solubility and stability of iron arsenates and their behaviour in acidic media and determined that scorodites are metastable, and can breakdown to form Fe (III) hydroxide species and arsenate ions (Dove and Rimstidt, 1985).

### 2.3 Hypothesis

From previous tin solubility testwork and observed plant process information, it was concluded that there is likely more than one mechanism of tin dissolution and precipitation from solution during the acidic sulphate reductive Releach process. Aqueous tin is of concern in the Releach process, as it limits indium extraction further downstream, resulting in lower indium recoveries.

Extensive studies of tin solubility have been reported. These predict higher tin solubility at acidic oxidizing conditions due to proton availability. Furthermore, other cations present in solution can affect bisulphate de-protonation and increase the total acidity of the solution. Temperature plays a role in Fe(III) reduction kinetics, and tin polymerization in iron-free acidic sulphate solutions. As was observed, the TCML Releach solutions show a strong correlation between total aqueous tin and total arsenic at the end of the leach cycle.

Fe(III)-As(V) precipitation studies have indicated that arsenate precipitates can be crystalline (stable), or amorphous (unstable), and subject to re-leaching. The rate of arsenate precipitation can also affect the stability of the arsenate precipitate. Rapid

precipitation of arsenates can produce an amorphous unstable ferric arsenate precipitate which can re-leach.

When aqueous anions, such as sulphate, increase in concentration relative to arsenate ions, the sulphate anions can displace adsorbed arsenate ions on the ferrihydrite precipitate by ligand substitution and produce an unstable precipitate, which can re-leach. Fe(III) in the arsenate matrix can be displaced by cations such as zinc or lead.

Arsenic in solution behaves like an acid and can complex with Fe(III) as well as precipitate with Fe(III) and form ferric arsenate precipitates. Based on the insights from the literature review, the following hypotheses are put forward to explain the behaviour of tin in the Reduction Re-leach.

### **2.3.1 Total Acidity:**

An increase in the total acidity of the Re-leach solution will increase the total aqueous tin concentration in solution by three governing mechanisms.

1. Total proton and sulphate availability: The higher the initial  $\text{H}_2\text{SO}_4$  concentration is at the start of the Re-leach, the higher the resulting total acidity and aqueous tin concentration will be during the Re-leach process.
2. Ligand substitution: The ratio of aqueous sulphate to arsenate typically increases as total acidity increases, leading to displacement of precipitated tin arsenates by sulphate. This results in a more unstable Re-leach precipitate which has a higher sulphate content and results in a higher aqueous tin concentration in solution.
3. Ionic strength of the Re-leach solution: Anions such as bisulphate, and acidic oxides such as arsenic increase the total acidity of the solution which should result in higher aqueous tin concentration.



### 2.3.2 Temperature:

1. Aqueous tin precipitation is driven initially by kinetics in the Releach process which corresponds to the rate of change in potential in the oxidizing range during the Releach, and that lower aqueous tin levels correspond to lower final REDOX potentials. The change in REDOX potential is a result of Fe(III) reduction, and the change in aqueous tin concentration profile will follow the change in Fe(III) concentration profile.
2. Tin (IV) oxide polymerization is a further precipitation mechanism that may occur in the Releach process. Increasing temperature may increase tin (IV) oxide polymerization and reduce final aqueous tin concentration in solution.

### 2.3.3 Reductant Ratio:

An increase in sulphide reductant amount relative to Ge Preconcentrate will increase the rate of arsenate precipitation and produce an amorphous, unstable precipitate, which will re-dissolve and increase the aqueous tin concentration. In the oxidizing leaching regime, lead compounds such as oxides/sulphates, sulphides, and arsenates have very low solubility and will precipitate.

### 2.3.4 Aqueous Arsenic (V) Concentration

1. Increased arsenic levels in the commercial Releach process do not lower the aqueous tin concentration in the Releach process trends due to the presence of Fe(III).
2. However, if Fe(III) is not present, then arsenic can react with Sn(II/IV) and precipitate tin in an acidic sulphate oxidizing solution as some type of sulphate, oxy-sulphate, sulphate peroxide, or oxide, and arsenic (III) as  $As_2O_3$  (Table 2.4).

The hypothetical mechanisms described above will be verified or disproved through test work:

1. Total acidity is tested at constant pressure and temperature, constant initial reductant amount ( $R_{PbCon}/PreCon = 0.6$ ), varying the initial acidity from 40 to

- 220 g/L H<sub>2</sub>SO<sub>4</sub>, and examining how aqueous tin concentration changes with total acidity, aqueous sulphate and arsenate concentrations, and precipitate composition versus time during the Reduction Releach Process.
2. Additional total acidity tests will be conducted at constant pressure and temperature, constant initial acidity (100 g/L H<sub>2</sub>SO<sub>4</sub>), and reductant amount ( $R_{\text{PbCon/PreCon}} = 0.6$ ), varying the initial arsenic concentration with reagent grade A<sub>2</sub>O<sub>5</sub> from 5 to 10 g/L As concentration, and examining how aqueous tin concentration changes with total acidity and aqueous sulphate and arsenate concentrations, and precipitate composition versus time during the Reduction Releach Process.
  3. A series of temperature tests will be carried out at constant pressure, initial acidity (100 g/L H<sub>2</sub>SO<sub>4</sub>), constant initial reductant amount ( $R_{\text{PbCon/PreCon}} = 0.6$ ), and varying the leach temperature from 30 to 90 °C. This test series will examine how aqueous tin concentration changes with temperature, ferric reduction profile, REDOX and time during the Reduction Releach Process.
  4. The test program for the proposed sulphide reductant ratio tests at constant pressure and temperature, and constant initial acidity (100 g/L H<sub>2</sub>SO<sub>4</sub>) will vary the reductant ratio from 0.2 to 1.0 g PbCon/g Precon. How aqueous tin and sulphur concentration, and total sulphur in leach residue change with reductant ratio (amount), REDOX, and time during the Reduction Releach Process will be examined.
  5. The proposed arsenic concentration tests at constant pressure and temperature, and constant initial acidity (100 g/L H<sub>2</sub>SO<sub>4</sub>) will vary the aqueous As(V) concentration from the baseline(BL) concentration of 1 g/L As(V) in 5 g/L As increments (BL, BL + 5 g/L as, BL + 10 g/L As). The change in total aqueous tin concentration, arsenic concentration, total acidity, Fe(III) concentration, and REDOX versus time will be examined during the Releach process.
  6. The proposed pure reagent arsenic concentration tests at constant pressure (1 atm) and temperature (90 °C), and initial acidity (100 and 220 g/L H<sub>2</sub>SO<sub>4</sub>) will vary the aqueous As(V) concentration and measure changes in aqueous tin and arsenic concentration, and REDOX versus time.

Other supporting testwork to provide corollary information includes:

1. Determine tin speciation/oxidation state in the Releach starting reagents ZnO fume, Ge Preconcentrate and in final Reduction Releach residue.
2. An investigation of tin solubility to compare against literature and theoretical tin solubility values.
3. Oxidation rate of stannous tin oxidation rates to determine the rate of Sn(II) oxidation as a function of tin concentration.
4. A valid Sn(II/IV) measurement method will be tested using iodometry and REDOX potential for use in the bench scale and pure reagent tests.

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### **3 EXPERIMENTAL**

#### **3.1 Reagents**

##### **3.1.1 Pure Components (Reagent Grade)**

Pure reagents for Sn(II/IV), As(III/V), and Fe(II) were reagent grade compounds, and were used for all the dissolution and solubility tests (Appendix A).

##### **3.1.2 Process Samples**

Germanium Preconcentrate, lead concentrate, and iron powder are used in the commercial Releach process. The thesis bench scale tests used lead concentrate, iron powder, and a composite Germanium Preconcentrate sample (Appendix B).

#### **3.2 Equipment**

The polyethylene reactor had a total volume of 4.5 L. The reactor dimensions were 17.2 cm I.D., height of 20 cm, and the operation level was 15.3 cm (3.5 L). The internal steam coil was made of 316L stainless steel, with dimensions of 162 cm long, 0.64 cm O.D., and 0.48 cm I.D. The agitator used was a dual impeller A310 mixer made of 316L stainless steel (Appendix C).

##### **3.2.1 Equipment Description**

The Reduction Releach apparatus (Figures 3.1 and 3.2) is comprised of the polyethylene reactor, variable speed dual impeller (A310) agitator, 4 baffles, steam heating/water cooling coils, thermocouple, and REDOX (Ag/AgCl) probe. The test apparatus is scaled down from the actual Releach process in terms of reactor geometry and mixing.

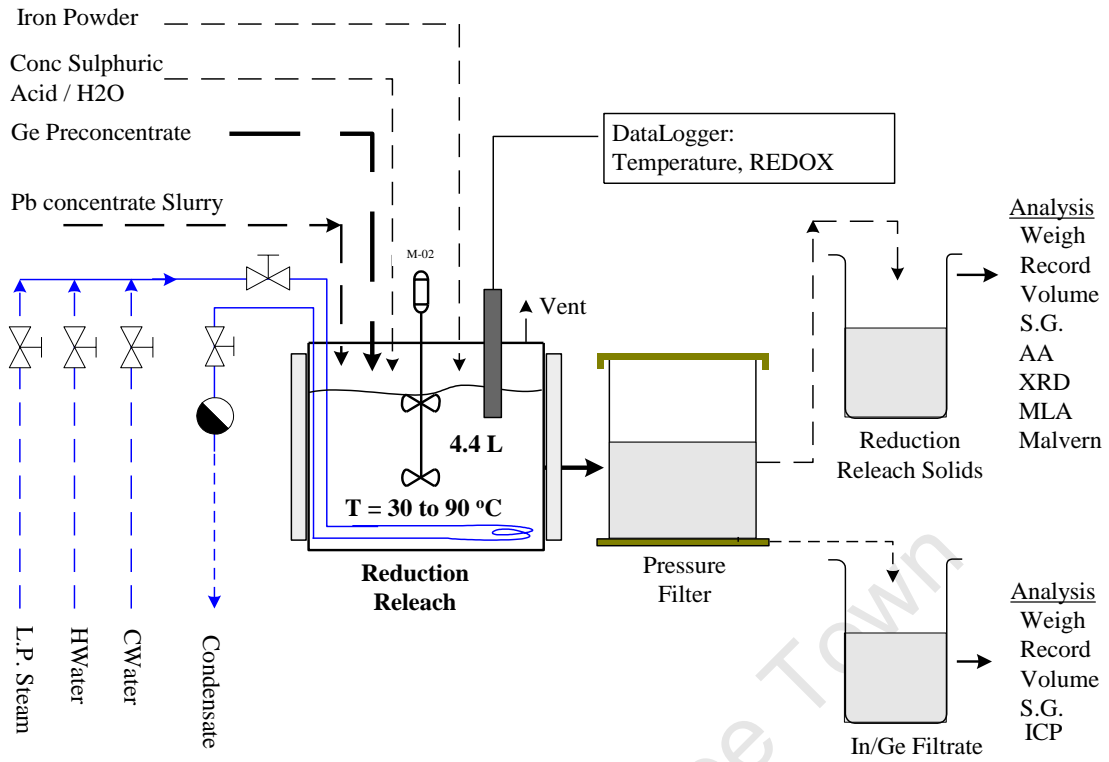


Figure 3. 1: Reduction Releach Apparatus



Figure 3. 2: Actual Reduction Releach Reactor (a) and Controls (b)

### **3.3 Methodology**

#### **3.3.1 Reduction Releach Procedure**

The diluted sulphuric acid reagent (40 to 220 g/L Initial H<sub>2</sub>SO<sub>4</sub>) was automatically heated to the operating temperature (30 to 90 °C) by a temperature-controlled steam heating coil. Once the operating temperature was reached, the Ge Preconcentrate was added as a slurry followed by the lead concentrate or PbS reductant, and then the pure reagent As<sub>2</sub>O<sub>5</sub> was added if required (Appendix D).

#### **3.3.2 Dissolution Test**

The diluted sulphuric acid solvent (40 – 220 g/L initial H<sub>2</sub>SO<sub>4</sub>) was heated to the operating temperature automatically by temperature-controlled steam heating coils. Once the operating temperature was reached the pure component being studied was added as a solid (Appendix D).

#### **3.3.3 Analytical Procedures for Reduction Releach Samples**

The samples taken during the releach tests were sent to TCML's Analytical Services lab for analysis. These samples were processed within seven days of submission (Appendix E).

##### Total Acidity Titration:

The total acidity (H<sub>2</sub>SO<sub>4</sub>) concentration was determined during the test using a sodium hydroxide titration procedure (Appendix E.1).

##### Ferrous Fe Titration:

The ferrous iron titrations were conducted during each test (Appendix E.2).

### Total Fe Titration:

The total iron titrations were conducted during each test, and then the ferric iron (Fe (III)) was determined as  $Fe_T - Fe^{+2}$  (Appendix E.3).

### Aqueous Sn (II/IV) Titration validation:

This test was used to determine an accurate method determination of Sn(II/IV) concentration using Iodometry as well as ORP (Appendix E.4).

### Sample Preparation: Solids:

Samples were filtered under vacuum, washed with demineralised water, sealed in a plastic container, and sent for analysis. Sample compositions were determined by inductive coupled plasma analysis ICP at the TCML Labs.

### Solid Speciation for Diagnostic Leaches (Sulphuric Acid, Acetic Acid):

These are leaches to increase certain impurity concentrations from <0.1 wt % to greater than 1 wt % using sulphuric acid and acetic acids in the residue. The increase in concentration was required for improved XRD and SEM resolution of low concentration elements in the residue matrix (Appendix H, I).

## 3.3.4 Controlled Variables and Baseline Conditions

### 3.3.4.1 Controlled Variables

**Table 3. 1: Controlled Variables**

<b>Controlled Variables:</b>	<b>Units</b>	<b>Baseline</b>		<b>Adjusted Variables</b>	
<b>Ge PreConcentrate(Basis)</b>	<b>g - dry</b>	<b>600</b>			
Temperature	°C	90	30	60	90
[Acidity]	(g/L H <sub>2</sub> SO <sub>4</sub> )	100	40	100	160
PbCon: PreCon	(g/g)	0.6	0.2	0.6	1.0
PbS:PreCon	(g/g)	0	0.1	0.4	0.6
Fe Powder	g- dry	Fixed	11 g/ kg PreCon., t = 100 min		
[As]	g/L (As <sub>2</sub> O <sub>5</sub> )	Baseline ~ 1	Baseline + 5	BaseLine + 10	
Mixing Speed (RPM)		400			
Sample times	minutes	1, 3, 10, 30, 60, 100, 150			

The controlled variable parameters (Table 3.1) for the Reduction Releach Process are temperature, acidity, and reductant concentration. The temperature of the process is traditionally 90 °C to ensure adequate Fe(III) reduction kinetics. At lower temperatures the ferric reduction reaction rates decrease rapidly. The acidity of 100 g/L H<sub>2</sub>SO<sub>4</sub> or greater is required to prevent silica dissolution during the commercial Releach which can cause downstream process problems in filtration of Releach residue and crud formation in SX operations. Adequate reductant (PbS) in the lead concentrate is required to ensure ferric reduction and impurity precipitation. In practice, temperature and acidity vary significantly and the experiments reflect the actual range of variation for acidity and temperature. As well, lead concentrate is added in the process via a slurry (with water) and can vary in addition amounts to Ge Preconcentrate. During the actual Releach process, temperature which increases as reagents are added may influence the chemistry of tin. Furthermore, initial acidity is based on fill volume at the beginning of the leach, and is then not further controlled during the Releach process.

### 3.3.4.2 Baseline Conditions (BL)

The purposes of the BL experiments (Table 3.2) are to determine the time for Fe(III) reduction, and to generate a BL for comparison against testwork around acidity, temperature, lead concentrate/PbS, and As<sub>2</sub>O<sub>5</sub>.

**Table 3. 2: Baseline Conditions**

<b>Baseline Conditions (No Fe Powder, with Fe Powder)</b>			
		<b>25A&amp;B<sup>a</sup></b>	<b>26A&amp;B<sup>b</sup></b>
<b>Conc H<sub>2</sub>SO<sub>4</sub>+H<sub>2</sub>O</b>	<b>g/L</b>	100	100
<b>Temperature</b>	<b>°C</b>	90	90
<b>Ge PreConcentrate:Dry</b>	<b>g</b>	600	600
<b>Ge PreConcentrate:Wet</b>	<b>g</b>	1154	1154
<b>PbCon:Ge PreConcentrate (Dry)</b>	<b>g/g</b>	0.6	0.6
<b>PbConcentrate: Dry</b>	<b>g</b>	360	360
<b>PbConcentrate:Wet</b>	<b>g</b>	391	391
<b>Fe Powder</b>	<b>g</b>	None	6.6
<b>Agitator</b>	<b>RPM</b>	400	400

**Notes: a = No Fe Powder, b = With Fe Powder**



The BL conditions represent actual process conditions for the commercial leach process. The Ge Preconcentrate mass is the basis for all other reagent addition experiments. Iron powder is not always added to the Releach process in practice. In all thesis tests using Ge Preconcentrate, the diluted H<sub>2</sub>SO<sub>4</sub> solution at the appropriate acid strength is added to the Releach reactor at room temperature. The diluted H<sub>2</sub>SO<sub>4</sub> solution is then heated indirectly using saturated steam in stainless steel coils inside the reactor to the desired operation temperature using a thermocouple and feedback temperature control loop. Once the operation temperature is reached, the reagents are added in the following sequence: Ge Preconcentrate, then Pb Concentrate. If iron powder is used, it is added at the t = 100 minute portion of the Releach cycle.

### 3.3.5 Controlled Variables: Description and Selection Criteria

#### 3.3.5.1 Ge Preconcentrate

Ge Preconcentrate is generated from an acidic sulphate iron precipitation purification process (pH=4), the residue contains the tin species of interest. The Ge Preconcentrate lead and arsenic compositions can vary widely (Table 3.3).

**Table 3. 3: Ge Preconcentrate Composition (%) Variability; TCML 2006**

	As [ % ]	Fe [ % ]	Pb [ % ]	SiO <sub>2</sub> [ % ]	Sn [ % ]	ASol/Zn [ % ]
<b>Average</b>	<b>1.91</b>	<b>11.68</b>	<b>24.28</b>	<b>2.33</b>	<b>0.90</b>	<b>6.16</b>
<b>MIN</b>	<b>0.83</b>	<b>5.50</b>	<b>13.80</b>	<b>1.10</b>	<b>0.39</b>	<b>1.70</b>
<b>MAX</b>	<b>3.80</b>	<b>19.00</b>	<b>42.00</b>	<b>3.80</b>	<b>1.60</b>	<b>14.50</b>
<b>95 % CI</b>	<b>0.05</b>	<b>0.17</b>	<b>0.34</b>	<b>0.04</b>	<b>0.02</b>	<b>0.13</b>
<b>STDEV</b>	<b>0.60</b>	<b>2.09</b>	<b>4.20</b>	<b>0.45</b>	<b>0.23</b>	<b>1.59</b>

A blended composite of several samples of Ge Preconcentrate (64 kg wet @ 48 % moisture; composition in Table 3.4) was used for all the benchscale Releach tests.

**Table 3. 4: Ge Preconcentrate Blended Composition (%); TCML 2006**

	As [ % ]	Fe [ % ]	Pb [ % ]	SiO <sub>2</sub> [ % ]	Sn [ % ]	ASol/Zn [ % ]
<b>Assay</b>	<b>1.20</b>	<b>10.00</b>	<b>14.60</b>	<b>1.60</b>	<b>1.10</b>	<b>14.40</b>

The balance of the composition is sulphur, oxygen, hydrogen, silica, and valuable impurities (indium, germanium). The composite Ge Preconcentrate sample was sealed in 2 - 20 L plastic pails with air tight lids. The Ge Preconcentrate mass added was 600 g (dry basis) for each bench scale test. The proportional amount of lead concentrate or PbS added was calculated from this basis amount.

#### 3.3.5.2 Iron Powder

For the commercial Releach process, iron in the Ge Preconcentrate varies from 5 to 19 wt % which results in significant variation of ferric and ferrous iron levels in the Reduction Releach (between 15 and 27 g/L total iron in the commercial Reduction Releach Process). The Releach reagents are added to the commercial reactor at room temperature and brought to leaching temperature (90 °C) in approximately 30 minutes from the start of the Releach cycle. The Releach cycle continues for approximately 45 minutes at leach temperature. At the end of the 45 minute leaching portion of the Releach cycle, the Fe(III) reduction and Cu removal is checked qualitatively (colourmetric analysis). If the Fe(III) has not been reduced by a reaction time interval of 45 minutes in the commercial Releach, iron powder can be added to reduce any remaining Fe(III) in solution to Fe(II), as well as precipitate any remaining Cu(II) from solution.

### 3.3.5.3 Acidity and Temperature

**Table 3. 5: Acidity and Temperature -- Test No. and g/L H<sub>2</sub>SO<sub>4</sub>, and Temperature °C**

<b>Initial Acidity and Temperature</b>		
<b>Δ H<sub>2</sub>SO<sub>4</sub> : Baseline (No Fe Powder), 90 °C</b>		
	<b>Test No.</b>	<b>g/L H<sub>2</sub>SO<sub>4</sub></b>
High Acid	<b>38A&amp;B</b>	<b>220</b>
Medium Acid	<b>27A&amp;B</b>	<b>160</b>
Baseline	25A&B	100
Low Acid	<b>28A&amp;B</b>	<b>40</b>
<b>Δ Temperature : Baseline (No Fe Powder), 100 g/L H<sub>2</sub>SO<sub>4</sub></b>		
	<b>Test No.</b>	<b>°C</b>
Med Temp	<b>29A&amp;B</b>	<b>60</b>
Baseline	25A&B	90
Low Temp	<b>30A&amp;B</b>	<b>30</b>

#### 3.3.5.3.1 Acidity

The bench scale acidity range (40 to 220 g/L H<sub>2</sub>SO<sub>4</sub>) was chosen to correspond to the actual range of terminal acidities (60 to 170 g/L total acidity) that are observed in the commercial Releach process. The terminal acidity targeted is 100 g/L total acidity to prevent silica dissolution, and eventual downstream filtering issues. The acidity change during the Releach process is a function of Ge Preconcentrate amount and composition, and mass of PbS reductant (lead concentrate) added relative to Ge Preconcentrate.

#### 3.3.5.3.2 Temperature

The temperature range chosen (30 to 90 °C) is the temperature range observed in the commercial batch leach process (30 to 90 °C). The higher temperatures are required for Fe(III) reduction and impurity precipitation, the lower temperatures are required for gypsum precipitation prior to filtering, as well as cooler temperatures for Indium SX feed solution. This testwork examines the absolute temperature and not “rate of change” of temperature as the batch Releach process has heating, leaching at temperature, and cooling steps.

### 3.3.5.4 Reductant Ratio: Lead Concentrate and PbS

Lead concentrate is required for Fe(III) reduction, and impurity precipitation during the Releach process, and is based on a mass ratio of 0.6 (t lead concentrate / t Ge Preconcentrate). The lead concentrate is added as a slurry (S.G. 2.8-2.9) and the additional amount is based on the change in fill level in the Releach batch reactor. The lead concentrate contains approximately 50 % lead and minor amounts of zinc and iron (Table 3.7). The sulphur (30 %) in lead concentrate is present as sulphides (Appendix B). Pure reagent grade PbS (galena) was also added to some experiments and the addition amount was based on the lead addition amount used in the lead concentrate tests, and then the mass was increased as equivalent PbS (Table 3.6). All reductant ratio tests varied the mass of lead concentrate or PbS to Ge Preconcentrate mass.

**Table 3. 6: Pb Concentrate and PbS Test No. and g/g**

<b>Pb concentrate and PbS versus Fe Powder</b>		
<b>Δ Pb concentrate : + BaseLine (No Fe Powder)</b>		
		<b>g/g</b>
PbCon: PreCon	<b>31A</b>	<b>1</b>
PbCon: PreCon	25A&B	0.6
PbCon: PreCon	<b>31B</b>	<b>0.2</b>
<b>Δ PbS : + BaseLine (No Fe Powder)</b>		
		<b>g/g</b>
PbS: PreCon	<b>32A</b>	<b>0.6</b>
PbS: PreCon	<b>32B</b>	<b>0.35</b>
PbS: PreCon	<b>32C</b>	<b>0.12</b>
<b>Δ PbS : + BaseLine (with Fe Powder)</b>		
		<b>g/g</b>
PbS: PreCon	<b>33A</b>	<b>0.6</b>
PbS: PreCon	<b>33B</b>	<b>0.35</b>
PbS: PreCon	<b>33C</b>	<b>0.12</b>

The lead concentrate assay is shown in Table 3.7. For more detailed lead concentrate assay, see Appendix B.

**Table 3. 7: Pb Concentrate Key Assays**

	As [ % ]	Fe [ % ]	Pb [ % ]	SiO2 [ % ]	Sn [ % ]	ASol/Zn [ % ]	S [ % ]
Assay	0.02	16.48	48.83	0.23	0.01	3.59	27.41

### 3.3.5.5 As(V) as As<sub>2</sub>O<sub>5</sub>

The As(V) tests were conducted at BL conditions with and without iron powder, and with varying amounts of As<sub>2</sub>O<sub>5</sub> (Table 3.8). In practice, arsenic concentrations vary widely from 1 to 7 g / L As in the Releach process. The source of arsenic variability in the Releach process is the Ge Preconcentrate (0.5 to 4 wt %). Furthermore, the lead content in Ge Preconcentrate can vary from 14 to 42 wt % (average is 24 wt %).

**Table 3. 8: Arsenic (As<sub>2</sub>O<sub>5</sub>) Test No. and Concentration**

<b>Arsenic addition (As<sub>2</sub>O<sub>5</sub>)</b>		
<b>Δ [As5+] : + Baseline (No Fe Powder)</b>		
		<b>g/L As</b>
As	<b>34A</b>	<b>BaseLine + 10</b>
As	<b>34B</b>	<b>BaseLine + 5</b>
As	<b>34C, 25A&amp;B</b>	Baseline
<b>Δ [As5+] : + Baseline (with Fe Powder)</b>		
		<b>g/L As</b>
As	<b>35A</b>	<b>BaseLine + 10</b>
As	<b>35B</b>	<b>BaseLine + 5</b>
As	<b>35C, 26A&amp;B</b>	Baseline

Pure component tests with no iron present and using reagent grade SnSO<sub>4</sub> and As<sub>2</sub>O<sub>5</sub> were also carried out in 100 and 220 g/L H<sub>2</sub>SO<sub>4</sub> at 90 °C over a 4-hour period, sampling every hour (Table 3.9). These tests were used for a comparison of the arsenic behaviour with that of the bench scale tests that have Fe(III/II) present.

**Table 3. 9: Pure As amd Sn Compound Reagent addition amounts.**

<b>Pure As<sub>2</sub>O<sub>5</sub>, SnSO<sub>4</sub>, and H<sub>2</sub>SO<sub>4</sub></b>			
<b>Δ [As<sup>5+</sup>] :As<sub>2</sub>O<sub>5</sub>, SnSO<sub>4</sub>, 100 g/L H<sub>2</sub>SO<sub>4</sub>, 90 °C</b>			
	<b>g As<sub>2</sub>O<sub>5</sub></b>	<b>g SnSO<sub>4</sub></b>	<b>ZnSO<sub>4</sub></b>
<b>39AB</b>	<b>2</b>	<b>20</b>	<b>0</b>
<b>40AB</b>	<b>20</b>	<b>2</b>	<b>550</b>
<b>41AB</b>	<b>2</b>	<b>20</b>	<b>0</b>
<b>42AB</b>	<b>20</b>	<b>2</b>	<b>0</b>
<b>Δ [As<sup>5+</sup>] :As<sub>2</sub>O<sub>5</sub>, SnSO<sub>4</sub>, 220 g/L H<sub>2</sub>SO<sub>4</sub>, 90 °C</b>			
	<b>g As<sub>2</sub>O<sub>5</sub></b>	<b>g SnSO<sub>4</sub></b>	<b>ZnSO<sub>4</sub></b>
<b>42CD</b>	<b>20</b>	<b>2</b>	<b>0</b>

## 4 RESULTS AND DISCUSSION

### 4.1 Speciation Studies

#### 4.1.1 ZnO Fume

Slag Fuming Furnace (SFF) fume samples leached with Return Acid (RA) to reduce the zinc oxide content, and increase the relative concentration of tin and other low concentration impurities for improved XRD analysis. The SFF fume was separated into size fractions (+75  $\mu\text{m}$ , +38  $\mu\text{m}$ ), polished and grain mounted. The XRD analysis (Figure 4.1) indicates that the main crystalline components are mimetite [ $\text{Pb}_5(\text{AsO}_4)_3\text{Cl}$ ] and zinc tin oxide ( $\text{Zn}_2\text{SnO}_4$ ) or  $(\text{ZnO})_2 \cdot \text{SnO}_2$ . Both arsenic and tin are present in their highest valence state of As(V) and Sn(IV) oxidation states, respectively. Partially reacted fume from the pH 4 iron precipitation step is present in the Ge Preconcentrate, so it is quite reasonable to expect some of these arsenic and tin compounds in the process.

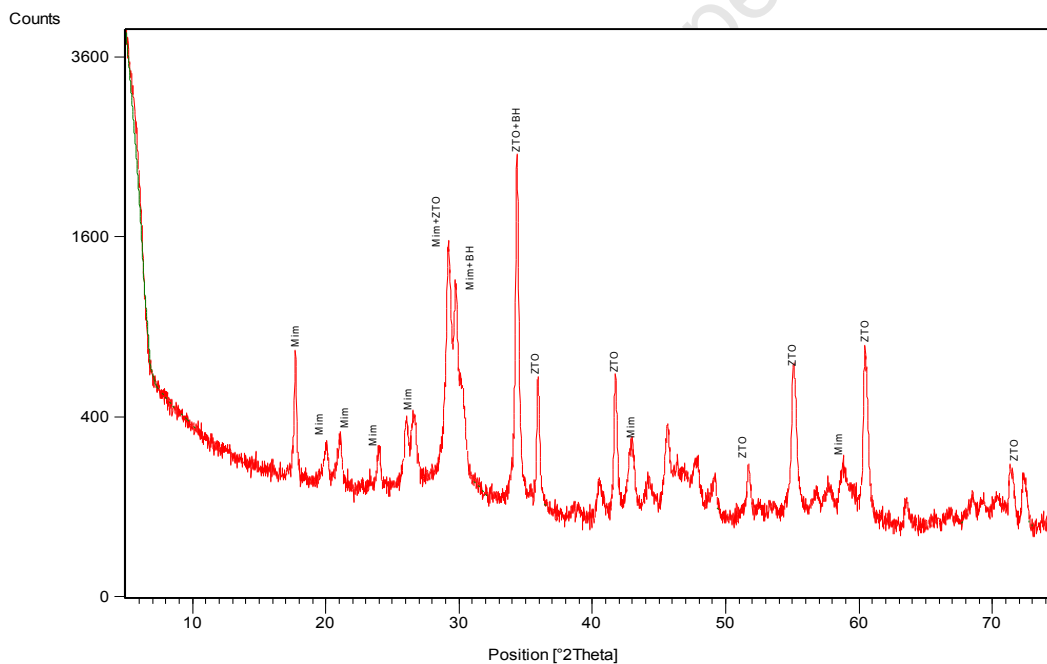


Figure 4. 1: XRD Scan - Return Acid Leached Fume (Sample 1)

A summary of the crystalline compounds in the fume is listed below (Table 4.1). Non-crystalline compounds are not included with this analysis.

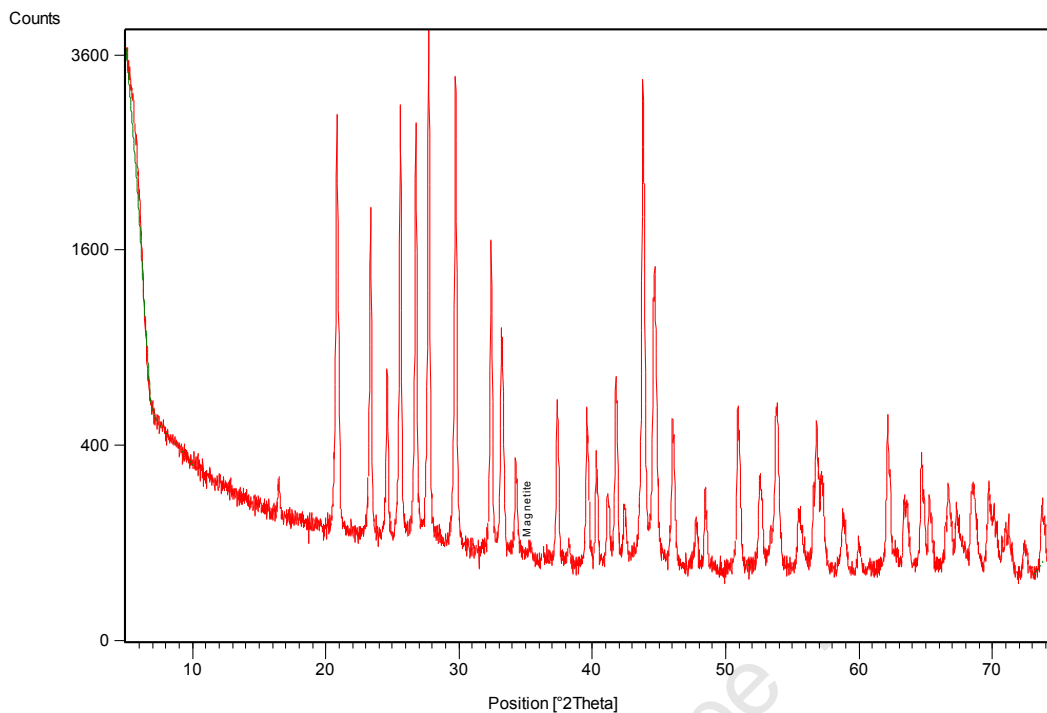
**Table 4. 1: ZnO Fume Crystalline Compounds**

Ref. Code	Compound Name	Chemical Formula	SemiQuant
01-080-2103	Mimetite (Mim)	$Pb_5 (AsO_4)_3 Cl$	Major
00-024-1470	Zinc Tin Oxide (ZTO)	$Zn_2 Sn O_4$	Major
01-075-1533	Zincite	$Zn O$	Trace
01-085-0711	Lithargite	$Pb O$	Trace
00-041-1493	Red lead	$Pb_3 O_4$	Trace
00-042-1355	Bindheimite (BH)	$Pb_2 Sb_2 O_7$	Minor

#### 4.1.2 Ge Preconcentrate

The germanium Preconcentrate was analyzed by SEM and XRD. The samples were grain-mounted and the -38  $\mu m$  size fraction was analysed. The majority of the crystalline tin was found to be associated with lead, iron and zinc oxides as  $(Zn,Fe,Pb,O)_2 \cdot SnO_2$ , which is the Sn(IV) state. Tin was present in a secondary crystalline phase on Al(Fe)-silicates, although no chemical formula was determined for this phase. Sometimes, indium and germanium are associated with tin. Lead is present in virtually all particles. The majority of arsenic could be present as As(V) with trace amounts of As(III). Both tin and arsenic may be present in their respective higher oxidation states as the iron precipitation process leach solution, which generates the Ge Preconcentrate, is air-sparged and oxidizing in nature. Tin concentration increased in the -38  $\mu m$  size fraction. XRD showed the sample was mainly anglesite ( $PbSO_4$ ), as well as lead arsenates  $Pb_3(AsO_4)_3$  or  $Pb_5(AsO_4)_3Cl$ . This indicates that lead is precipitating with sulphate and arsenate due to the low solubility of these compounds in acidic sulphate media. The undersized fraction was studied by SEM-EDX analysis.





**Figure 4. 2: XRD Scan – Ge Preconcentrate (Sample 3 - 38  $\mu\text{m}$  Size Fraction)**

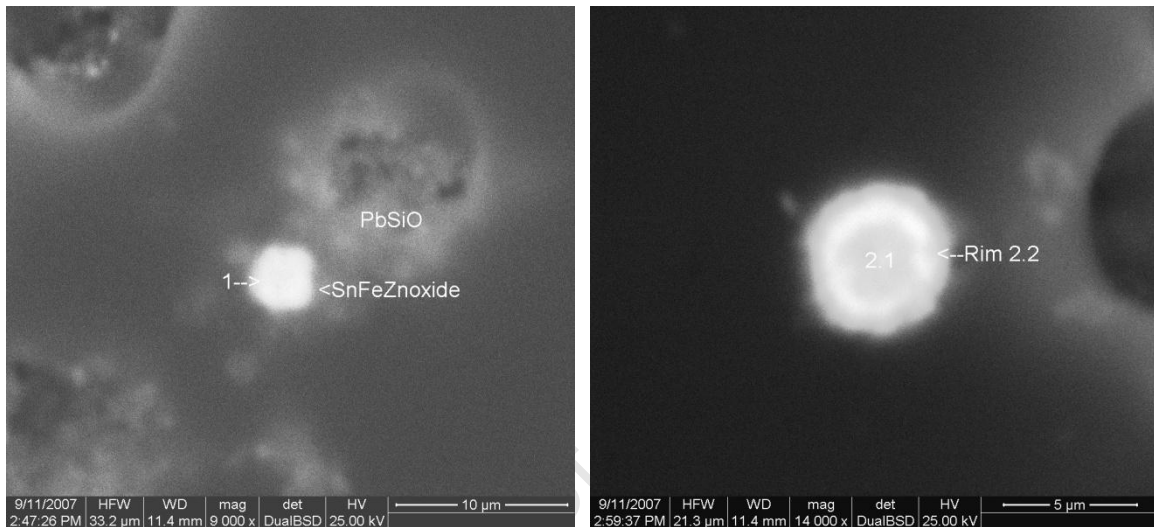
The crystalline compounds identified in the Ge Preconcentrate XRD scan (Figure 4.2) are listed below (Table 4.2). Tin increased from 1.2 % in the unleached sample to 3.2 % in the leached -38  $\mu\text{m}$  portion but decreased to 0.6 % in the leached +38  $\mu\text{m}$  fraction. All non-labelled significant peaks are anglesite.

**Table 4. 2: Ge Preconcentrate Crystalline Compounds - Pattern List**

Ref. Code	Compound Name	Chemical Formula	SemiQuant
01-083-1720	Anglesite	$\text{Pb}(\text{SO}_4)$	major
01-077-0049	Arsenic Oxide	$\text{As}_2\text{O}_3$	trace*
01-086-1346	Magnetite	$\text{Fe}_{2.962}\text{O}_4$	low

The major lead compound identified by XRD analysis is lead sulphate. Interestingly, trace amounts of As(III) were detected. Crystalline iron is present as magnetite, most likely from the fume (unreacted from the iron precipitation process).

Shown in Figure 4.3 for particle one and two are the Ge Preconcentrate SEM micrographs. Tin is associated with zinc, iron, and lead as an oxide.



**Figure 4. 3: SEM - Ge Preconcentrate (Sample #3 - 38μm Size Fraction)**

Tin is found in the Ge Preconcentrate as both oxide particles, as well as in a layered lead oxide particle as crystalline particles and residue. The compositions of particles 1 and 2 are summarized below (Table 4.3). Tin appears to be heavily concentrated in the core of the particle, as well as the outer surface (particle 2). Possibly, tin is present in the unreacted fume and has precipitated tin on the surface of the particle.

**Table 4. 3: Ge Preconcentrate Crystalline Compounds Part A**

Particle 1			Particle 2 – core			Particle 2 - outer surface		
Fe	21.9	%	Pb	35.6	%	Pb	70.2	%
Zn	18	%	Fe	24.4	%	Fe	7	%
Sn	13.4	%	Zn	11.7	%	Sn	5.4	%
O	29.7	%	Sn	5.7	%	Zn	3.9	%
			O	37.7		O	26.7	%

Further analysis of Ge Preconcentrate using SEM analysis revealed that tin is present in layers on the Ge Preconcentrate particle (Figure 4.4). The particle (particle 8) is layered with a core, and two identified outer layers (An2, An3) both containing tin as a mixed zinc and tin oxide.

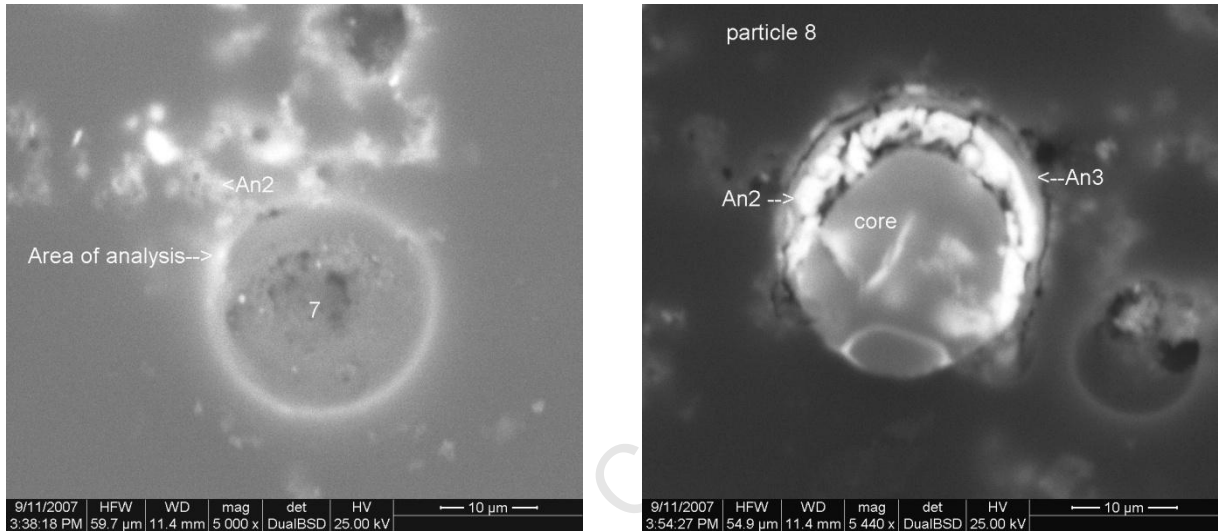


Figure 4. 4: Ge Preconcentrate SEM Pictures

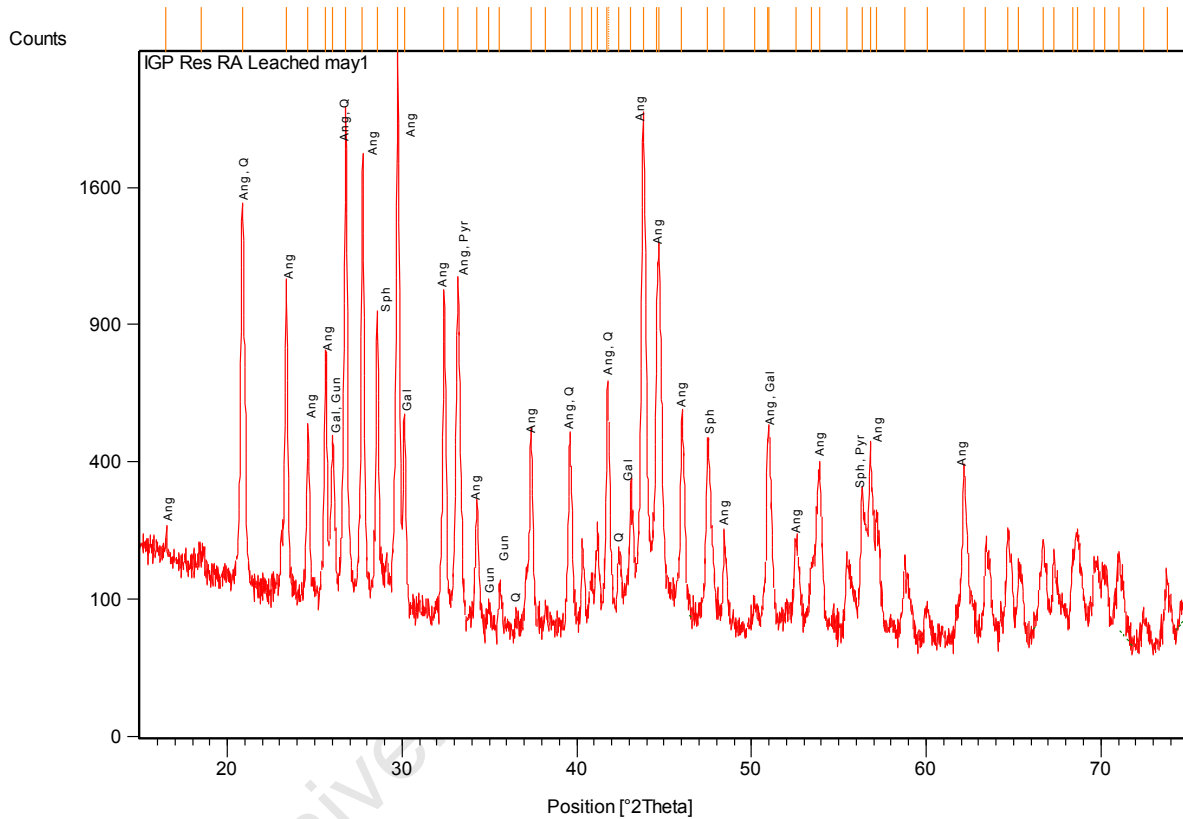
Tin is associated with zinc and oxygen as a zinc tin oxide or zinc tin iron oxide (Table 4.4). The highest concentration of tin (>8 %) being in the outer layer/core of the particle.

Table 4. 4: Ge Preconcentrate Crystalline Compounds Part B

Particle 7 - outer skin			Particle 7 -hollow part			Particle 8 - An2			Particle 8 - core			Particle 8 - An3		
Pb	24.2	%	Pb	40.1	%	Pb	64.7	%	Si	21.5	%	Pb	22	%
Sn	6.8	%	Sn	7.1	%	S	3.5	%	Pb	12.9	%	Sn	8.5	%
Si	2.5	%	Fe	3	%	Sn	1.8	%	Sn	8.2	%	Si	8.1	%
Sb	2.1	%	Sb	2.6	%	Si	0.7	%	Sb	6.8	%	Zn	3.4	%
Fe	1.7	%	S	2.2	%	O	29.4	%	Ge	2.3	%	Fe	3.1	%
S	1.2	%	Si	1.4	%				In	1.7	%	Cd	2.1	%
O	61.5	%	As	1.3	%				As	0.6	%	Ti	1.1	%
			O	42.4	%				S	0.5	%	As	0.4	%
									O	45.6	%	O	51.3	%

### 4.1.3 Reduction Residue

The XRD analysis showed that the sample consists mainly of anglesite ( $\text{PbSO}_4$ ), galena and sphalerite. The XRD scan of the residue found anglesite (major), galena (medium), sphalerite (medium) and minor levels of quartz, pyrite and gunningite (Figure 4.5)



**Figure 4. 5: XRD Scan – Reduction Residue**

The presence of galena ( $\text{PbS}$ ) and sphalerite ( $\text{ZnS}$ ) indicates unreacted lead concentrate in the sample, either due to excess lead concentrate addition or poor mixing, and combined with the low solubility of sulphides in acidic media (atmospheric pressure,  $90\text{ }^\circ\text{C}$ ) (Table 4.5). The Releach sample had excessive residual levels of galena ( $\text{PbS}$ ) and sphalerite ( $\text{ZnS}$ ) from the lead concentrate used in the reduction treatment, and was not further studied. The presence of lead and zinc sulphides indicates that excessive lead concentrate was added, or that the concentrate was not mixed sufficiently.

**Table 4. 5: Reduction Residue Compounds - Pattern List**

Ref. Code	Compound Name	Chemical Formula	SemiQuant
01-083-1720	Anglesite (Ang)	Pb(SO <sub>4</sub> )	high
01-078-1900	Lead Sulfide (Gal)	PbS	medium
01-077-2100	Zinc Sulfide (Sph)	ZnS	medium
01-071-1680	Pyrite (Pyr)	FeS <sub>2</sub>	low
01-078-2066	Cervantite, syn	Sb <sub>2</sub> O <sub>4</sub>	trace*
01-078-1253	Quartz (Q)	SiO <sub>2</sub>	low
00-033-1476	Gunningite (Gun)	ZnSO <sub>4</sub> · H <sub>2</sub> O	low

Furthermore, crystalline tin was found to be associated with Pb, Fe and zinc oxides with Al(Fe)-silicates, in the Sn(IV) state. This is not surprising as the highest concentration of ferric iron (15 g/L) is at the beginning of the Releach. The REDOX reaction between Fe(III) and Sn (II) is very thermodynamically favourable and will readily oxidize any Sn(II) present to the Sn(IV) oxidation state. Although not shown here, amorphous residue solids showed low levels of indium and germanium. The grain mount of the -38 µm size fraction was analysed by SEM-EDX.

## 4.2 Pure Tin–H<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O System

### 4.2.1 Solubility Level of Pure SnSO<sub>4</sub> versus Temperature

Diluted H<sub>2</sub>SO<sub>4</sub> (100 g/L total acidity) was heated to three different temperatures (30, 60, 90 °C, P = 1 atm), and then SnSO<sub>4</sub> (s) was added successively in 30 g Sn/L increments over four hours until the solution was saturated and the solid would no longer dissolve (Figure 4.6). These tests were done to validate theoretical tin solubility calculations done with OLI v3.1, 2006). The total aqueous tin concentration was measured by inductive coupled plasma analysis (ICP). The maximum solubility of Sn for all three temperature cases was approximately 99 g [Sn]/L. This indicated that temperature did affect total tin solubility, which decreased from 99 to 95 g/L with an increase in temperature from 30 to 90°C (Weiser, 1926). With respect the thesis benchscale tests using Ge Preconcentrate, the total measured tin levels during the Releach dissolution phase did not exceed 1 g Sn /L concentration at the one minute time frame

into the Release, however, the solution may have exceeded 1 g/L prior to the one minute time frame, but was not sampled.

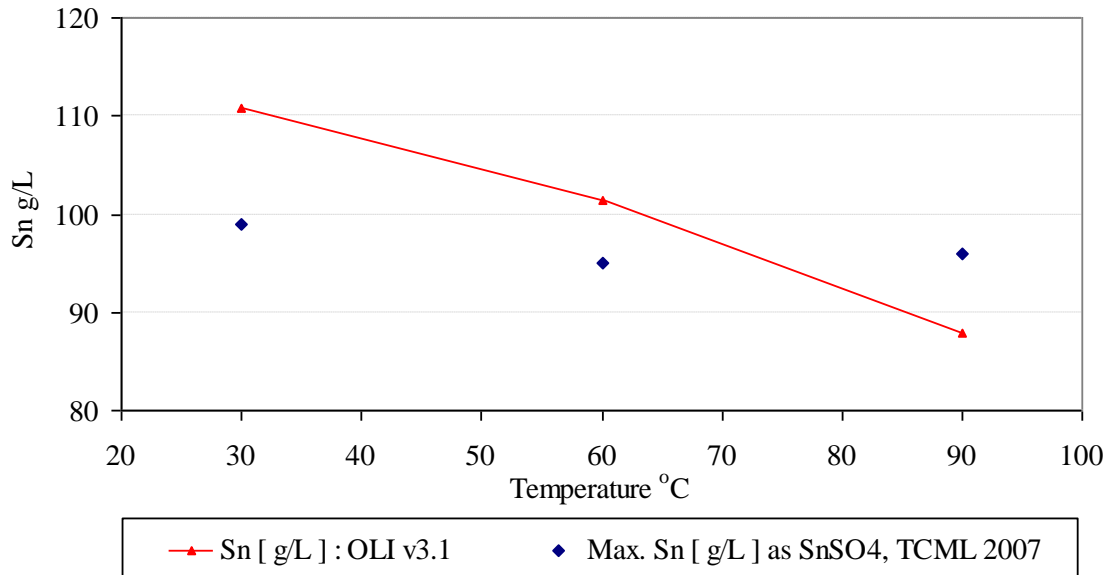


Figure 4. 6: SnSO<sub>4</sub> Solubility versus Temperature

The low tin solubility early in the Release may indicate that other kinetic effects other than temperature alone may influence tin solubility. Although total aqueous tin concentration was measured for the stannous sulphate solubility experiments (Figure 4.6), it may be assumed from previous Sn (II) oxidation work, that aqueous Sn(II) most likely had converted to Sn(IV) as dissolved and entrained oxygen and is present throughout these pure reagent saturation tests. From previous tin speciation work in the Ge Preconcentrate, it was determined that tin is predominantly Sn(IV), with minor amounts of Sn(II) (Table 2.1). Tin speciation work completed for the Ge Preconcentrate blended sample used in all the thesis tests was determined to be in the Sn(IV) oxidation state. Therefore, the blended composite sample assumes homogenous mixture, and the assay determined for the particular size fraction analyzed represents all size fractions of the analysis, which may not be true (see section 4.1.2).

#### 4.2.2 Sn(II) Oxidation versus $\text{Sn}_{\text{T(aq)}}$ Concentration

Stannous sulphate oxidation in sulphate media oxidizes to stannic sulphate in the presence of dissolved oxygen by the following reaction:

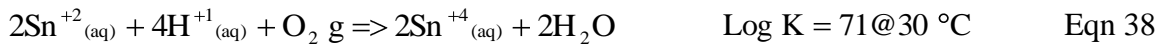


Figure 4.7 shows tin concentrations between 500 and 700 mg/L which demonstrate first order kinetics and have similar rates of 0.0002 mg Sn/L s. Tin concentrations below 500 mg/L follow first order kinetics, but not as closely.

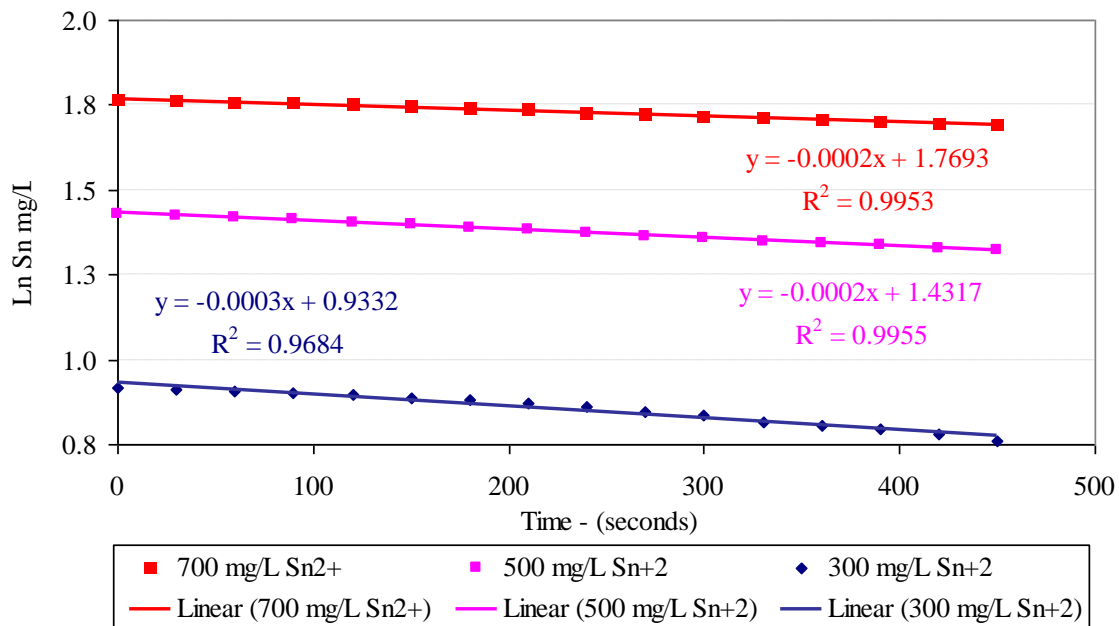


Figure 4. 7: Sn(II) Oxidation versus Time: Pure Reagents (20 °C, 100 g/L  $\text{H}_2\text{SO}_4$ )

The slow Sn(II) oxidation kinetics are most likely due to low dissolved oxygen concentrations present in the solution which ranged between 5 mg/L initial to 0.7 mg/L final dissolved  $\text{O}_2$  concentration range for all initial Sn(II) concentration experiments. The lower than theoretical dissolved concentration may be due to poor mass transfer by inefficient mixing, or possibly, if  $\text{SnO}_2$  is present, is similar to what can occur with iron oxides. Lower tin concentration in solution increases the rate of tin oxidation after 100 seconds due to more dissolved oxygen in solution relative to the higher tin

concentration in solution, which has consumed more oxygen earlier ( $t < 100$  s) in the reaction.

The first order rate constants for oxidation of Sn(II) to Sn(IV) are shown for the three different tin concentrations (Table 4.6). The dissolved oxygen consumption increases as the tin concentration increases.

**Table 4. 6: Sn(II) Oxidation Kinetics versus Time**

Reductant R	Order	k	Units	R <sup>2</sup>
300 mg/L Sn	1	0.0003	s <sup>-1</sup>	0.9684
500 mg/L Sn	1	0.0002	s <sup>-1</sup>	0.9955
700 mg/L Sn	1	0.0002	s <sup>-1</sup>	0.9953

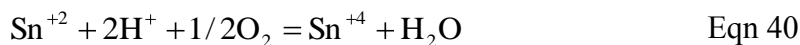
All three oxidation rates are very slow which is consistent with low O<sub>2</sub> mass transfer rates.



### 4.3 Reliability of Sn(II) and Sn(IV) Measurements

#### 4.3.1 Sn(II) Concentration (Pure Compound) – Iodometry

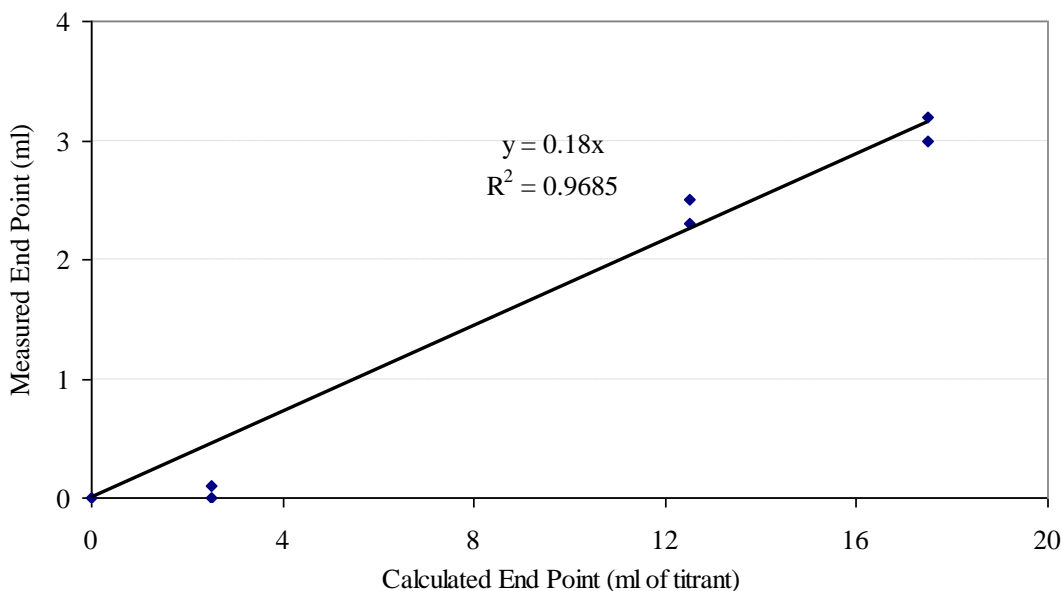
From other Sn(II) oxidation kinetics analysis work, iodometry is a method recommended for Sn(II) analysis in sulphate media (Martyak and Seedfeldt, 2005). The reaction in sulphuric acid is:



As well, iodide reacts with dissolved oxygen in acidic media (Christian, 1986).



There was a fairly good trend between calculated and measured endpoint for the pure SnCl<sub>2</sub> and diluted H<sub>2</sub>SO<sub>4</sub> (100 g/L) at 20 °C system (Appendix E, Table E.5).



**Figure 4. 8: Calculated versus Measured Iodine/Starch Endpoint; Pure SnCl<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>**

The calculated endpoint is the mL of titrant multiplied by the strength of iodine titrant (0.001 g/L Sn (II) equivalent). The deviation from unity and error could be from the estimate of the blue colour starch endpoint. In addition, the addition of the starch indicator was not at the exact time near the endpoint. As well, further reading mentions not using starch indicators in strong acid solutions which can decompose starch and affect endpoints (Christian, 1986).

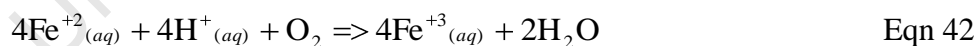
For the pure Sn(II) solutions (300, 500, and 700 ppm Sn(II)) in 100 g/L H<sub>2</sub>SO<sub>4</sub> at 20°C, the end point REDOX (Eh) ranged between 550 to 630 mV(Appendix E).

#### 4.3.2 Sn (II) Concentration (Pure and Pure + Impurities) – Iodometry

The objective of these tests is to examine the effect of other ions (Fe (II)) in solution with respect to REDOX potential for solutions containing tin ions using iodometry.

##### Iodine/Starch Method

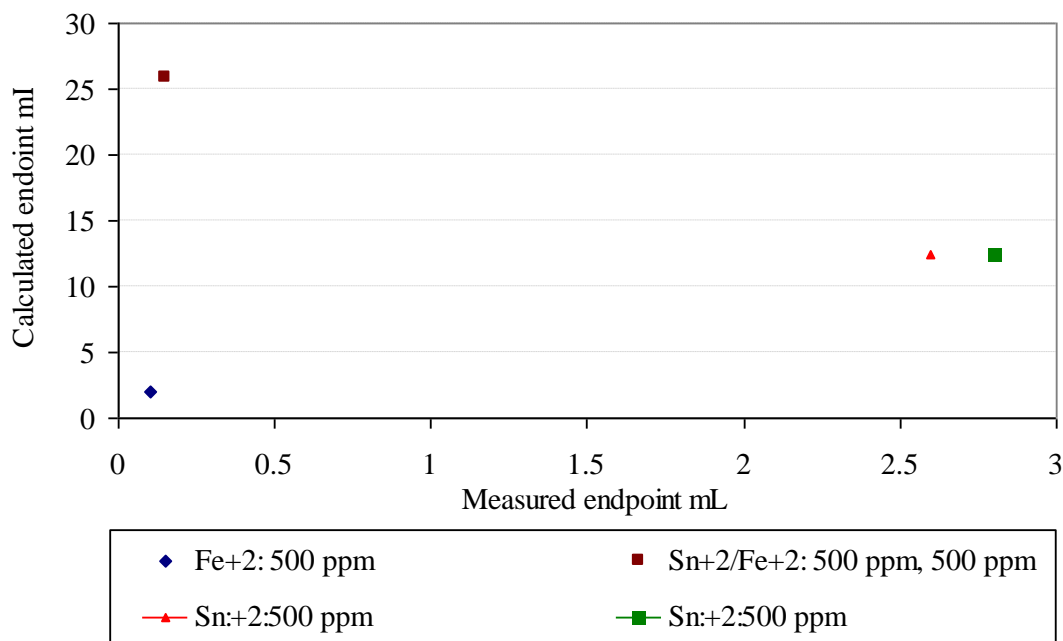
The objective is to determine: (1) if Fe(II) oxidation occurs in a solution containing 500 ppm Fe(II) (using FeSO<sub>4</sub>·7H<sub>2</sub>O) over a 10-minute interval; (2) if Fe(II) and Sn(II) oxidation occur in a solution containing 500 ppm Sn and 500 ppm Fe over a 10-minute interval; and (3) to perform a titration on both of these two solutions.



The iodine starch method for determining Sn(II) in solution became unreliable as impurities were added. Tests were conducted with pure Sn(II) solution, pure Fe(II) solution, and a mixed solution of Sn(II) and Fe(II). Shown on Figure 4.9 is a graph of calculated versus measured iodine/starch endpoint indicating how much tin is in solution. The mixed tin and iron solution have unexplained endpoints which could not be used to determine aqueous tin concentrations in solution. The iodine starch endpoint for the mixed tin and iron system should have been between 0.1 mL Fe(II), and 12.5 mL Sn(II) (not 25.6 mL). The reduction tests contained an average 16 g/L total iron concentration,

so from these tests it was determined to abandon the iodine/starch method and use total aqueous tin in solution determined by inductive coupled plasma ICP analysis.

When an impurity (Fe(II)) was introduced in the iodine starch titration, the measured starch endpoint did not match the calculated endpoint. Error in endpoint other than those mentioned above (4.3.1) may have also been compounded by the fact that Fe (II) also reacts with iodine, as well as oxygen.



**Figure 4. 9: Calculated vs. Measured Iodine/Starch Endpoint (Sn(II) + Fe(III))**

In summary, the iodine/starch method of analysis can be used for aqueous Sn(II/IV) concentration determination. However, for mixed ion solutions with impurities other than tin, this method is not suitable. Based on these results, iodometry was abandoned as a method for determining aqueous tin (II) concentration and inductive coupled plasma analysis (ICP) was chosen for measurement of total aqueous tin concentration for the thesis benchscale tests.

## 4.4 Commercial System (Complex)

### 4.4.1 Reproducibility of Reduction Tests

#### 4.4.1.1 Acidity

Acidity tests were carried out at four different acid concentrations: 220, 160, 100 (BL), and 40 g H<sub>2</sub>SO<sub>4</sub>/L. Two tests were conducted at each acid concentration, the highest acidity having the largest tin concentration (Table 4.7). The largest source of error for the 100 g/L H<sub>2</sub>SO<sub>4</sub> experiments seems to be from addition procedure of the Ge Preconcentrate slurry, and the homogeneous nature of the Ge Preconcentrate slurry. There was some difficulty adding the Ge Preconcentrate to the leach reactor due to a narrow opening in the reactor lid. The lid openings were minimized in diameter and sealed during the leach to minimize evaporation losses during the 150 minute leach cycle. The Ge Preconcentrate consumes the free acid in the reduction reaction.

**Table 4. 7: Aqueous Tin Variability -- Acidity Tests, 90 °C, R R<sub>PbCon/PreCon</sub> = 0.6**  
**t = 60 minutes, tin concentration variability - mg/L aqueous Sn**

Variable	Average	STDeviation	No. Experiments
BL 100g /L H <sub>2</sub> SO <sub>4</sub>	4.8	2.1	6
220g /L H <sub>2</sub> SO <sub>4</sub>	20.5	not applicable	2
160g /L H <sub>2</sub> SO <sub>4</sub>	8.0	not applicable	2
40g /L H <sub>2</sub> SO <sub>4</sub>	1.0	not applicable	2

The 160 g/L tests had the same tin concentration and, therefore, zero standard deviation because equilibrium tin concentration had been established in both tests. The 40 g/L tests had lower tin solubility, and both experiments maintained 1 mg/L Sn after 3 minutes test duration.

#### 4.4.1.2 Temperature

Reproducibility of aqueous tin concentration measurements was satisfactory for temperatures greater than or equal to 60 °C (Table 4.8). The greatest error occurred for

the lowest temperature case (30 °C). In this case, the standard deviation was greater than the average value. This large source of error could be due to impurity removal kinetics, Ge Preconcentrate addition to the reactor, Ge Preconcentrate sample homogeneity, and number of Ge Preconcentrate storage containers. The impurity removal mechanisms for the process are strongly temperature dependent, therefore, once tin dissolution had occurred from the Ge Preconcentrate the tin did not precipitate significantly.

**Table 4. 8: Aqueous Tin Variability -- Temperature Tests, 90 °C,  $R_{PbCon/PreCon} = 0.6$   
t = 60 minutes, tin concentration variability - mg/L aqueous Sn**

Variable	Average	STDeviation	No. Experiments
BL 90 °C	4.8	2.1	6
60 °C	8.5	not applicable	2
30 °C	138.0	not applicable	2

The second source of error may have been the addition method to the reactor, as it was difficult to add the Ge Preconcentrate to the reactor due to the non-homogeneous condition of the Ge Preconcentrate sample. Every effort was made to ensure an evenly blended residue sample, however, all the bench scale tests were conducted over about a month, and the Ge Preconcentrate sample may have stratified to some degree in the 20 L plastic pail. As well, there were two 20 L plastic pails, and each one of the 30 °C tests samples could have been taken from different Ge Preconcentrate storage pails.

#### 4.4.1.3 PbS Reductant

Variability of tin due to the powdered PbS is most likely due to reaction with the Ge Preconcentrate during addition to the reactor as mentioned previously. The highest error occurred at addition ratios less than  $R_{PbCon/PreCon} = 0.6$  (Table 4.9). The test at  $R_{PbCon/PreCon} = 0.35$  had the largest source of error. Again, the source of error might have been attributed to Ge Preconcentrate addition/storage issues mentioned above. The lowest PbS addition tests had the highest aqueous tin concentration, which is expected due to insufficient reductant.

**Table 4. 9: Aqueous Tin Variability -- PbS Reductant Tests, 90 °C, 100 g/L H<sub>2</sub>SO<sub>4</sub>  
t = 60 minutes, tin concentration variability - mg/L aqueous Sn**

Variable	Average	STDeviation	No. Experiments
BL R = 0.6	7.5	not applicable	2
R =0.35	5.5	not applicable	2
R = 0.12	36.0	not applicable	2

#### 4.4.1.4 Arsenic Concentration

The average aqueous tin value increases for an increase in arsenic (arsenic acid) concentration due to increasing total acidity.

**Table 4. 10: Aqueous Tin Variability - Arsenic Tests, 90 °C, R<sub>PbCon/PreCon</sub> = 0.6  
t = 60 minutes, tin concentration variability - mg/L aqueous Sn**

Variable	Average	STDeviation	No. Experiments
Baseline (BL)	4.8	2.1	6
BL + 5 g/L As	11.0	not applicable	2
BL + 10 g/L As	29.0	not applicable	2

Reproducibility of tin concentration measurements was poorest for the baseline case. One reason could be these experiments were the first experiments done when technique for reagent addition, such as Ge Preconcentrate addition, lead concentration) was not as precise. As well, the BL tests were at a lower total acidity when less sulphate was available for precipitation.

## 4.4.2 Total Acidity

The following section discusses total acidity in terms of the proton concentration of the solution in terms of varying initial H<sub>2</sub>SO<sub>4</sub> and arsenic concentrations.

### 4.4.2.1 Acidity and Proton Concentration

#### (1) Acidity (H<sub>2</sub>SO<sub>4</sub>), 40 to 220 g/L H<sub>2</sub>SO<sub>4</sub>, 90 °C

The increase in tin solubility shown in Figure 4.10 has been explained by Pourbaix: as the acid concentration increases (below pH 1) the solubility of Sn(IV) species increases dramatically for oxidizing environments. The 220 g/L initial acidity tests had the highest total aqueous tin levels in solution. Pourbaix indicates that Sn(IV) solubility is very high below pH 1 with REDOX potentials greater than 100 mV. The lower acidity curves correspond to reduced tin solubility of tin at the lower concentrations of H<sub>2</sub>SO<sub>4</sub> due to less bisulphate ion availability to complex tin.

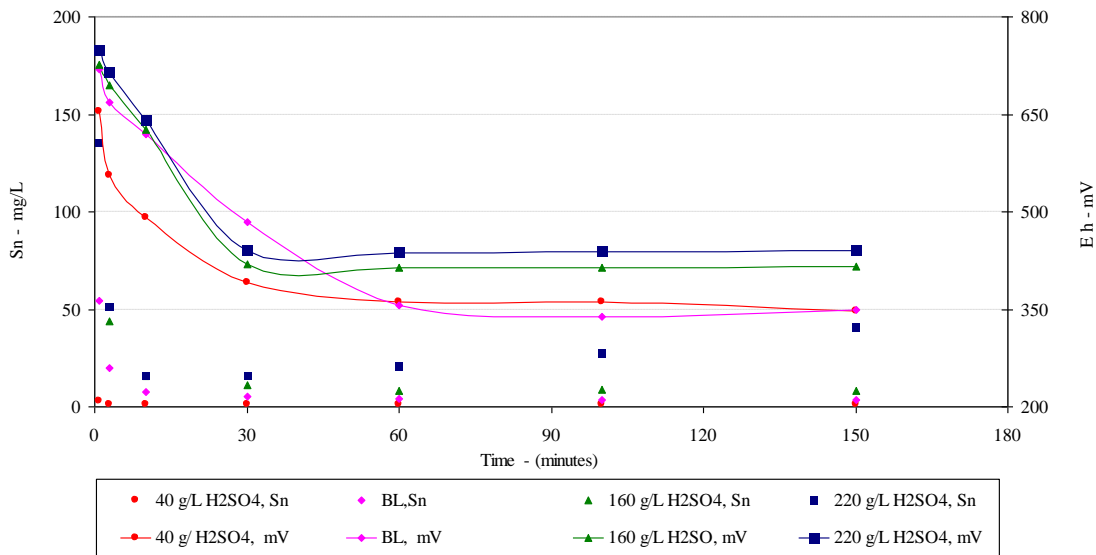
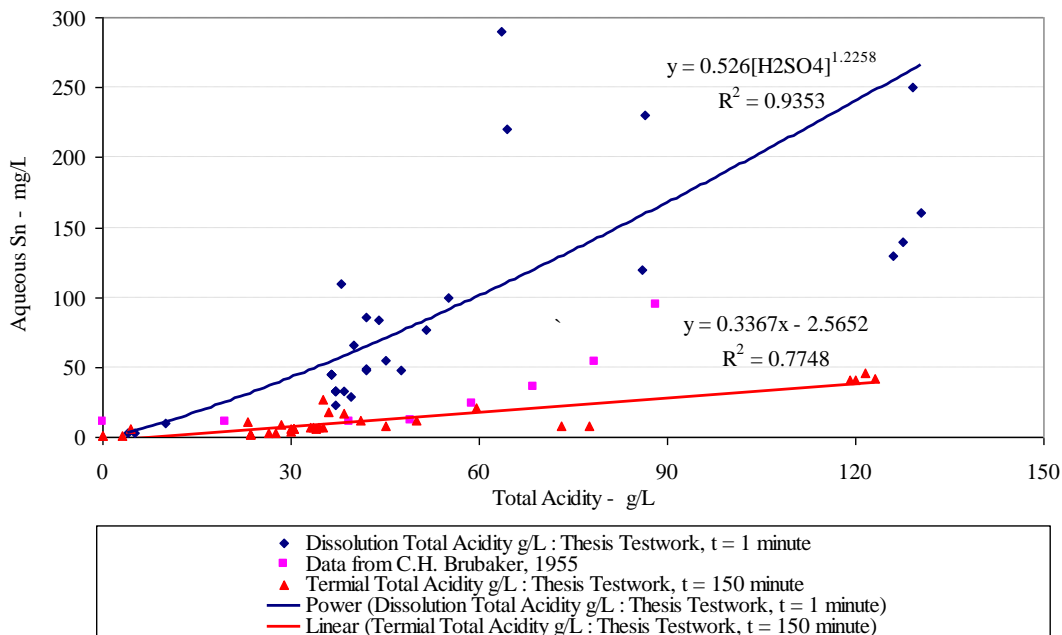


Figure 4. 10: Aqueous Tin Concentration (aged) and REDOX versus time

At the higher acidities, there exists a greater concentration of sulphate and bisulphate ions for Sn(II/IV) to complex within the Releach solution.

Aqueous tin (not averaged) is plotted against total acidity at all time intervals as shown below (Figure 4.11). The reason proposed for increased tin solubility was the formation of soluble Sn(II) complexes utilizing the greater availability of sulphate and bisulphate ions at the higher acid concentrations. At the beginning of the Releach, tin undergoes dissolution from the Ge Preconcentrate into solution. The amount of tin taken into solution depends on acidity and temperature. The tin dissolution phase of the Releach occurs within one minute of the Releach when the acidity is greatest. At the same time, zinc and arsenic are pulling out sulphate and bisulphate ions from the solution and competing with tin for protonation. Also, in this regime there are precipitation reactions occurring. Therefore, the competing ions during dissolution and tin precipitation or co-precipitation reactions contribute to the variability of tin during the tin dissolution phase of the Releach.



**Figure 4. 11: Aqueous Tin Concentration (not averaged) versus Total Acidity**

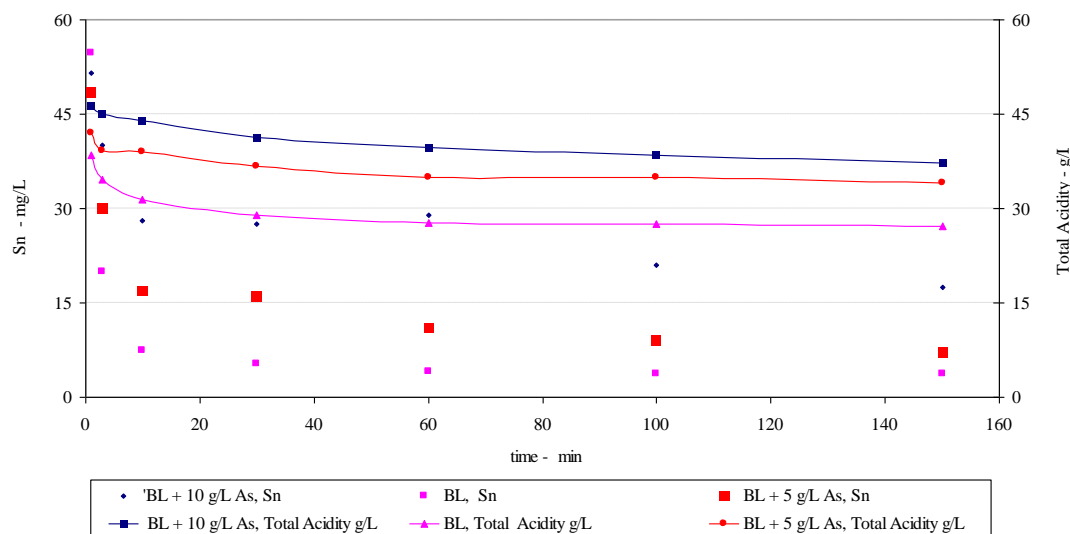
In both dissolution and terminal acidity cases, the higher tin concentration values correspond to higher total acidities which follows Pourbaix Eh-pH theory. Furthermore, the largest tin concentration values for both dissolution and terminal acidity experiments occurred at the start of the leach cycle. The dissolution rate of tin from Ge Preconcentrate is so rapid (occurs in less than one minute) that kinetic data could not be determined. There was one measurement just after the addition of the



reagents at the one minute mark in the thesis bench scale experiments. The experimental tin solubility values reported by Brubaker (Brubaker, 1955), fall between values of dissolution total acidity and terminal total acidity. Two possible reasons for this difference could be ionic strength and temperature. The ionic strength of thesis work was higher than for Brubaker's work and anions such as chloride, fluoride, arsenate and arsenite anions (~1 g/L As) may have complexed tin in the present work. This would make sense for the thesis test work dissolution curve tin values which had higher tin values compared to the Brubaker results. The temperature of the thesis tests was 90 °C versus 25 °C for Brubaker's tests, and tin polymerization may have occurred which may explain the lower equilibrium thesis test tin concentration values compared to Brubaker. In summary, when the total acidity was less than 60 g/L, the thesis terminal acidity tin values were similar to Brubaker's results most likely due to equilibrium conditions being approached for the solution chemistry. The thesis testwork tin values for the dissolution test work do not compare very well to Brubaker's results most likely due to other non-equilibrium behaviour such as kinetics and co-precipitation which are occurring to a great degree at the beginning of the leach cycle (Brubaker, 1955; Gordon and Brubaker, 1960).

(2) Acidity ( $H_3AsO_4$ ), BL to BL + 10 g/L As, 90 °C

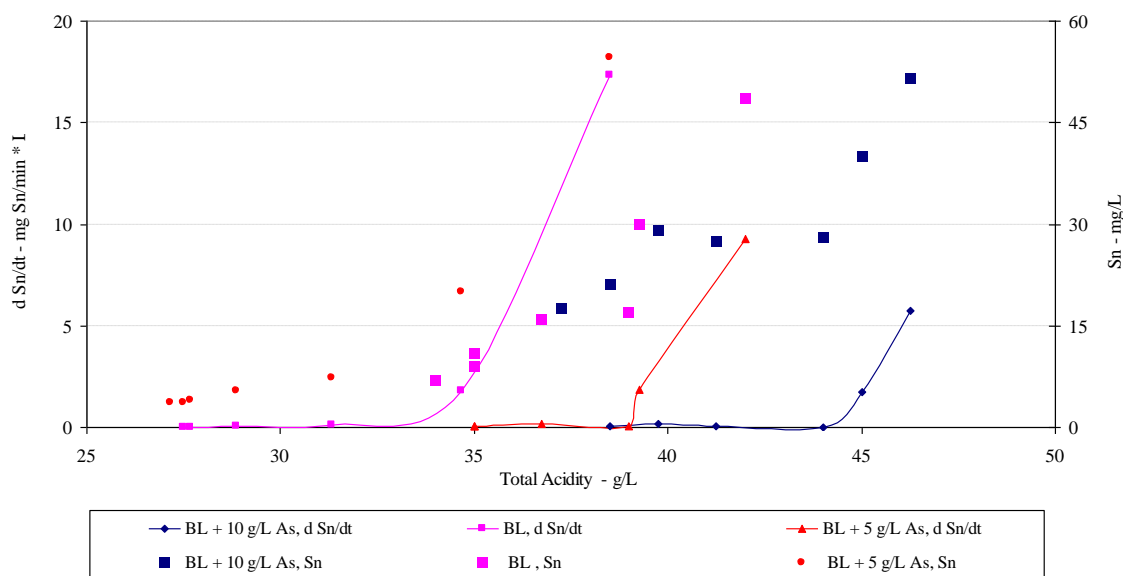
Initial acidity and the total aqueous concentration of arsenic can affect the total acidity of the leach solution during the Reduction Process. The higher the total aqueous arsenic concentration, the higher the total acidity (Figure 4.12).



**Figure 4.12: Aqueous Tin Concentration and Acidity versus Arsenic in Solution**

The increasing arsenic addition ( $\text{As}_2\text{O}_5$ ) increased the total acidity of the solution due to increased arsenic acid concentration. The BL case (BL  $\sim 1$  g/L As) reached acidity equilibrium in approximately 30 minutes into the leach cycle with a value of 27 g/l total acidity. As the arsenic addition increased, the total acidity increased as did the time required to reach this value. The total acidity for the BL + 5 g/L As case reaches equilibrium in approximately 60 minutes with a value of 34 g/L total acidity. The highest arsenic addition case of BL + 10 g/L As does not reach a total acidity equilibrium and has a value of 37 g/L total acidity at the 150-minute position of the leach cycle. Arsenic oxides behave as acids in acidic media. The pKa1 and pKa2 values for arsenic acid are 2.2 and 6.98, respectively. The pKa1 for bisulphate ion is 1.99. Therefore, the addition of  $\text{As}_2\text{O}_5$  to acidic media will increase the total acidity of the solution.

Tin precipitation rate and aqueous concentration both increase as total acidity increases (Figure 4.13). As the aqueous arsenic concentration increases, the aqueous tin concentration increases due to increased acidity which agrees with Pourbaix Eh-pH theory. Similarly, the Eh for these tests ranged between (350 to 800 mV), and the precipitation rate of tin decreases with increasing arsenic concentrations due to higher equilibrium aqueous tin values.



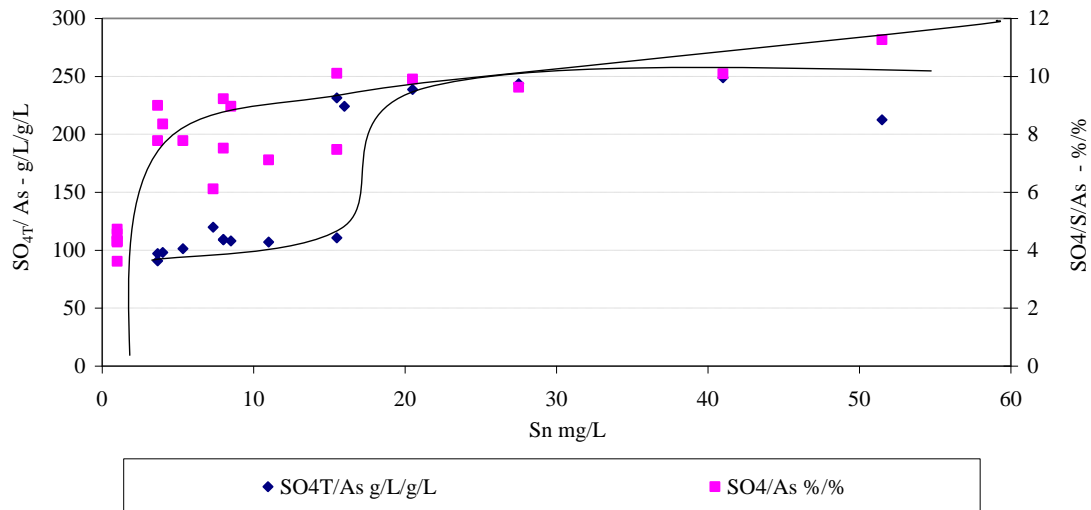
**Figure 4.13: Aqueous Tin Precipitation and Concentration versus Total Acidity**

This may imply indirectly that arsenic or sulphate is not available for tin precipitation as  $\text{Sn}_3(\text{AsO}_4)_3$ ,  $\text{SnSO}_4$  or  $\text{SnSO}_4\text{O}_2$ , or precipitation or co precipitation as  $\text{Pb}_3(\text{AsO}_4)_3$ , and, essentially, tin is complexed with some other ionic species and not available for the tin precipitation mechanism.

#### 4.4.2.2 Ligand Substitution (Sulphate and Arsenate)

##### (1) Change in Sulphate Concentration, 40 to 220 g/L $\text{H}_2\text{SO}_4$ , 90 °C

Sulphate concentration was increased using change in  $\text{H}_2\text{SO}_4$  concentration. As the ratio of sulphate to arsenate in acidic media increases, the aqueous tin concentration increases dramatically. At 15 mg/L, the aqueous ratio doubles and remains fairly constant as tin concentration increases (Figure 4.14). Similarly, as aqueous tin concentration increases, the residue sulphate to arsenic ratio increases as well. The increase in  $\text{SO}_4/\text{As}$  aqueous ratio is a result of the increased acidity. The aqueous values decrease sharply at approximately 15 mg/L Sn when the total initial acidity is reduced from 220 g/L  $\text{H}_2\text{SO}_4$ , and the aqueous  $\text{SO}_{4\text{T}}/\text{As}$  values correspond to 100 and 160 g/L initial  $\text{H}_2\text{SO}_4$ .



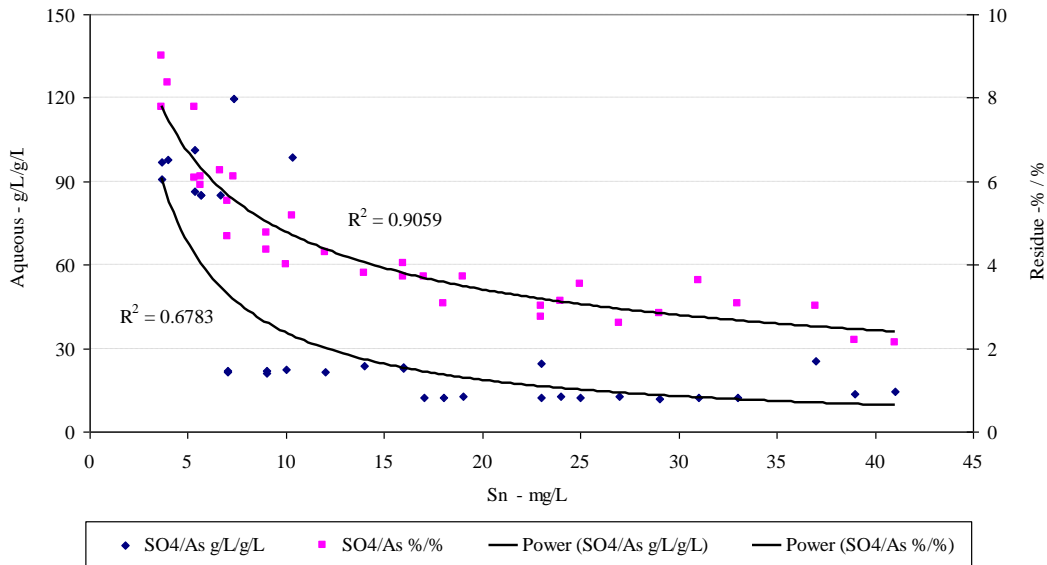
**Figure 4. 14: SO4:As Ratios (Aqueous, Residue) versus Aqueous Tin Concentration**

The sulphate to arsenic ratio in residue does not follow as closely the same sharp aqueous  $\text{SO}_4/\text{As}$  ratio trend at 15 mg/L Sn. The  $\text{SO}_4/\text{S}/\text{As}$  ratio in residue follows a similar trend, although not as defined due to other impurities that are precipitating that are in greater concentration relative to tin such as lead, zinc, and iron. The lower values of tin concentration were towards the end of the Releach cycle. Both aqueous and residue sulphate to arsenic ratios increase as the acidity and tin concentration increase, and may be due to ligand substitution, however, cannot be proven.

(2) Arsenate Concentration – BL, BL+5, and BL + 10 g/L As, 90 °C

Increased addition of  $\text{As}_2\text{O}_5$  was done to decrease the ratio of aqueous sulphate to arsenate ions in the Releach solution. Figure 4.15 shows aqueous and residue ratios of sulphate to arsenate versus aqueous tin concentration. The higher aqueous  $\text{SO}_4/\text{As}$  ratios correspond to the baseline experiments, the lower ratio values are the elevated arsenic addition experiments (BL + 10 g/L As). The residue  $\text{SO}_4/\text{As}$  ratio follows a similar trend with the lowest residue  $\text{SO}_4/\text{As}$  ratios occurring with the highest arsenic addition experiments, and the highest ratios occurring for the baseline experiments with no arsenic addition. Both aqueous and residue ratios increase with time as the Releach progresses. As the tin concentration in the solution increases, the amount of sulphate relative to arsenic in solution and residue both decrease. The increased amount of arsenic in solution led to higher tin concentrations in solution. This

increase in aqueous tin concentration is due to the increase in total acidity from the presence of aqueous arsenic and not ligand substitution. The removal of additional arsenate from solution with the elevated arsenic addition experiments is due to arsenate (Pb, Zn, Fe) precipitation.

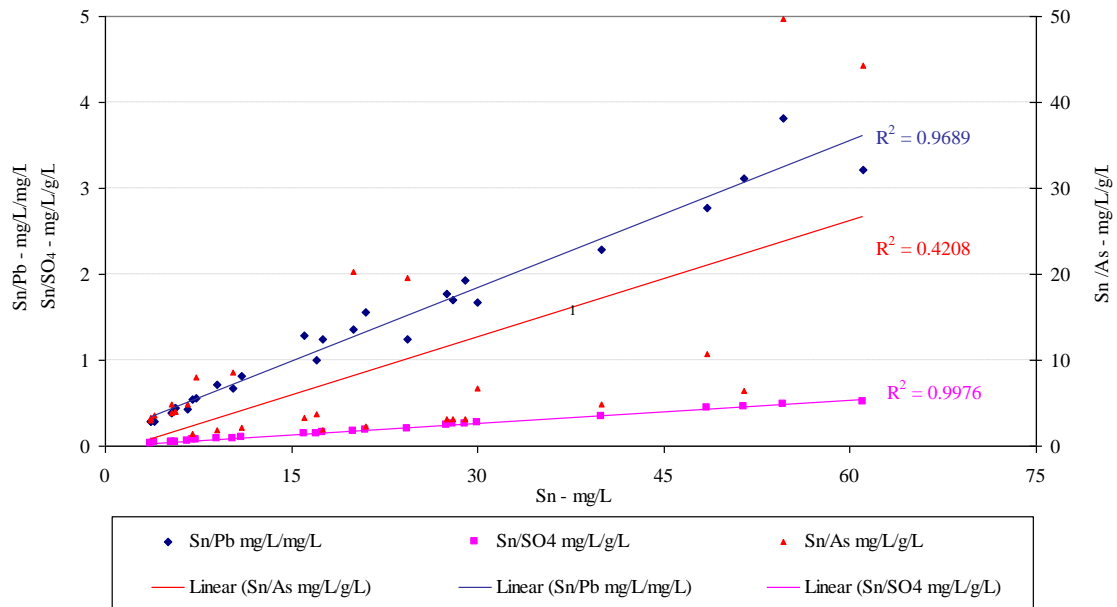


**Figure 4.15: SO<sub>4</sub> : As Ratio (Aqueous, Residue) versus Aqueous Tin Concentration**

In fact, as the aqueous tin concentration decreases, both ratios increase exponentially, which is not indicative of possible ligand substitution (as compared to Figure 4.14). Some other mechanism(s) of tin precipitation exist with elevated aqueous arsenic concentrations relative to sulphate concentrations. Relative amounts of other ions present in the Releach such as zinc, lead, or other may affect arsenic and tin interactions.

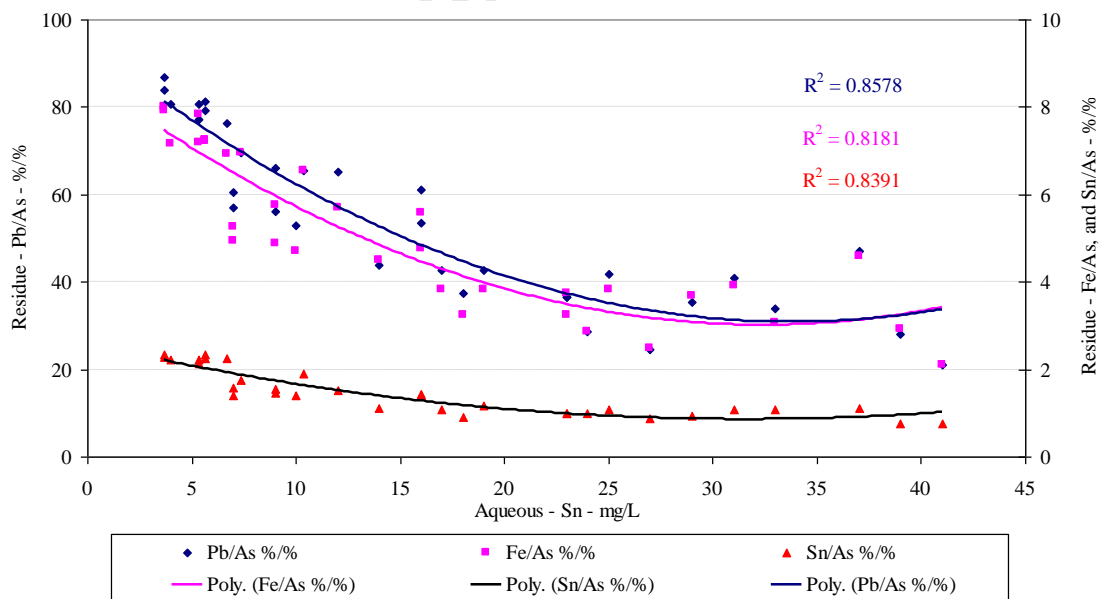
The aqueous phase of tin, sulphate, lead, and arsenate, aqueous ratios of tin to lead, sulphate, and arsenic were examined for the duration of the leach (Figure 4.16). In terms of arsenic correlations with tin concentration, there are two distinct precipitation regimes for tin, which seem to transition at approximately 40 mg/L. Both lead and sulphate ratio trend well with tin above 40 mg/L, and seem to have fairly linear correlations, however the correlation between tin and arsenic is very non-linear. This may imply that both lead and sulphate have some type of association with tin at the

higher aqueous tin concentrations present at the start of the Releach at high REDOX conditions, whereas the correlation between tin and arsenic is less pronounced.



**Figure 4.16: Aqueous Sn: (Pb, As, SO<sub>4</sub>) vs. Aqueous Sn (BL to BL + 10 g/L As)**

Further investigations of the tin concentration profile of less than 40 mg/L, and the corresponding trends for lead, iron, and tin to arsenic ratios in residue, are illustrated in Figure 4.17.

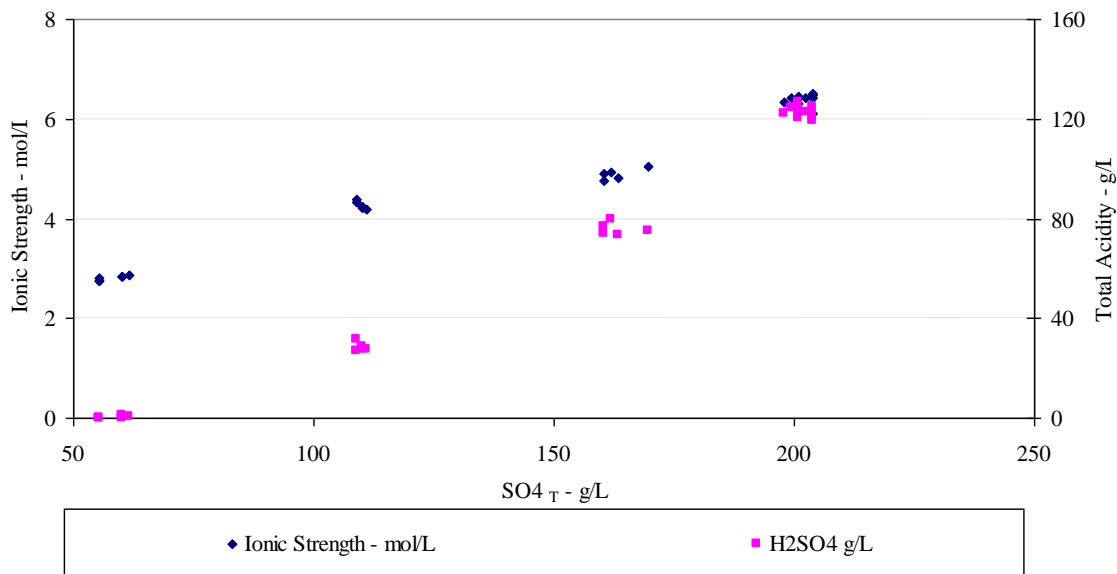


**Figure 4.17: Pb/ Fe/ Sn:As Residue Ratios vs. Aqueous Sn (BL to BL+10g/L As)**

As the tin concentration decreases in solution, all the residue ratios increase due to precipitation of lead, iron and tin. The two most closely related ratios are Pb/As and Fe/As, most likely due to arsenate precipitation. The lead to arsenic ratio showed the greatest correlation with aqueous tin due to the low solubility of lead compounds in acidic sulphate media, whereas the iron to arsenic ratio is not quite as good due to the complexation of tin with iron and precipitation with lead. This is further illustrated as aqueous tin correlates better for Pb/As in residues than Fe/As. The worst correlation was for Sn/As, most likely because tin precipitation has been shown to correlate well with sulphate either from precipitation as a Sn(IV/II) sulphate, or co-precipitation with lead sulphate.

#### 4.4.2.3 Ionic Strength: 40 to 220 g/L H<sub>2</sub>SO<sub>4</sub>, BL to BL+5, BL+10 g/L As

Total sulphate increases with total acidity as expected (Figure 4.18). The ionic strength increases as total acidity (40 to 220 g/L H<sub>2</sub>SO<sub>4</sub>) and is mainly due to the increase in aqueous sulphate concentration.

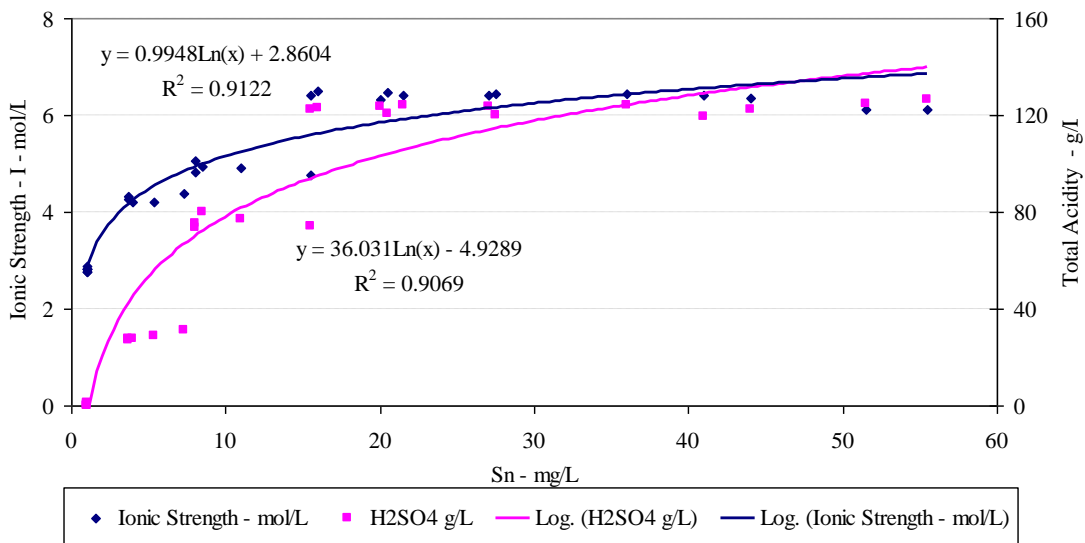


**Figure 4. 18: Ionic Strength and Total Acidity vs. Sulphate (40 to 220 g/L H<sub>2</sub>SO<sub>4</sub>)**

The slopes of the ionic strength and total acidity curves diverge as the total sulphate concentration is decreased, which is expected as there is less dominance of the sulphate anion concentration contribution to ionic strength because of the predominance

to bisulphate. In addition, there is less cation dissolution from the Ge Preconcentrate into the solution at the lower acidity. The lowest total acidity values in Figure 4.18 were for the initial 40 g/L H<sub>2</sub>SO<sub>4</sub> thesis experiments. The total aqueous sulphate concentration is composed of sulphate contributions from ionic salts ([SO<sub>4</sub>] ionic) and free acid ([SO<sub>4</sub>/HSO<sub>4</sub>] H<sub>2</sub>SO<sub>4</sub>). The change in aqueous sulphate concentration from H<sub>2</sub>SO<sub>4</sub> (SO<sub>4</sub>/HSO<sub>4</sub>) concentration changes is much more significant than changes in total sulphate, and sulphate associated with ionic salts. This may indicate that tin precipitation is associated with sulphate and bisulphate from H<sub>2</sub>SO<sub>4</sub> contribution to total acidity. As shown below, the change in H<sub>2</sub>SO<sub>4</sub> (SO<sub>4</sub>/HSO<sub>4</sub>) concentration is much more rapid than the sulphate contribution from the ionic salts, indicating that the acidic sulphate and bisulphate is being bound by tin.

As tin concentration increases, there seems to be correlation between total acidity and ionic strengths less than a value of six (Figure 4.19).



**Figure 4. 19: Ionic Strength and Total Acidity vs. Aqueous Tin (40 to 220 g/L H<sub>2</sub>SO<sub>4</sub>)**

For ionic strengths less than six, the increase in tin concentration is due to higher bisulphate availability for complexing tin. For ionic strengths greater than six, there is less dependence of aqueous tin concentration on ionic strength and more dependence on total acidity. The ionic strength appears related to the total acidity which can be expected to affect tin concentration substantially. Possibly, Sn(IV) (as SnO<sub>2</sub>) dissolution by acidity varies with activity [H<sup>+</sup>]<sup>4</sup>, and therefore small changes in acid concentration can



significantly affect tin concentration. The ionic strength and total acidity reached its maximum value at the beginning of the Release cycle before tin and other impurity precipitation reactions (Pb, As, Fe) occurred, and total acidity was greatest in concentration. The lowest values of tin and ionic strength are found at the end of the Release when all the impurity precipitation reactions have taken place and the resulting aqueous ionic values are the equilibrium values, or near the equilibrium values, and total acidity was fairly constant.

The ionic strength was increased from addition of As(V) as  $As_2O_5$  and the total acidity increased which is expected from arsenic acids (Figure 4.20). The tin concentration increased as both the ionic strength and total acidity increased. The increase in acidity is expected with increased arsenic addition, however, the correlation of tin and ionic strength is less conclusive ( $R^2=0.4394$ ) with arsenic addition compared to the ionic strength change using sulphate/bisulphate ions (Figure 4.19 above). From these two results, the increase in tin concentration is due to increase in total acidity, and the ionic strength of the Release solution is of less importance in terms of tin concentration.

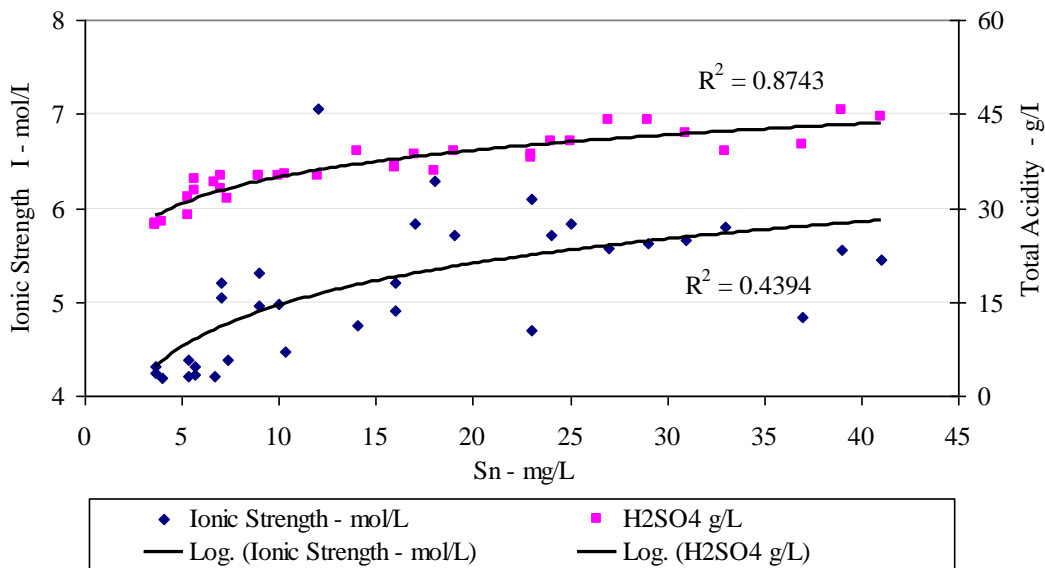
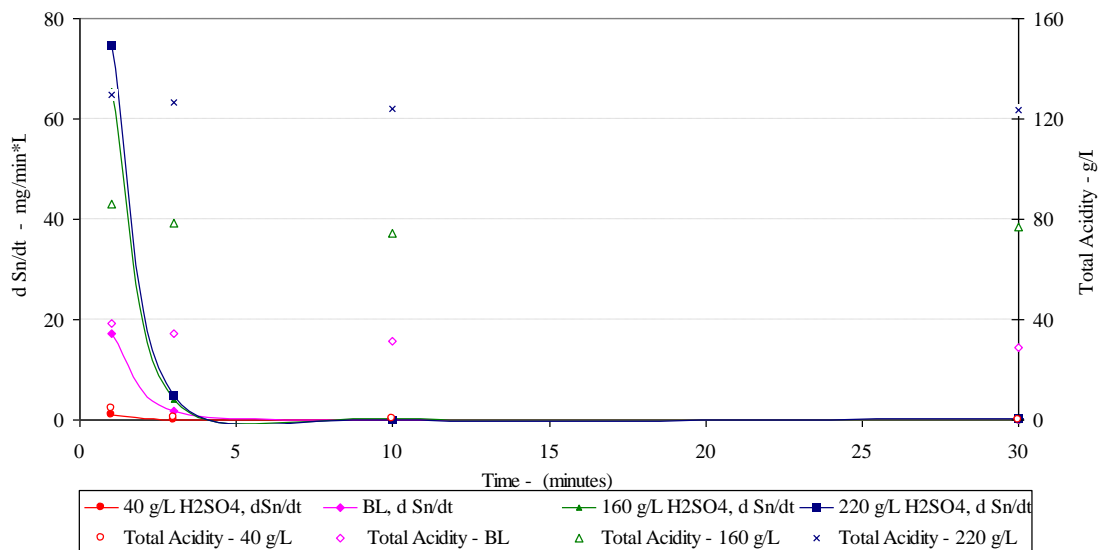


Figure 4. 20: Ionic Strength, Total Acidity vs. Aqueous Tin (BL to BL + 10 g/L As)

Kinetics:

The rate of tin precipitation was affected by acidity as shown in the Figure 4.21. The highest tin precipitation rate corresponds to the highest acidity case (220 g/L  $H_2SO_4$ )

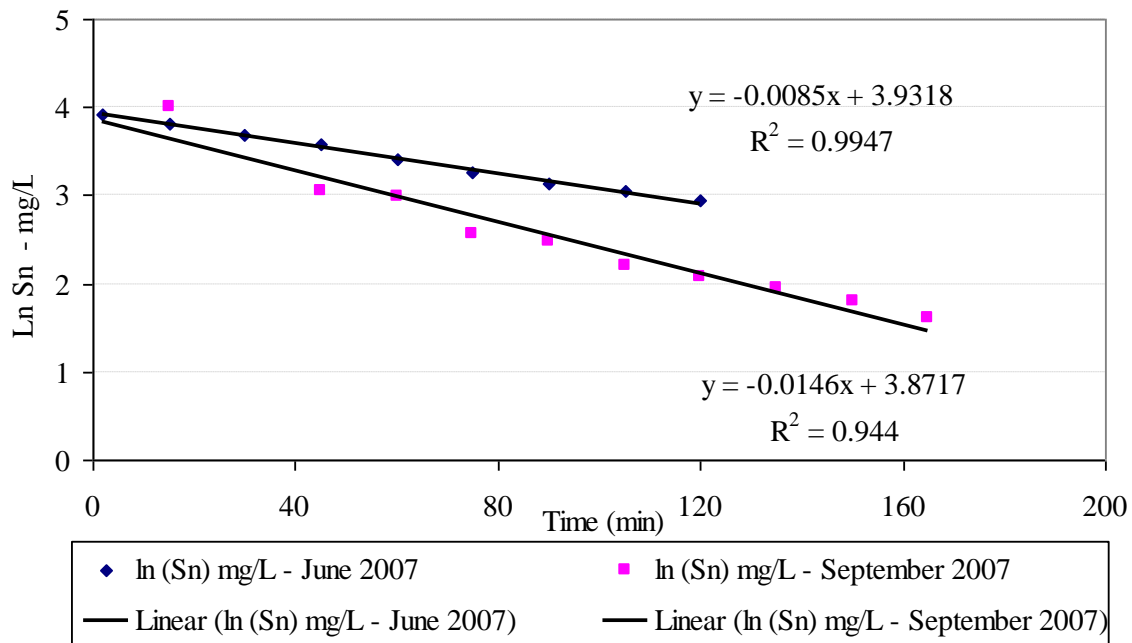
and occurs before 10 minutes. The 160 g/L H<sub>2</sub>SO<sub>4</sub> acidity case has a slightly lower precipitation rate. However, the rate profile is almost identical to the higher acidity case. This implies that above an initial acidity of 160 g/L, acidity is not affecting the tin removal significantly, and may in fact be detrimental with higher equilibrium concentrations, as shown previously. All tin precipitation at the lower acidities is essentially complete within twenty minutes at 90 °C with the majority of tin being removed from solution in less than 10 minutes. In the lowest acidity case of 40 g/L H<sub>2</sub>SO<sub>4</sub> tin did not precipitate to any discernible amount during the entire process. This is most likely due to the high concentration of other cations (Zn, Fe, In, Ge, etc.), rather than tin, reacting with the sulphate and bisulphate available for precipitation. Both zinc and iron sulphate complexes have much higher stability constants compared to tin, and will complex sulphate before tin, therefore, reducing the ability of tin to precipitate as a bisulphate, sulphate or oxy-sulphate. Also, the lowest acidity case had the smallest tin concentration after dissolution, most likely due to the limited availability of complexing sulphate and bisulphate ions to effect primary dissolution. The high tin precipitation rate occurs for tin concentrations exceeding 35 mg/L tin and then the precipitation rate is reduced significantly with the total acidity remaining unchanged (Figure 4.21).



**Figure 4. 21: Tin Precipitation Rate and Total Acidity versus Time**

The higher concentrations of tin occur early in the leach just after dissolution of the Ge Preconcentrate, and then at the end of the leach with the highest terminal acidity. The highest residual acidity concentrations below 40 mg/L tin concentration are for the 220 g/l H<sub>2</sub>SO<sub>4</sub> experiments showing that an excess initial acidity (>160 g/L H<sub>2</sub>SO<sub>4</sub>) has no effect on tin precipitation.

The commercial Reduction process starts the leach with approximately 220 – 240 g/L H<sub>2</sub>SO<sub>4</sub> total acidity. The commercial process typically has first order tin precipitation kinetics with respect to tin concentration (Figure 4.22).



**Figure 4. 22: Commercial Kinetics, TCML 2006**

The differences in kinetics between the thesis benchscale experiments and the commercial Releach may have been due to reagent addition sequence relative to temperature profile. The thesis tests were done at constant temperature, where the commercial releach is changing temperature as reactants (PbCon, Ge Preconcentrate, diluted H<sub>2</sub>SO<sub>4</sub> or spent electrolyte) are added.

The precipitation rate approximately follows second-order kinetics for the 100 g/L and 160 g/L H<sub>2</sub>SO<sub>4</sub> experiments and first order for the 220 g/L H<sub>2</sub>SO<sub>4</sub> acid concentrations (Table 4.11).

**Table 4. 11: Tin Kinetics versus Acidity, 40 to 220 g/L H<sub>2</sub>SO<sub>4</sub>, 90 °C**

**Temperature = 90°C, R<sub>PbCon:PreCon</sub> = 0.6**

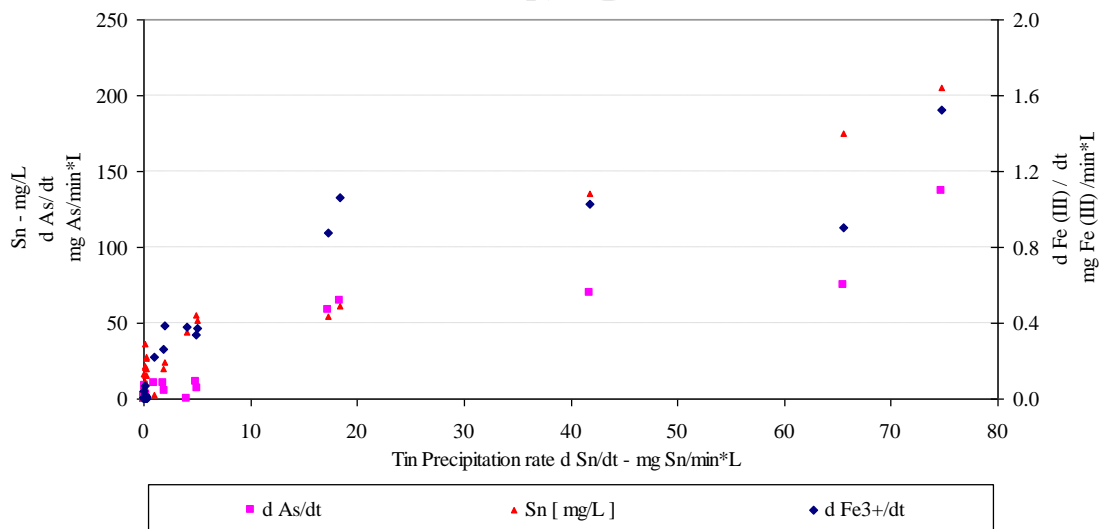
Reductant R	Order	k	Units	R <sup>2</sup>
BL 100g /L H <sub>2</sub> SO <sub>4</sub> , nFe				
0.6	2	0.0009	1/mg Sn /min * L	0.7678
40g /L H <sub>2</sub> SO <sub>4</sub> , nFe				
0.6	n/a	n/a	n/a	n/a
160g /L H <sub>2</sub> SO <sub>4</sub> , nFe				
0.6	2	0.0004	1/mg Sn /min * L	0.6462
220g /L H <sub>2</sub> SO <sub>4</sub> , nFe				
0.6	1	0.0072	min <sup>-1</sup>	0.9748
Plant Data 2007				
0.6	1	0.0085	min <sup>-1</sup>	0.9947
0.6	1	0.0146	min <sup>-1</sup>	0.944

The best overall kinetic fit for tin precipitation for the thesis tests was the 220 g/L H<sub>2</sub>SO<sub>4</sub> case. This kinetic fit is similar to the plant data most likely due to similar initial acidity (220 g/L H<sub>2</sub>SO<sub>4</sub>). However, the high acidity experiment shows dissolution occurring after approximately 30 minutes. The plant process starts with an initial acidity of 240 g/L. A good kinetic fit was not possible for the 40 g/L H<sub>2</sub>SO<sub>4</sub> experiments due to no clear tin dissolution or precipitation regimes. Overall, polymerization kinetics of Sn(IV) species such as SnO<sub>2</sub>, may be difficult to prove or understand, except perhaps that the polymerization rate should be dependent to some extent on aqueous tin concentration as shown below in Figure 4.23.

#### 4.4.2.4 Sn, As, Fe(III) versus Tin Precipitation: 40 to 220 g/L H<sub>2</sub>SO<sub>4</sub>, 90 °C

Total Acidity does not only affect tin precipitation, it may also affect the kinetics of precipitation of other species in the leach solution. Arsenates have been discussed

earlier and both lead and iron arsenates can precipitate at the Releach Process conditions. There appeared to be three different tin precipitation regimes when the acidity was varied from 40 to 220 g/L H<sub>2</sub>SO<sub>4</sub>. The highest precipitation rate of tin was between 75 to 60 mg Sn/min·L (Figure 4.23). During the 75 to 60 mg/min·L tin precipitation interval, the tin, arsenic, and lead are precipitating, and tin is possibly precipitating or co-precipitating as an arsenate or sulphate. During the tin precipitation regime from 65 to 20 mg Sn/min·L tin is still precipitating; however, the Fe(III) reduction and arsenate precipitation are both relatively constant which may mean some other tin precipitation mechanism is taking precedence, and the majority of lead and iron arsenate precipitation has taken place. Perhaps tin is precipitating as sulphate or oxide (SnSO<sub>4</sub>O<sub>2</sub> or SnO<sub>2</sub>) during this time. When the tin precipitation rate is less than 20 mg Sn/min/L, both arsenic precipitation and ferric reduction are occurring. The majority of the values in this tin precipitation regime are for the 100 g/L H<sub>2</sub>SO<sub>4</sub> acidity experiments, and the tin precipitation rate increases as the initial H<sub>2</sub>SO<sub>4</sub> acidity increases. This correlation also occurs in the early stages of the Releach cycle when the tin concentration is the highest.



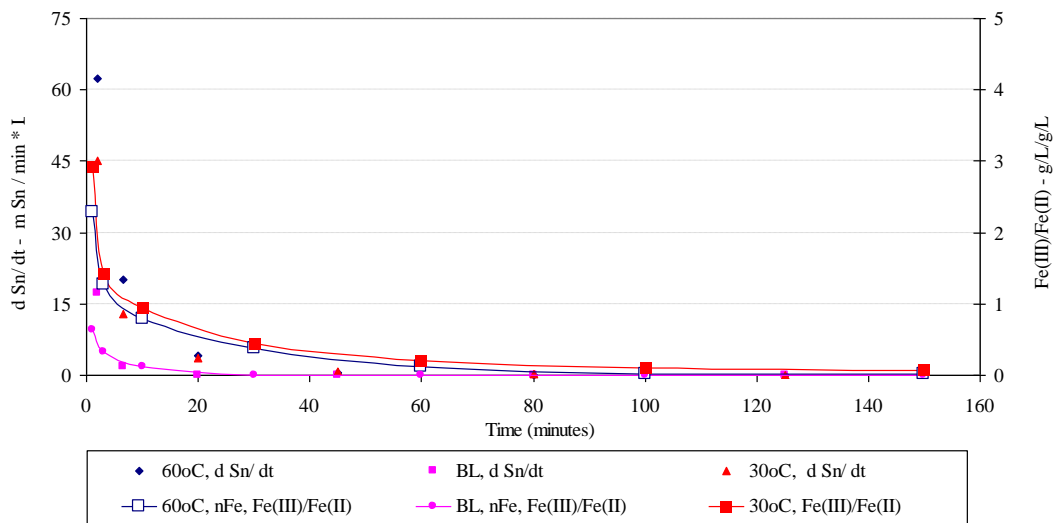
**Figure 4. 23: Sn, As, Fe(III) versus Tin Precipitation Rate**

#### 4.4.3 Temperature

##### 4.4.3.1 Tin Precipitation and Fe(III) Reduction

Kinetic studies using Fe(III) to precipitate Sn(IV) below 80 °C have shown that the rate of Sn(IV) precipitation increases with increasing temperature by overcoming the

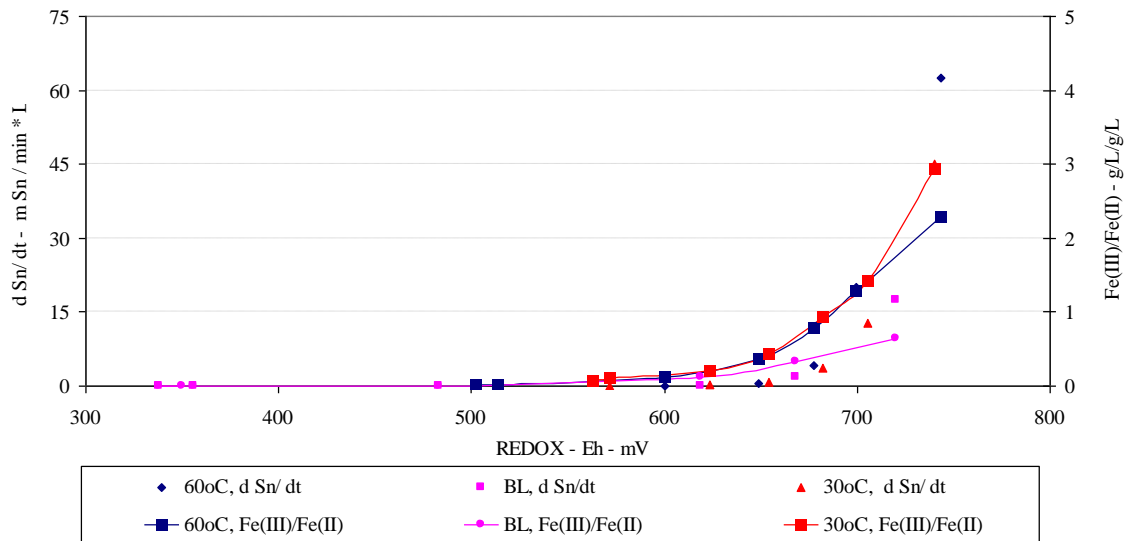
activation energy required (Danilov and Tsygankov, 1975). The rate of removal of tin from solution is greatest for the 90 °C curve and decreases as the temperature is reduced. The “colloidal hypothesis” does not entirely explain tin precipitation kinetics. Furthermore, tin is most likely present as Sn(IV) during the Fe(III) reduction period as any Sn(II) would be readily oxidized to Sn(IV) by Fe(III). For all temperatures tested, the majority of tin removal is complete during the first 30 to 60 minutes of the Releach, and the aqueous tin concentration profile closely follows the ferric to ferrous reduction ratio for all temperatures (Figure 4.24). The greatest rate of tin precipitation occurs in less than 10 minutes in oxidizing leaching conditions (> 100 mV). As expected, the Fe(III) reduction was fastest at 90 °C as was the tin precipitation rate. The BL temperature case tin concentration after one minute of reaction time was approximately 50 mg/L tin, whereas the lower temperature cases were both above 200 mg/L tin. The Sn(IV) sulphate or oxy sulphate compounds may be precipitating during this time frame, however, other reduction or metathesis reactions may be occurring as well.



**Figure 4. 24: Tin Precipitation and Ferric to Ferrous Ratio versus Time**

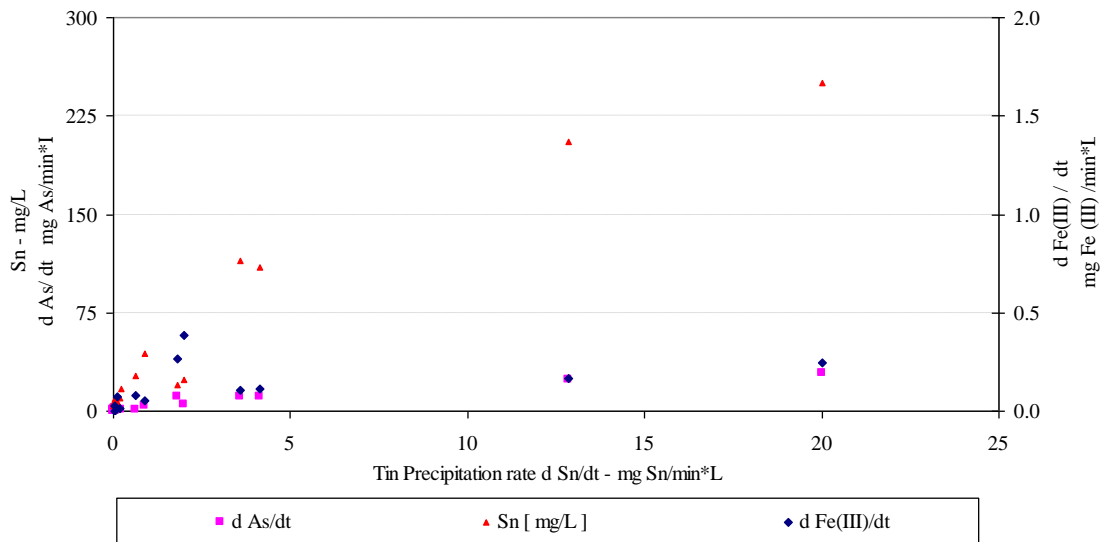
The major portion of the tin precipitation occurs between REDOX values of 750 mV and 350 mV (Figure 4.25). In the BL case, ferric reduction is approximately completed at a REDOX value of 500 mV with reduction continuing until 350 mV is reached. In the lower temperature cases, reaching ferric reduction is also completed at approximately 500 mV, but the REDOX does not drop much below the 500 mV value.

The reason may be insufficient energy required for the activation of other precipitation reactions, which are occurring in the lower REDOX range. There is also little difference between tin precipitation rates below 700 mV for the lower temperature cases. The Fe(III) reduction is so rapid that after one minute the Fe(III) reduction is 75 % complete. The Fe(III) concentration has decreased from 15 g/L Fe(III) to 4 g/L Fe(III) after one minute.



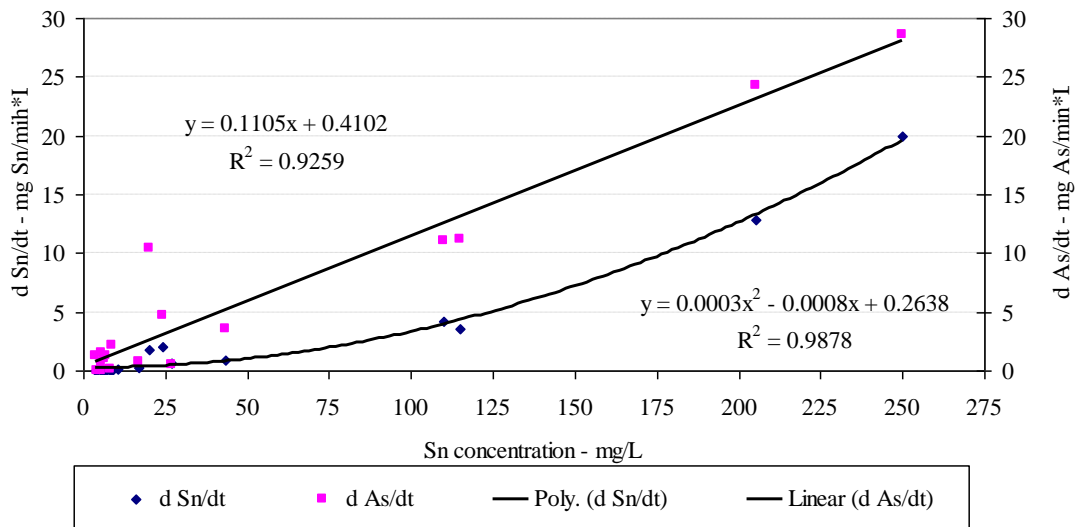
**Figure 4.25: Tin Precipitation and Ferric to Ferrous Ratio versus REDOX**

For all the temperatures tested (30, 60, 90 °C) with initial H<sub>2</sub>SO<sub>4</sub> acidity of 100 g/L, the arsenic precipitation rate corresponds to the ferric reduction timeline quite well (Figure 4.26). The Fe(III) reduction and arsenic precipitation profile matched each other closely indicating that the Fe(III) reduction was involved in the arsenic precipitation mechanism. The arsenic precipitation followed a fairly linear precipitation rate, whereas the tin precipitation rate decreased in a non-linear fashion, which implies that some other tin precipitation mechanism was occurring simultaneously. The lower tin precipitation rate values and corresponding ferric values were more variable at the lower ferric and tin concentrations.



**Figure 4. 26: Aqueous Sn, As Precipitation, and Fe(III) Reduction vs. Sn Precipitation**

The highest tin and arsenic precipitation rates occur at higher tin concentrations early on in the Release. Again, the tin precipitation is non-linear whereas the arsenic precipitation is linear indicating that other tin precipitation mechanisms are occurring. (Figure 4.27).



**Figure 4. 27: Tin Precipitation, Arsenic Precipitation vs. Tin Concentration**



#### 4.4.3.2 Tin Precipitation and Polymerization

The precipitation of tin with respect to temperature has been explained by condensation and hydration theories, where the stannic acids dehydrate and polymerize as the temperature is increased from ambient conditions to boiling (Weiser, 1926), (Mellor, 1924). The tin concentration decreases at each time interval as well as the REDOX potential as the temperature is increased from 30 °C to the baseline temperature of 90 °C (Figure 4.28). The baseline temperature (90 °C) reaches REDOX equilibrium 40 minutes prior to either of the lower temperature cases. It has been mentioned previously that the Sn(IV) precipitation with Fe(III) requires less activation energy as the temperature is increased. The aqueous tin concentration is less than 1 g/L, and it is unlikely that this tin concentration and subsequent precipitation would reduce the REDOX by as much as 400 mV. The reduction of Fe(III) to Fe(II) is 771 mV, and iron is present in significantly higher concentration (~15 g/L Fe<sub>T</sub>). Once the Fe(III) reduction is complete, in approximately 60 minutes, there is negligible tin precipitation for the remainder of the Releach for the BL case, and minor tin precipitation for the two lower temperature cases. These findings do not rule out tin precipitation by polymerization which could be occurring simultaneously.

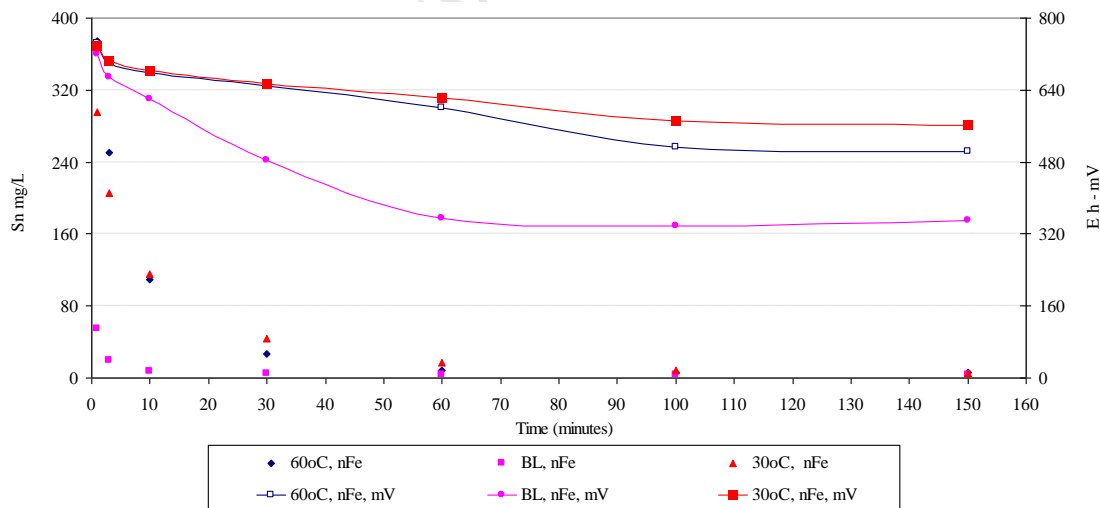
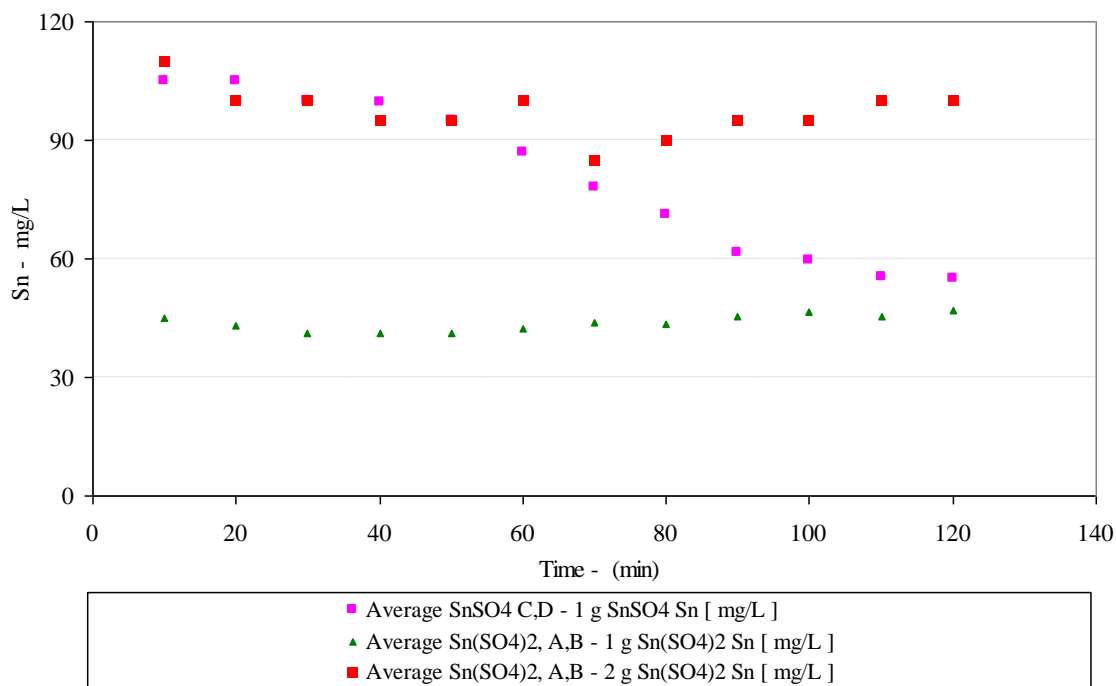


Figure 4. 28: Tin Concentration and Eh versus Time

Pure reagent tests were carried out using different Sn(II/IV) compounds at initial acidity at 100 g/L H<sub>2</sub>SO<sub>4</sub>, at 90 °C to determine if tin polymerization can occur (Figure 4.29).



**Figure 4. 29: Tin Speciation (Sn(II/IV) Sulphate ) vs. Time, 100 g/L H<sub>2</sub>SO<sub>4</sub>, 90 °C**

These tests were all 120 minutes in duration, and sampled every 10 minutes. There was dissolved oxygen present in these tests in a continuous stirred reactor, and the oxidation of Sn(II) to Sn(IV) is rapid. Approximately 80 % of the tin (as SnSO<sub>4</sub>) precipitated in the first 10 minutes of the leach. Overall, tin precipitation occurred during the entire leach cycle and the measured tin concentration decreased from 110 mg/L to 55 mg/L. From a thermodynamic perspective, tin can precipitate as a sulphate or oxide type compound in an oxidizing E<sub>h</sub> REDOX range greater than +200 mV. The decrease in REDOX potential during the tin precipitation period was approximately 100 mV. Therefore, tin precipitation by polymerization may occur but cannot be proven, as tin sulphate and oxide precipitation products are possible as well.

The experimentally determined activation energies varied in value from 11 to 8 kJ/mol. The calculated value depended upon which time interval they were based on (Table 4.12). The experimentally determined activation energy value of 18 kJ/mol for the 10 to 60 minute time-frame compares to the previous Sn(IV) precipitation activation energy value of 18 kJ/mol for 10 to 70 °C solutions of 0.5 to 1.5 mol/L Malic acid (Table 4.12).

Table 4. 12: Tin Kinetics versus Temperature

Acidity = 100 g/L H<sub>2</sub>SO<sub>4</sub>, R<sub>PbCon:PreCon</sub> = 0.6

	Temperature	Order	k	Units	R <sup>2</sup>	Ea - kJ/mol
<b>t = 1..150 minutes</b>						
BL	90 °C, nFe	~2	0.0009	1/mg Sn /min*L	0.7678	11
	60 °C, nFe	2	0.0014	1/mg Sn /min*L	0.9572	
	30 °C, nFe	2	0.0014	1/mg Sn /min*L	0.9938	
<b>t = 10..60 minutes</b>						
BL	90 °C, nFe	1	0.2023	min <sup>-1</sup>	0.9063	18
	60 °C, nFe	1	0.1313	min <sup>-1</sup>	0.9863	
	30 °C, nFe	1	0.0945	min <sup>-1</sup>	0.969	
<b>t = 1..10 minutes</b>						
BL	90 °C, nFe	2	0.0129	1/mg Sn /min*L	0.9976	12
	60 °C, nFe	2	0.0007	1/mg Sn /min*L	0.9998	
	30 °C, nFe	2	0.0005	1/mg Sn /min*L	0.9955	

The correlation coefficient for the BL case of 90 °C condition improved if the time period over which data was analysed was decreased to the initial stages of the leach, indicating that after 10 minutes other mechanisms for tin removal were occurring. In this sense, different activation energies were determined over different time periods. The decrease in value of the correlation coefficient with increasing temperature may be attributed to other tin precipitation mechanisms occurring at higher temperatures, such as arsenate precipitation, which will be discussed in the next section. The best second order fit was obtained for the time interval of less than 10 minutes, and this time interval

follows the Fe(III) reduction profile very closely, indicating that tin is precipitated by direct precipitation or co precipitation mechanisms.

#### 4.4.4 Reductant Mass Ratio (PbConcentrate, and PbS /Preconcentrate)

##### 4.4.4.1 Reductant Ratio and Rate of Arsenate Precipitation

The initial tin concentrations for samples at the one minute mark in the Releach for reductant ratios of  $R_{PbCon/PreCon} = 0.2$ , BL (0.6), and  $R_{PbCon/PreCon} = 1$  experiments were 220 mg/L, 55 mg/L and 23 mg/L tin, respectively (Figure 4.30). The excess and baseline reductant addition ratios ( $R_{PbCon/PreCon} = 1$ ,  $R_{PbCon/PreCon} = 0.6$ ) have the lowest equilibrium REDOX value of 350 mV. However, the excess reductant case reached this value in 10 minutes at 90 °C versus 60 minutes for the BL case. The  $R_{PbCon/PreCon} = 0.2$  case nearly reached equilibrium. The equilibrium values of tin for the reductant ratios of 0.2, 0.6, and 1 were 12 mg/L, 4 mg/L and 9 mg/L, respectively (Figures 4.30, 4.31).

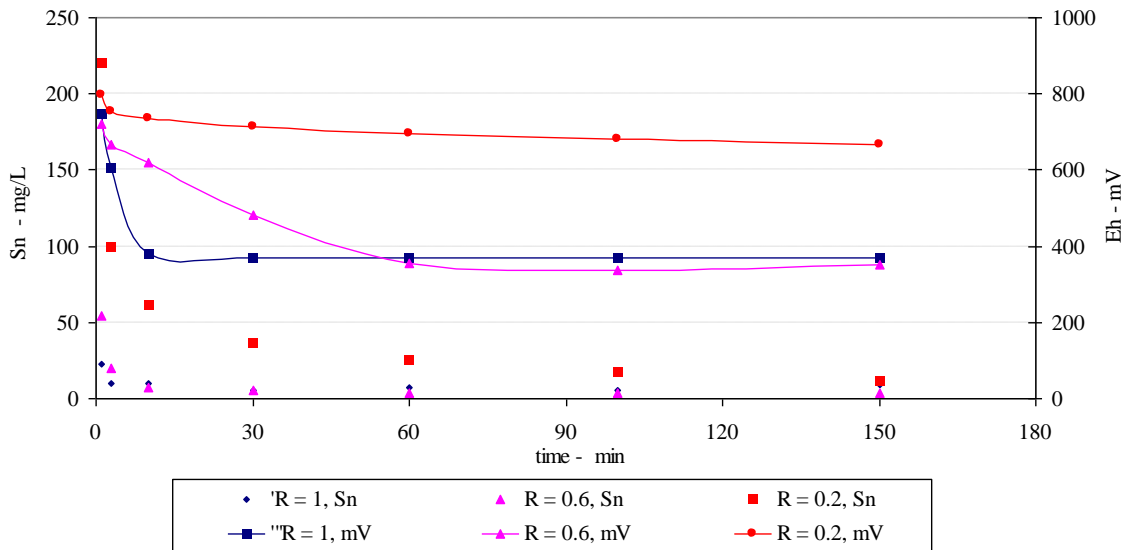
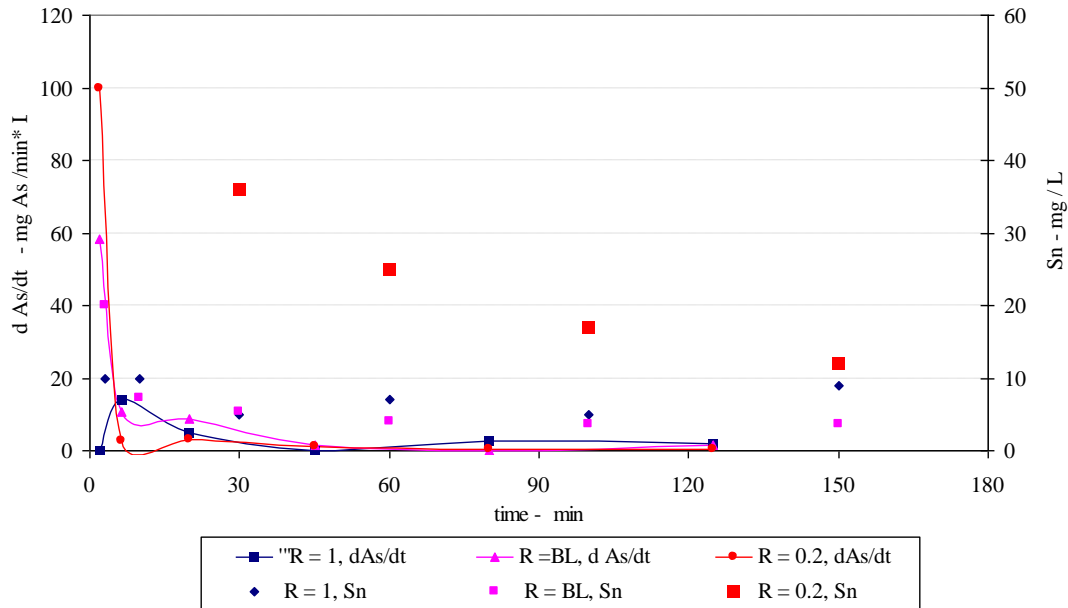


Figure 4. 30: Aqueous Tin and REDOX vs. Time, 100 g/L H<sub>2</sub>SO<sub>4</sub>, and 90 °C

The lowest equilibrium value of 4 mg/L was achieved using the BL reductant ratio of  $R_{PbCon/PreCon} = 0.6$ . The highest reductant ratio ( $R_{PbCon/PreCon} = 1$ ) had the greatest initial tin removal rate and lowest concentration of tin. However, after 30 minutes duration, re-dissolution occurred and the tin concentration started increasing from 5 mg/L to 9 mg/L at the end of leach cycle.

The rate of arsenate precipitation can affect the stability of the precipitate making a more amorphous solid which has the ability to releach (Figure 4.31). The highest rate of arsenic precipitation occurs with excess reductant ( $R_{PbCon/PreCon} = 1$ ) and is complete at one minute duration in the leach, and immediately undergoes dissolution at a rate of 14.5 mg As/min·L at approximately six minutes into the leach.



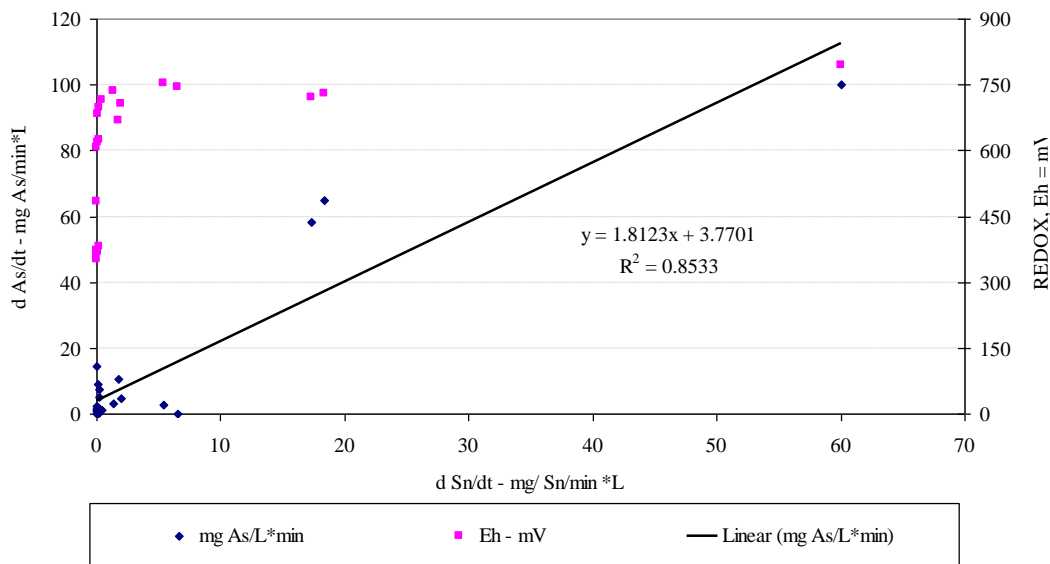
**Figure 4. 31: Arsenic Precipitation and Aqueous Tin Concentration vs. Time**

The  $R_{PbCon/PreCon} = 1$  case then re-precipitates until  $t = 60$  minutes, where again, arsenic undergoes dissolution for the next 20 minutes and the tin level increases approximately 80 % from 5 mg/L to 9 mg/L at the end of the leach. There was no arsenate dissolution for the BL case, which reached an equilibrium tin concentration value of 4 mg/L.

The limiting reductant case ( $R_{PbCon/PreCon} = 2$ ) never reached equilibrium and tin precipitation continued during the entire leach. The excess reductant case was the most unstable in terms of variable tin concentrations compared to the other reductant ratio experiments ( $R_{PbCon/PreCon} = 0.2, 0.6$ ).

The curve is plotted for the entire leach duration. It is not clear what arsenate species (Pb, Fe, Zn) are precipitating, and are thermodynamically possible at these

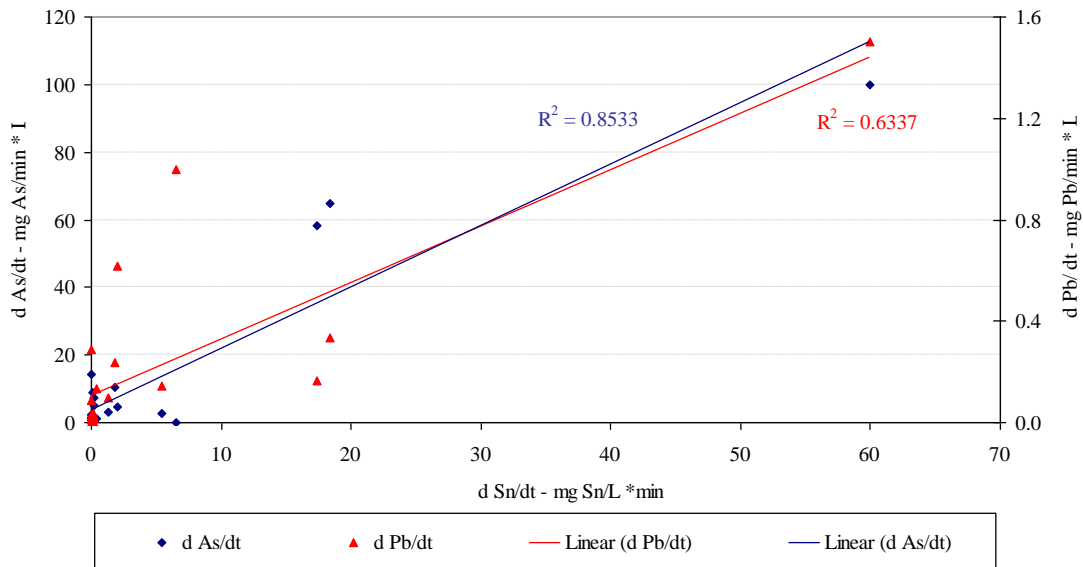
REDOX conditions, so the rate of arsenic precipitation is plotted. The tin precipitation rate followed very closely the arsenic precipitation rate. The tin could be precipitated or co-precipitated with the arsenate (Figure 4.32). The majority of the tin precipitation occurs at 750 mV, and then decreases rapidly to 350 mV at the final stages of tin precipitation. This indicates that different tin precipitation mechanisms are occurring above REDOX values of 600 mV. With respect to Eh, many factors such as acidity, cation and anion concentrations are changing, and that it is difficult to correlate Eh with tin precipitation rate.



**Figure 4. 32: As Precip. and REDOX vs. Sn Precipitation, 100g/L H<sub>2</sub>SO<sub>4</sub>, and 90 °C**

The total arsenic and lead precipitation rate is plotted against tin precipitation rate, and there is a very good correlation between the two (Figure 4.33). The highest rates of tin precipitation occur at the beginning of the Releach cycle when the tin and lead concentrations are the highest. The high lead precipitation rates at the lower tin precipitation rates are for the excess reductant case ( $R_{PbCon/PreCon} = 1$ ). Furthermore, this tin precipitation rate should have been much higher, however, the majority of tin had already precipitated before the  $t = 1$  minute mark sample time. Also plotted is the lead precipitation rate which shows some correlation between lead and tin, however, it is not as strong a correlation as that of arsenic due to lead precipitating as sulphate and

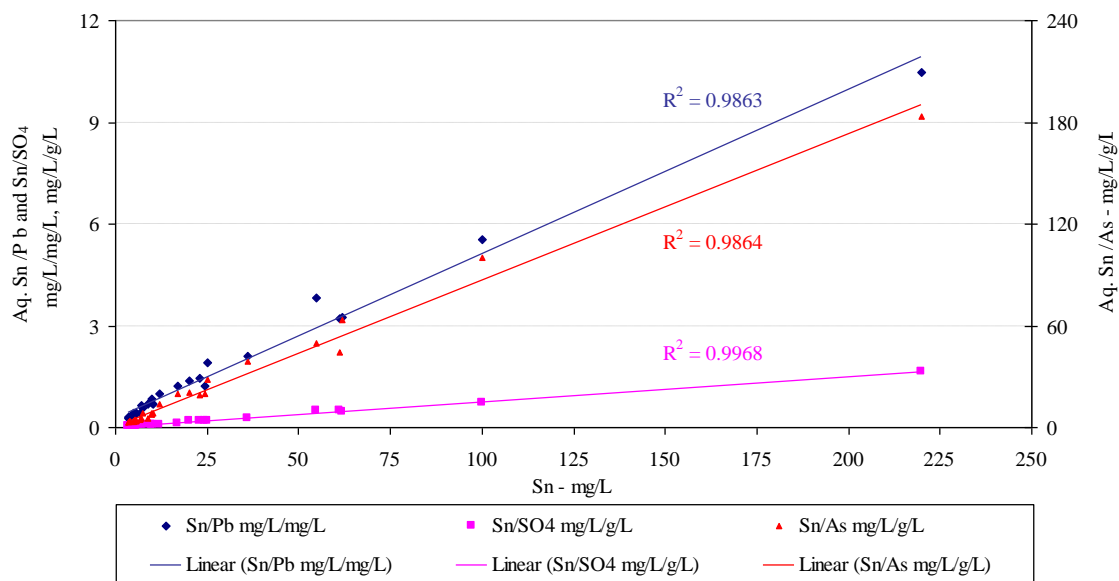
sulphide, in addition to arsenates. The higher arsenic precipitation rates at the lower tin precipitation rates correspond to the excess reductant case ( $R_{PbCon/PreCon} = 1$ ).



**Figure 4. 33: Arsenic and Lead Precipitation Rate vs. Tin Precipitation Rate**

In summary, the lower tin precipitation rates (< 20 mg Sn/L·min) do not have clear correlation with arsenic or lead.

Tin has been normalized with aqueous lead, arsenic, and sulphate, and compared to see how these ratios vary with tin concentration (Figure 4.34).



**Figure 4. 34: Tin Aqueous Ratios with (Pb, As, SO<sub>4</sub>) vs. Tin Concentration**

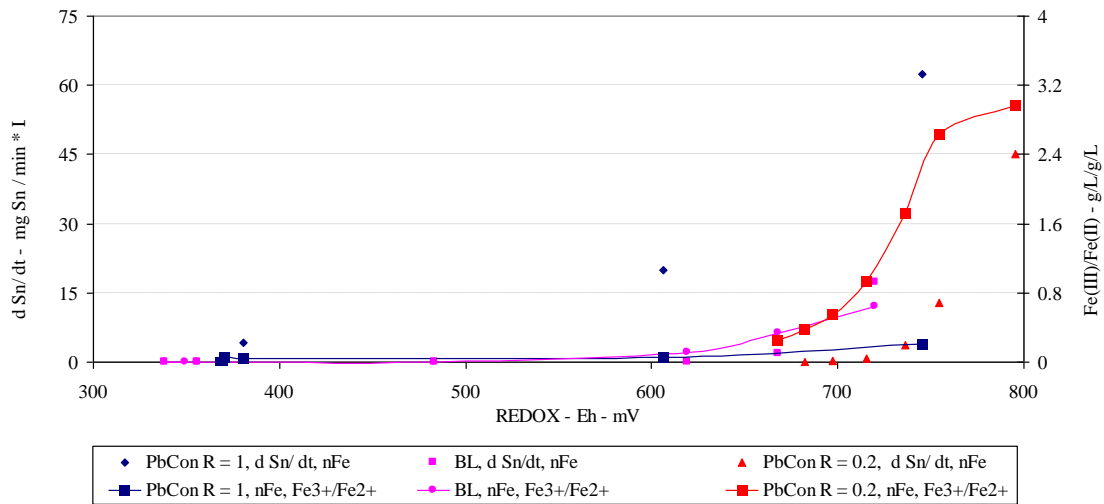
The best correlation for aqueous tin was with sulphur as sulphate indicating that tin was precipitating as a sulphate type compound, or tin was correlating with aqueous sulphate due to changing acid concentration. There is good correlation between both tin and arsenic, and tin and lead which may mean tin is also precipitating directly (cation substitution) or co-precipitating with a lead arsenate type compound. The highest measured tin precipitation values correspond to the highest aqueous ratios value for both arsenic and lead and were for the minimum reductant case ( $R_{PbCon/PreCon} = 0.2$ ). As tin precipitation decreases, so do the values of the aqueous ratios as both tin and the impurities are decreasing in value in the aqueous phase.

#### 4.4.4.2 Reductant Ratio and REDOX

Lead concentrate is a source of sulphide reductant (PbS) and is added primarily for Fe(III) reduction, and copper removal by metathesis reaction, and other impurity removal. The greatest rate of tin removal occurred during REDOX potentials greater than 600 mV for all reductant ratios tested (Figure 4.35). The Fe(III) reduction occurs at REDOX values greater than 700 mV. All tin removal reactions occurred between REDOX range of 750 mv and 325 mV, the greatest tin precipitation rates occurring at a REDOX value greater than 600 mV. The highest reductant mass ratio ( $R_{PbCon/PreCon} = 1$ ) experiment REDOX had already been reduced to 613 mV within one minute, and the



measured tin precipitation rate at this REDOX potential was the 62.5 mg Sn/min·L tin precipitation rate.



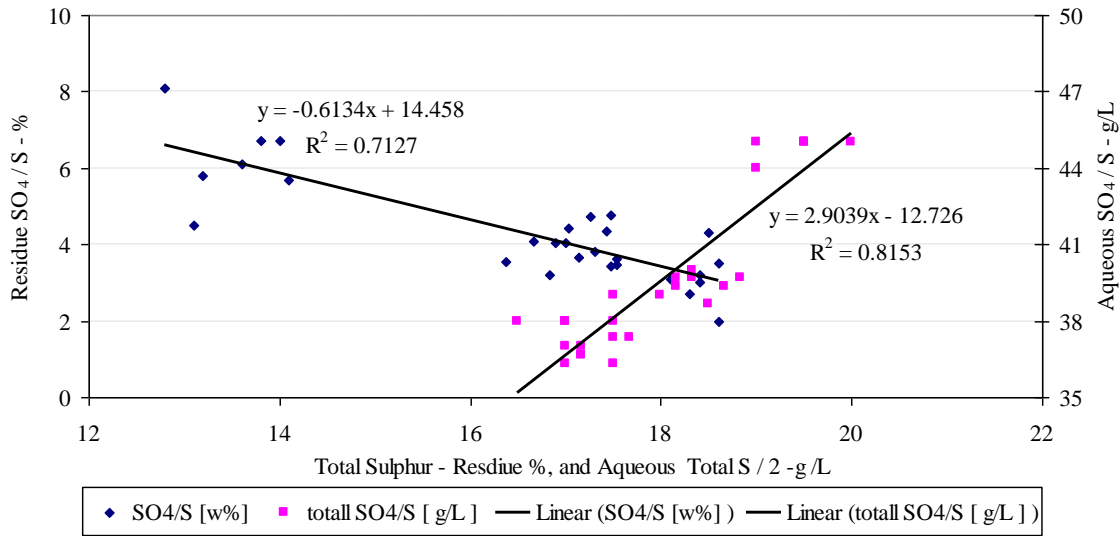
**Figure 4.35: Sn Precip. and Fe(III) Red. vs. REDOX, 100g/L H<sub>2</sub>SO<sub>4</sub>, and 90 °C**

The majority of tin removal occurred at REDOX potential greater than 600 mV indicating that there are different tin precipitation mechanisms for REDOX regimes between 600 and 300 mV. For REDOX value greater than 600 mV thermodynamically favourable tin precipitation reactions identified are arsenate precipitation (Pb, Zn, Fe), then tin sulphate precipitation reactions such as Sn(IV) sulphates, peroxy-sulphates, or hydrous oxides. Most likely, tin is present as Sn(IV) in this REDOX regime which would agree with thermodynamics theory (Pourbaix). For REDOX values less than 600 mV, other tin precipitation mechanisms could be occurring such as tin precipitation by polymerization and Sn(II) sulphide precipitation. The excess reactant experiments ( $R_{\text{PbCon/PreCon}} = 1$ ) had the greatest tin removal initially. However, after the dissolution period the tin kept precipitating as the Release cycle reached conclusion. The excess and BL reductant experiments exhibited no difference in tin precipitation rates for REDOX values below 600 mV, indicating that the additional reductant serves no benefit in terms of tin removal.

#### 4.4.4.3 Reductant Ratio and Sulphur

The sulphate sulphur in the residue decreases as total sulphur increases in all the reductant mass ratio tests ( $R_{\text{PbCon/PreCon}} = 0.2 \dots R_{\text{PbCon/PreCon}} = 1$ ). This trend is a result of

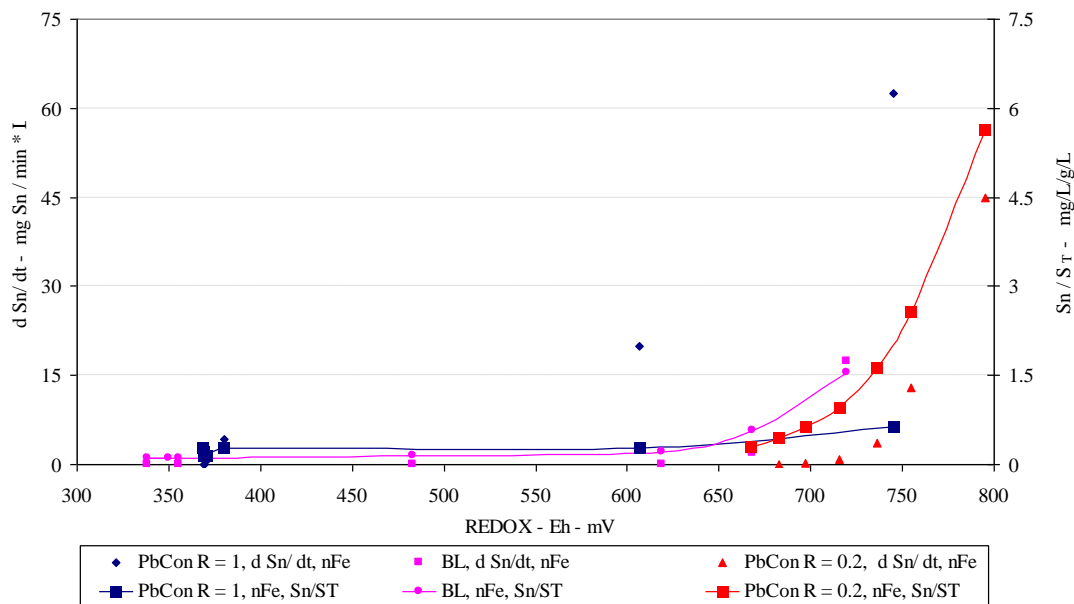
the higher reductant ratio, which increases the amount of unreacted reductant deporting to the residue (Figure 4.36).



**Figure 4. 36: S in Residue and Aqueous vs.  $S_T$ , 100g/L  $H_2SO_4$ , and 90 °C**

For all reductant addition experiments the sulphur in residue increases from 0.5 to 1 % (approximately) during the Releach cycle. The highest reductant experiment ( $R_{PbCon/PreCon} = 1$ ) achieved a steady state residue sulphur concentration in approximately 10 minutes compared to 100 minutes for the BL case ( $R_{PbCon/PreCon} = 0.6$ ). The lowest reductant addition experiment ( $R_{PbCon/PreCon} = 0.2$ ) had the greatest increase in residue concentration of 1.3 % in 30 minutes and never reached equilibrium in terms of residue sulphur concentration (Figure 4.36).

Sulphur oxidation to sulphate and subsequent precipitation occurred in the leach solution while it was still oxidizing between REDOX values of 800 to 600 mV (Figure 4.37) and follows Fe(III) closely (previous Figure 4.35). The lowest reductant ratio ( $R_{PbCon/PreCon} = 0.2$ ) has tin precipitation occurring in the highest REDOX range between 800 and 675 mV, as well as the highest ratio of aqueous tin to total aqueous sulphur ratio. This result is expected as the REDOX is at the highest value, and it corresponds to Sn(IV) solubility behaviour. The lowest reductant ratio also had the highest total acidity values.



**Figure 4.37: Sn Precip. and Aqueous  $S_T$  vs. REDOX, 100g/L  $H_2SO_4$ , and 90 °C**

Essentially, by the time REDOX reaches a value of 600 mV the ratio of tin total sulphur in solution has reached an approximate steady value until the lower value of REDOX is reached around 350 mV. For the highest reductant case ( $R_{PbCon/PreCon} = 1$ ), tin is still precipitating below 600 mV, indicating perhaps that tin is precipitating by some other non-sulphur precipitation or REDOX mechanism, such as Sn(IV) arsenate, or cation substitution or co-precipitation with lead arsenate during the 600 mV to 350 range, which is in line with Eh-pH regime for precipitation of lead arsenate. The tin precipitation rate was greatest for the aqueous tin to total sulphur profile meaning that sulphate is also precipitating during reduction of Fe(III) and not just as a result of the solubility behaviour of lead. Tin and sulphate concentration may have been significantly higher than measured in the one minute sample for the BL and highest reductant ratio cases, but due to the rapid nature of iron reduction were sampled too late.

As excessive reductant is present, the aqueous ratio of terminal tin and lead concentration in solution decrease (Figure 4.38). As more reductant is added, either  $PbSO_4$  or  $S^0$  covers the surface of  $PbS$ , and the rate of  $PbS$  dissolution decreases, and the available aqueous phase sulphide ion for Fe(III) reduction decreases, resulting in an increase of the final tin concentration in the aqueous phase. As the rate of  $PbS$

dissolution diminishes, the terminal  $\text{H}_2\text{SO}_4$  and  $\text{Fe(III)}$  concentrations both increase which results in higher aqueous tin concentrations. At the lower reductant ratios ( $R_{\text{PbCon}} = 0.2$ ,  $R_{\text{PbS}} = 0.12$ ) there is insufficient sulphide present to precipitate the tin as either  $\text{Sn(IV)}$  or  $\text{Sn(II)}$  sulphides resulting in higher terminal tin concentrations.

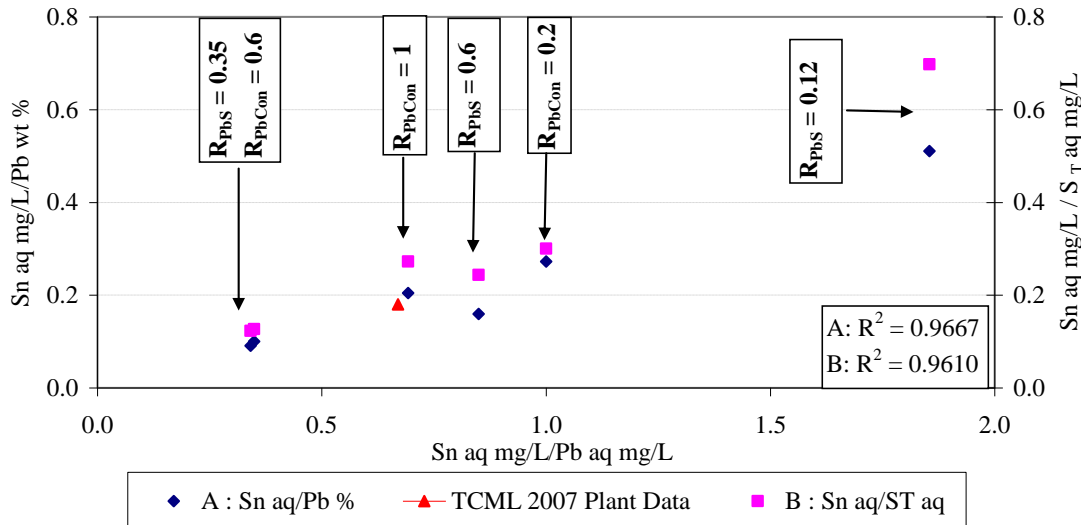


Figure 4. 38: Aqueous Sn, S, Pb Ratios at  $t=150$  minutes,  $100\text{g/L H}_2\text{SO}_4$ , and  $90^\circ\text{C}$

The final tin levels in the Releach are affected by the amount of reductant added. The lowest tin levels are achieved using  $\text{PbS}$  at a ratio of 0.35 ( $R_{\text{PbCon/PreCon}} = 0.60$  equivalent) and represents an equilibrium value. The highest levels of tin remaining in solution occurred at the lowest levels of reductant added for both lead concentration and lead sulphide. The tin levels started increasing as an excess of sulphide was present in the Releach solution due to lead sulphate and elemental sulphur formation which reduced the lead sulphide dissolution rate. Furthermore, insufficient reductant will not cause tin precipitation as sulphide or hydrous oxide. The lowest reductant ratio had the highest residual tin levels. Excess reductant shown on the 1  $\text{PbCon}$ :  $\text{PreCon}$  curve had higher residual tin levels than the intermediate reductant. The greatest rate of tin precipitation with lead concentrate and pure  $\text{PbS}$  occurs within 10 minutes as compared to the plant data which occurs within 15 minutes.

## Kinetics:

The tin kinetics are approximately second order for the base case ( $R_{\text{PbCon/PreCon}} = 0.6$ ) and minimum addition case ( $R_{\text{PbCon/PreCon}} = 0.2$ ). No meaningful kinetic fit could be made for the excess reductant case ( $R_{\text{PbCon/PreCon}} = 1$ ). The excess reductant case underwent tin and arsenic re-dissolution which may have contributed to difficulty finding an accurate kinetic fit for this experiment.

**Table 4. 13: Tin Kinetics versus Reductant Mass Ratio**

<b>100 g/L H<sub>2</sub>SO<sub>4</sub>, 90°C</b>				
<b>Reductant</b>	<b>Order</b>	<b>k</b>	<b>Units</b>	<b>R<sup>2</sup></b>
<u>PbCon</u>				
0.2	2	0.0005	1/mg Sn /L*min	0.9988
0.6 (BL)	2	0.0009	1/mg Sn /L*min	0.7678
1	na	na	na	na
<u>PbS</u>				
0.12	2	0.0001	1/mg Sn /L*min	0.9313
0.35	2	0.0002	1/mg Sn /L*min	0.8343
0.6	na	na	na	na
<u>Plant Data 2007</u>				
0.6	1	0.0085	min <sup>-1</sup>	0.9947
0.6	1	0.0146	min <sup>-1</sup>	0.944

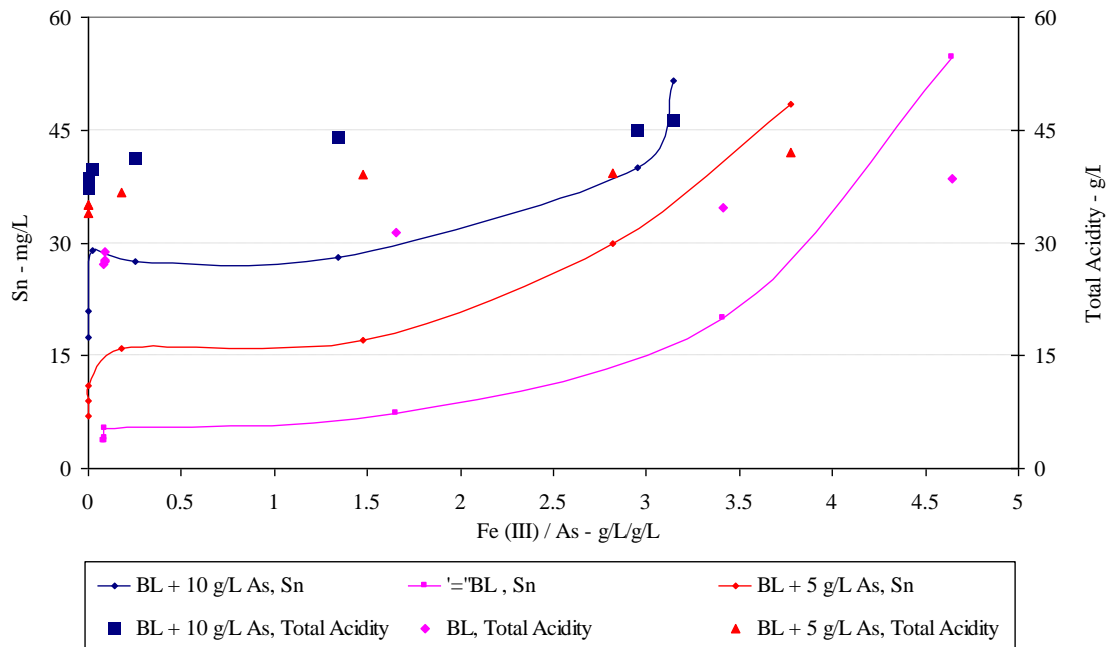
### **4.4.5 Aqueous Arsenic (V) Concentration, BL to BL + 10 g/L As**

From previous TCML 2006 commercial Reduction process observations, the concentration of arsenic correlated ( $R^2 = 0.9072$ ) very well to aqueous tin concentration.

#### **4.4.5.1 Fe(III) – As(V) Complexation**

Arsenic may be complexed with Fe(III) and exist as metastable phase in which initial acidity or Fe(III/II) concentrations are important with respect to the stability of the precipitated amorphous ferric arsenate, or crystalline scorodite phase (Singhania et al., 2006). However, the ferric iron present also affects the aqueous tin concentration. Ferric

iron can complex arsenic creating a metastable phase of arsenic. Furthermore, acidity increases the concentration of aqueous tin in solution as described by Pourbaix's equilibrium theory. As the amount of aqueous arsenic increases relative to Fe(III), the aqueous tin decreases (Figure 4.39). However, both the higher arsenic addition experiments (BL + 5 and 10 g/L As) have a higher total acidity and higher aqueous tin concentrations.



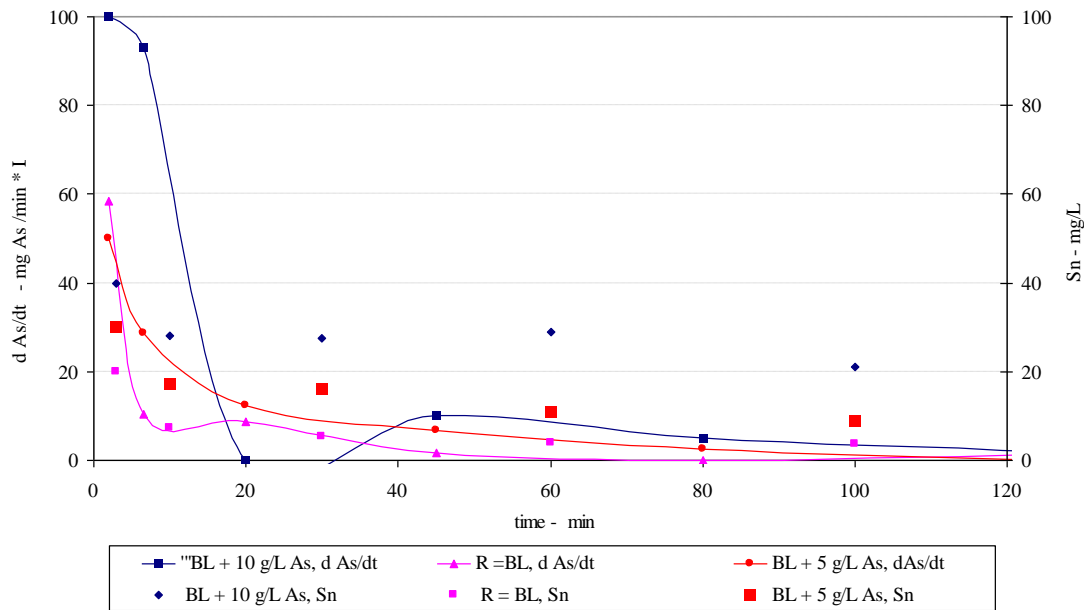
**Figure 4. 39: Aqueous Tin and Acidity vs. Fe(III)/As Ratio (Aqueous)**

The higher tin concentrations occur at lower Fe(III)/As(V) ratios for two possible reasons. The acidic nature of aqueous arsenic and resulting increase in total acidity and increasing tin solubility agrees with theory. Further, the ferric ion complexed/associated with arsenic and reduced the ability of arsenic to react with tin directly, or indirectly as an arsenate, both of which will precipitate at these conditions. As the Fe(III)/As ratio is increased there is less available arsenic for Fe(III) to complex with and both total acidity and aqueous tin concentrations increase. Aqueous iron concentrations in the solution are in excess of arsenic (15 g/L total Fe versus 1 g/L As for the BL case). During the first minute of the reaction the Fe(III) is reduced from 14 g/L to 8 g/L, and the corresponding Fe(III)/As(V) ratio at one minute is 4.5 in the first minute of the leach cycle, then approximately zero in 30 minutes. Chemical association of tin with arsenate may be possible as well. Previous Fe(III)-As(V) precipitation studies have found other trivalent

ions such as Al(III) can replace Fe(III), and divalent cations such as Pb, Zn, Ca, Mn, and Mg may precipitate with iron arsenate precipitates. Therefore, perhaps, Sn(II) or Sn(IV) can precipitate with the arsenate precipitate as well.

Kinetics:

Also, kinetic effects such as aqueous arsenic concentration can affect final aqueous tin levels. The highest arsenic concentration test (BL + 10 g/L As) had the greatest rate of arsenic precipitation and underwent re-dissolution after approximately 20 minutes into the Releach. The resulting tin concentration increased slightly after re-dissolution and then re-precipitated after 60 minutes (Figure 4.40).

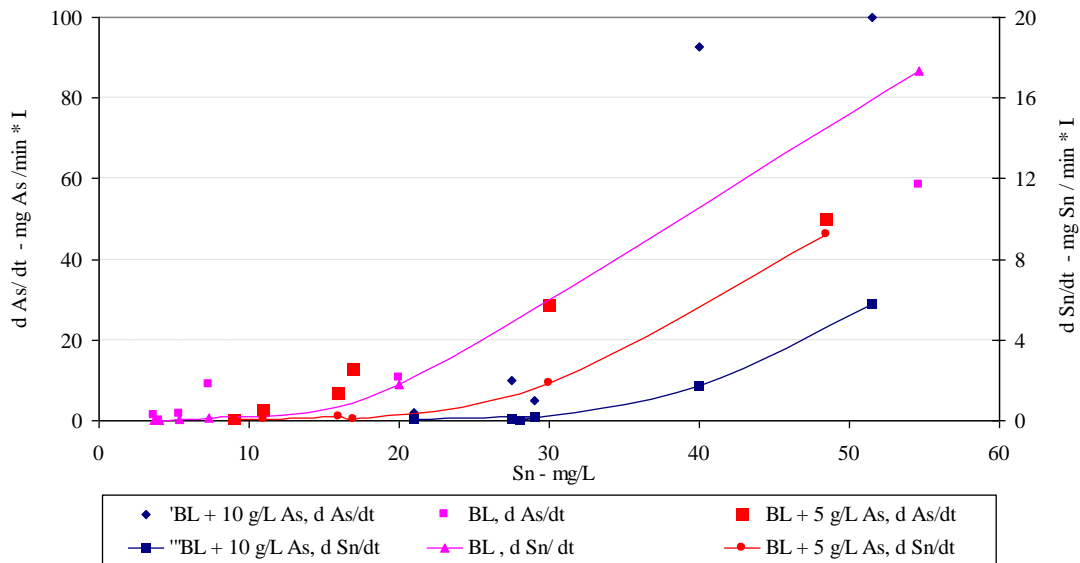


**Figure 4.40: As<sub>2</sub>O<sub>5</sub> Precipitation and Sn Concentration versus Time**

The tin concentration profile followed the arsenic precipitation rate closely for all the arsenic addition (As<sub>2</sub>O<sub>5</sub>) experiments. Both the BL experiment and BL + 5 g/L experiments had completed arsenic precipitation by 100 minutes into the Releach cycle. The aqueous tin concentration increases with increasing arsenic concentration due to increased total acidity. However, the effect of arsenic concentration on tin precipitation with higher arsenic concentrations is still not clear. The higher arsenic concentration resulted in an increased rate of arsenic precipitation and subsequent unstable precipitate

which underwent re-dissolution, and a higher terminal tin concentration, due to total acidity.

The rates of tin precipitation for all three of the arsenic concentration experiments are similar for tin concentrations above 40 mg/L tin. For all three different initial arsenic concentrations, the higher arsenic addition experiments resulted in a shorter tin precipitation regime due to either sulphate (Pb, Sn) or direct arsenate precipitation or co-precipitation with (Pb, Fe, Zn) arsenates (Figure 4.41). The BL, BL +5 g/L As, and BL + 10 g/L As tin precipitation transition times were 10, 20, and 30 mg/L Sn, respectively. Below 40 mg/L tin concentration, the higher arsenic concentrations delay the tin concentration transition point where the tin precipitation rate increases, possibly due to higher total acidity and subsequent increase in tin solubility. As well, there is better correlation agreement between tin concentration and aqueous Sn/SO<sub>4</sub> ratio versus Sn/As ratio in this tin concentration range (< 40 mg/L Sn).



**Figure 4. 41: As and Sn Precipitation versus Sn Concentration**

From Table 4.14, the rate of tin precipitation increased as did the order of the reaction with increasing arsenic concentration. This was due to increased lead and ferric arsenate precipitation. In the benchscale tests the tin precipitation kinetics were found to



be second to third order as the arsenic concentration increased. Furthermore, the BL tests were approximately first order tin precipitation kinetics. The best second order fit was for the BL + 5 g As/L experiments, and the higher arsenic addition case (BL + 10 g/L As) precipitate was unstable and underwent re-dissolution during the leach test. The tin precipitation kinetics for the commercial process data was a first order fit.

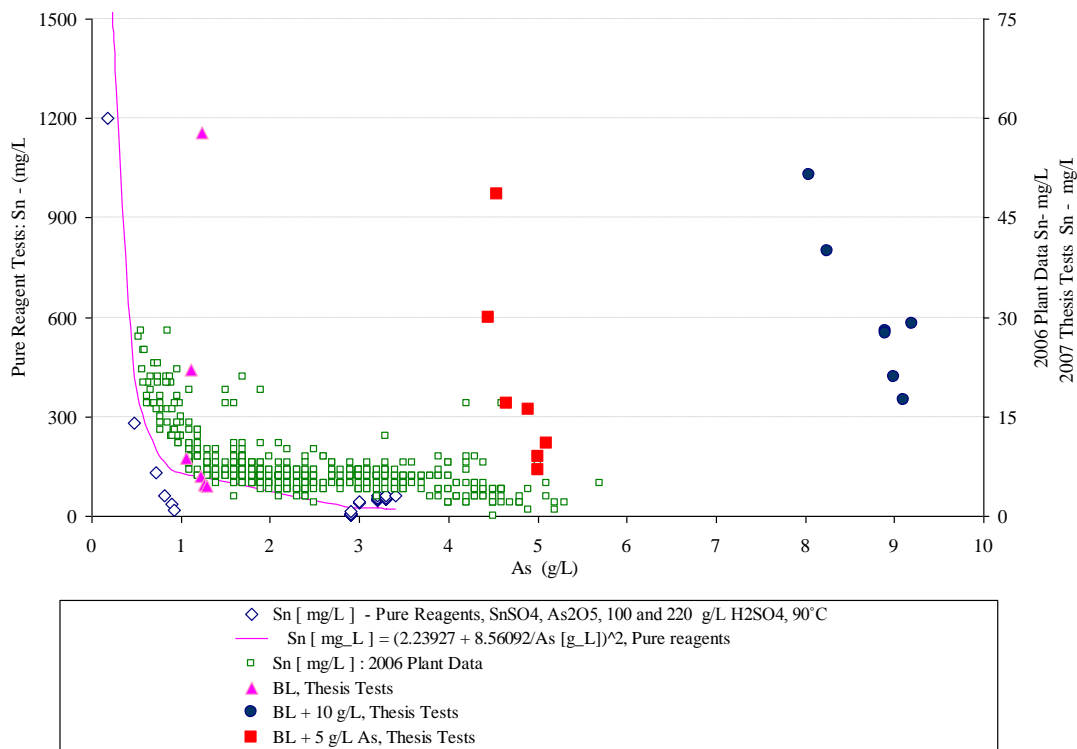
**Table 4. 14: Reaction Order for Tin versus Arsenic in Solution, 100 g/L H<sub>2</sub>SO<sub>4</sub>, 90 °C**  
**100 g/L H<sub>2</sub>SO<sub>4</sub>, 90 °C, R<sub>PbCon:PreCon</sub> = 0.6**

Reductant R	Order	k	Units	R <sup>2</sup>
BL, nFe R = 0.6	2	0.0009	1/mg Sn /L*min	0.7678
BL + 5 g/L As, nFe R = 0.6	2	0.0006	1/mg Sn /L*min	0.984
BL + 10 g/L As, nFe R = 0.6	3	0.00001	(1/mg Sn /L*min) <sup>2</sup>	0.8858
Plant Data 2007 R = 0.6	1	0.0085	min <sup>-1</sup>	0.9947
R = 0.6	1	0.0146	min <sup>-1</sup>	0.944

#### 4.4.5.2 Pure Reagent Tests – No Fe(III):

Tin behaves differently in acidic sulphate solutions with iron compared to solutions without iron present. Several pure reagent tests using stannous and stannic sulphate, arsenic pentoxide, and sulphuric acid were conducted (Figure 4.42). The pure reagent tests (Fe(III) free) were used to compare against TCML 2006 plant data, and the benchscale thesis test data that did contain Fe(III), and the results are shown in Figure 4.42. The pure reagent tests were done at 100 g/L and 220 g/L H<sub>2</sub>SO<sub>4</sub> cases (initial plant conditions), and the thesis bench scale tests were done at 100 g/L initial H<sub>2</sub>SO<sub>4</sub>.

From these tests, it can be determined that aqueous arsenic concentration by itself does not reduce aqueous tin concentration, as long as the arsenic concentration is greater than 1 g/L As. The solids precipitated during these tests could be SnSO<sub>4</sub>O<sub>2</sub>, As<sub>2</sub>S<sub>3</sub>, As<sub>2</sub>O<sub>3</sub>, or SnS, as well as possibly Sn<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>, although they are all thermodynamically possible.



**Figure 4. 42: Pure Reagent, TCML 2006 Plant Data, Thesis Benchscale Tests**

The pure reagent and 2006 plant data correlates well with the final Releach aqueous tin and arsenic concentrations. The thesis benchscale data follows a similar trend for aqueous arsenic and tin concentrations. The pure reagent tests show that aqueous tin in the presence of Fe(III) and dissolved oxygen can react and precipitate tin. The BL benchscale thesis tests do follow the commercial Releach tin trend more closely than the benchscale tests with elevated arsenic concentrations. All the benchscale tests follow the 2006 plant data aqueous tin profile, although the results of the thesis benchscale tests are not as pronounced as the pure reagent data tests. The benchscale tests with elevated arsenic also had higher total acidity, and may have complexed Fe(III), therefore, becoming unavailable for Fe(III) reduction and tin precipitation.

Furthermore, the different acidities used during the pure reagent tests produced different colour precipitates. The higher acidity case of 220 g/L H<sub>2</sub>SO<sub>4</sub> produced a darker grey precipitate within the first hour. The colour proceeded to change to a darker grey/brown with time, as shown in Figure 4.43.

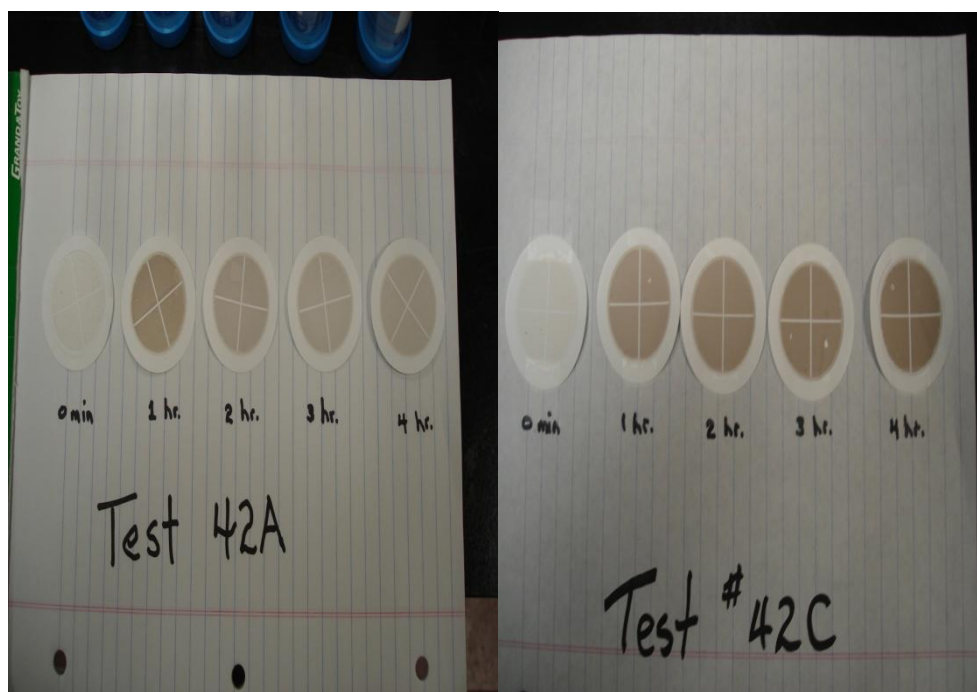


Figure 4. 43: Tests 42A and 42C

The grey/brown precipitates could be  $\text{SnSO}_4\text{O}_2$ , or  $\text{Sn}_3(\text{AsO}_2)_2$ , and or  $\text{SnS}$  or  $\text{As}_2\text{S}_3$ . All the indicated precipitates are thermodynamically possible at the leaching conditions. However, there was not enough precipitate for XRD analysis. Also, in those benchscale tests which were using Ge Preconcentrate, other arsenate precipitates, such as  $\text{Pb}_3(\text{AsO}_3)_2$ ,  $\text{PbSO}_4$ , and  $\text{PbO}$ , are also thermodynamically possible.

## 5 CONCLUSION

### 5.1 Key Findings and Future Work

In the iron precipitation residue, the feed material to the Releach, most of the tin is present in the stannic state and is associated with zinc, iron and lead oxides. This result implies that if zinc and iron are leached from this material, tin will also dissolve. Tin concentrations are indeed highest early in the leach, before precipitation starts to dominate tin chemistry. The association of tin with zinc and iron in the iron precipitation residue is also consistent with higher tin levels in the dissolution phase for leaches conducted at higher acidities. Since the zinc- and iron-oxide material is an acid consumer, starving the leaches of acid will limit the extent of leaching of the iron residue, and thus the level of tin in solution early in the leach.

Tin precipitation rates are fastest early in the leach when the change in solution REDOX potential is greatest. This is explained by co precipitation with, or adsorption on, lead arsenates or sulphates which occurs during the Fe(III) reduction step in the first 30 minutes of the leach. Tin precipitation rates observed in the full-scale process are best simulated in the benchscale tests for comparable leach acidity (220 g/L H<sub>2</sub>SO<sub>4</sub>). High leach acidities promote tin precipitation rates. However, in the absence of arsenic, this high acidity promotes tin re-dissolution beyond a retention time of 30 minutes. There is no observed re- dissolution in the plant surveys at similar starting acidities, and this warrants further work.

For a comparable acidity regime (100 g/L H<sub>2</sub>SO<sub>4</sub> starting acidity), the addition of arsenic to the leach results in higher tin concentrations in the dissolution regime of the leach. This is believed to be the result of higher total acidity due to the presence of arsenic acid in solution. The final tin concentration in the leach is also higher when soluble arsenic is present in the leach. This could be explained by the slower precipitation rate constant with arsenic present (precipitation rate slows at high arsenic levels), or that tin is complexed with arsenic and Fe(III) in solution, preventing precipitation; both of which warrant further study. The presence of iron may explain why this trend is different than the plant trend of high As and low Sn, perhaps because of the

iron complexation. Although not discussed in this paper, from other Releach testwork there was a clear correlation with initial lead reductant levels and corresponding aqueous arsenic and tin concentrations. However, the role between iron and arsenic with tin precipitation was not conclusive and provides opportunity for further work, especially with arsenic addition experiments at the Releach initial 220 g/L acidity.

#### Thesis Supporting Testwork:

Iodometry could not be validated as an accurate measure of Sn(II/IV) concentrations with Fe(II) present in solution, therefore, ICP was used for total aqueous tin concentration. The aqueous oxidation of Sn(II) to Sn(IV) increases with increasing tin concentration. The oxidation rate of Sn(II) was first order kinetics with a rate constant between 0.0002 to 0.0003 mg Sn/L·s, and may be low due to poor mass transfer of oxygen and inefficient mixing. The REDOX potential (Eh) varied between 550 to 650 mV. The different methods used for speciation of tin in Ge Preconcentrate, and Reduction Releach residue were X-Ray Absorption Near Edge Structure Spectroscopy (XANES), Mineral Liberation Analysis (MLA), and X-Ray Diffraction (XRD). Crystalline tin in the Ge Preconcentrate and Reduction Releach residue is primarily present as Sn(IV), as a mixed zinc tin oxide, with tin as SnO<sub>2</sub> type compound with minor amounts of Sn(II) as SnO or SnSO<sub>4</sub>. The amorphous phase of tin was not studied. Future speciation work would investigate the amorphous phases of the Ge Preconcentrate and Reduction Releach residue.

#### Main Thesis Test Work.

##### Total Acidity:

##### Higher acidity and proton availability:

The tin re-dissolution observed with the benchscale thesis tests at 220 g/L H<sub>2</sub>SO<sub>4</sub> initial acidity did not occur with the observed tin dissolution in the commercial Releach at similar initial acidity, which warrants further study.

The higher acidity (40 to 220 g/L H<sub>2</sub>SO<sub>4</sub>, 90 °C) benchscale tests were proven to increase the tin solubility during the Reduction process. Equilibrium theory by Pourbaix predicts higher tin solubilities at higher acidities. However, the type of tin in the aqueous

phase was not determined. The higher observed speciation of aqueous tin may have been ionic, or a colloidal polymer which did not filter well.

The 220 g/L H<sub>2</sub>SO<sub>4</sub> experiment had higher aqueous tin concentrations and Eh values compared to the lower acidity experiments. The terminal Eh, and aqueous tin concentration increased as total acidity increased. The highest acidity experiments had terminal Eh and tin concentrations of 450 mV and 75 mg/L Sn versus 350 mV and 5 mg/L Sn for the lower acidity case (40 g/L H<sub>2</sub>SO<sub>4</sub>). Increasing total acidity increases tin dissolution during the initial stages of the Releach. For dissolution conditions (t = 1 minute sample) below 60 g/L H<sub>2</sub>SO<sub>4</sub>, the terminal tin concentrations were less than 5 mg/L, and agreed well with previously reported literature values. Dissolution acidities exceeding 60 g/L H<sub>2</sub>SO<sub>4</sub> have tin concentrations which exceed the literature values. Tin concentrations varied from 120 to 220 mg/L compared to 100 mg/L from previously reported literature. The increase above literature values may have been due to other anions in solution which may complex tin.

Initial acidity was also increased by the addition of acidic arsenic oxides (As<sub>2</sub>O<sub>5</sub>). The highest arsenic addition experiments had a total acidity of 38 g/L and tin concentration of 40 mg/L Sn versus 27 g/L total acidity and 25 mg/L Sn for the baseline acidity case with no As<sub>2</sub>O<sub>5</sub> addition. Both the total acidity and aqueous tin concentrations increased as total acidity increased. Aqueous tin most likely precipitates or co-precipitates with arsenates for Eh greater than 600 mV; and predominately as a sulphate or oxide below 600 mV.

#### Ligand Substitution:

Sulphate and arsenate ligand substitution was proven for higher aqueous sulphate to arsenate concentration ratios using a change in total acidity (H<sub>2</sub>SO<sub>4</sub>). The sulphate to arsenate concentration ratio ((SO<sub>4</sub>/As)<sub>aq</sub>) was increased by increasing the H<sub>2</sub>SO<sub>4</sub> concentration from 40 to 220 g/L, and resulted in unstable precipitates which releached and resulted in higher aqueous tin concentrations. The aqueous sulphate to arsenate concentration ratio was varied by changing the initial concentrations of H<sub>2</sub>SO<sub>4</sub> and comparing the sulphate to arsenate concentration ratio in both aqueous and precipitate phases. The highest ratios obtained were 5000 to 6000 g/L/g/L and were for the lowest

acidity case of 40 g/L H<sub>2</sub>SO<sub>4</sub>. The corresponding tin concentrations were quite low as well (< 5 mg/L Sn). The ratio was so high and tin concentrations so low due to minimum proton availability to effect arsenic dissolution. The balance of the ratios varied between 100 to 300 g/L/g/L; the higher ratios were for the higher initial acidities. As the aqueous tin concentration increased, the SO<sub>4</sub> content of the precipitate increased as well. The highest value of aqueous tin and sulphate in residue corresponds to high initial acidity experiments. It was generally found that increasing initial total acidity increased Fe(III) dissolution, which in turn has the ability to complex arsenic in solution.

Ligand substitution was not proved by decrease in sulphate to arsenate concentration ratio ((SO<sub>4</sub>/As)<sub>aq</sub>), and was adjusted by the addition of As<sub>2</sub>O<sub>5</sub> to achieve an initial arsenic concentration ranging between 1 to 10 g/L arsenic @ 100 g/L initial H<sub>2</sub>SO<sub>4</sub>. As the aqueous sulphate to arsenic ratio decreased from 120 to 15 g/L/g/L, the aqueous tin concentration increased from 5 to 40 mg/L. Furthermore, the corresponding ratio in residue follows the same aqueous ratio trend and decreases as well, and the aqueous tin concentration increases. Some of the additional arsenic is precipitating and the increased aqueous tin could be due to total acidity or, arsenic in residue could be displacing tin that has precipitated or adsorbed as some other precipitated compound. The lead precipitated from the Releach solution between 600 and 800 mV, and thermodynamically could precipitate as sulphates, oxides, or arsenates (Pb, Fe, Zn). The tin to lead and tin to sulphate aqueous ratios had the best R<sup>2</sup> correlation with each other of 0.9689 and 0.9976, respectively, with aqueous tin concentration most likely due to the low solubility of lead compounds. Aqueous ratios Sn/Pb and Sn/As followed each other in the REDOX range between 600 to 800 mV, while tin may have been precipitating directly or co-precipitating with arsenate compounds (Pb, Zn, Fe). The aqueous ratio of Sn/SO<sub>4</sub> was the most consistent over the entire REDOX range and may have indicated that tin is precipitating or co-precipitating with sulphate as lead sulphate, or some type of Sn(IV) sulphate. The correlation for aqueous tin to arsenic had the worst correlation with aqueous tin of R<sup>2</sup> = 0.4208. This could be due to complexation with Fe(III), as well as arsenic precipitating with lead and iron. From the data, the Sn/As ratio behaviour becomes very different above 30 mg/L Sn; perhaps indicating a different precipitation mechanism. By investigating arsenic as a ratio of Pb/As, Fe/As, and Sn/As in residue, it

becomes clear that tin correlates with Pb/As best at  $R^2 = 0.8578$ . Pb/As and Fe/As follow the same trend in terms of aqueous tin concentration.

### Ionic equilibrium:

Ionic equilibrium due to increase in sulphate ions does not by itself affect tin concentration of the Releach solution, but is due to the total acidity (40 to 220 g/L  $H_2SO_4$ ) and subsequent solubility of tin. There seems to be a different ionic behaviour for ionic strengths less than six, which corresponds to tin concentrations less than 20 mg/L. The lower tin concentrations correspond to the end of the Releach cycle when most of the impurity precipitation has taken place, i.e., there are less ions in solution. The experiments showed a wide range of aqueous tin concentration for little change in ionic strength. For the increased initial total acidity  $H_2SO_4$  experiments, the ionic strength increased from 2.5 to 7 mol/L, and aqueous tin increased as well. Possibly,  $SnO_2$  dissolution by acid varies with activity  $[H^+]^4$ , therefore, a small change in acid concentration can significantly affect aqueous tin concentration. Increasing arsenic (BL to BL + 10 g/L As) concentration correlates directly to increasing ionic strength of the Releach solution, which in turn increases the aqueous tin concentration, which is in agreement with acidity and equilibrium theory. However, the increases in tin are due to the acidic nature of arsenic and not ionic strength.

Tin precipitation kinetics resulting from change in acidity ranged between first and second order kinetics. TCML trials were done using a diluted concentration of  $H_2SO_4$  with rate constants ranging from 0.0085 to 0.0146 mg Sn/min·L. The thesis benchscale tests were first order in terms of kinetics for 220 g/L initial  $H_2SO_4$ , which is closer to the commercial TCML Releach initial acidity of 220 to 240 g/L  $H_2SO_4$ . The thesis benchscale tests with acidities less than 220 g/L  $H_2SO_4$  resulted with second order fit with rate constants ranging from 0.0004 to 0.0009 mg Sn/min·L. The tin precipitation decreases rapidly below 220 g/L  $H_2SO_4$  total acidity. The decrease in rate constant is due to reduced proton availability for Sn(IV), and possibly Sn(II) precipitation reactions from varying total acidity (40 to 220 g/L  $H_2SO_4$ ). The Fe(III) reduction during the Releach went through three distinct stages in terms of tin precipitation from tin concentrations of 60 to maximum mg/L, 30 to 60 mg/L, and less than 20 mg/L.



### Tin polymerization:

Tin precipitation by polymerization could not be proven. Tin did precipitate at 90 °C in acidic sulphate media (100 g/L H<sub>2</sub>SO<sub>4</sub>) in the absence of reductants or other impurities (As(V), Fe(III) from 110 mg/L to 55 mg/L Sn). However, thermodynamically, the Sn(IV/II) precipitate could have been some other type of Sn(IV) precipitate (hydrous oxide, sulphate, or sulphate-peroxide). There was not enough precipitate for analysis and further work is recommended. This work may involve taking filtrate from the Releach tests using Ge Preconcentrate and lead concentrate, and using a sugar reductant to precipitate the tin; then using XRD, MLA speciation analysis for identification of the tin precipitate. The activation energies for the tin precipitation kinetics for the Releach process varied from 11 to 18 kJ/mol during the Releach cycle. The lowest activation calculation for the first 10 minutes of the Releach was for a value of 12 kJ/mol. However, during the Fe(III) portion of the Releach, the solution reached above a REDOX potential of 600 mV. The 10 to 60 minute portion of the Releach had the highest activation energy of 18 kJ/mol. There were no REDOX potential or tin concentration driving forces after 10 minutes of the Releach; which most likely caused the activation energy to increase for the balance of the Releach. The tin precipitation kinetics were approximately second order for the first 10 minutes of the Releach and then first order for the balance of the Releach. Overall kinetics for the entire Releach approached closer to second order kinetics. The best kinetic fit for tin precipitation was during the first 10 minutes of the Releach where tin precipitation was second order and the R<sup>2</sup> correlation values were greater than 0.99.

As the temperature (30 to 90 °C) is increased, the rates of tin precipitation, Fe(III) reduction and subsequent arsenate precipitation are correspondingly increased during the Reduction Releach process. Tin precipitation is very closely tied with ferric reduction above 30 to 40 mg/L aqueous tin, and REDOX potentials above (600 to 800 mV). In this oxidizing regime, tin can precipitate as a sulphate, sulphate peroxide, oxide, or a polymer in a purely acidic sulphate media. Tin precipitation follows Fe(III) reduction concentration profile. In terms of thermodynamics, aqueous Fe(III) can oxidize aqueous Sn(II) to Sn(IV) readily. It is not clear what type of tin precipitated or co-precipitated.

From data analysis of aqueous and residue ratios of tin to lead, iron, and sulphate, tin could have readily precipitated as an arsenate or sulphate in the REDOX potential range of 600 to 800 mV. Literature review provides the possibility that tin could have precipitated directly with lead arsenate from cation substitution or as  $\text{Sn}_3(\text{AsO}_4)_3$  at 90 °C, or co-precipitated with the lead sulphate or lead arsenate. Below 550 mV, there is little difference in the rate of tin precipitation.

#### Reductant Amount:

An increased reductant amount (Pb Concentrate, PbCon: PreCon ((g/g); 0.2 to 1) is proven to increase the rate of tin precipitation, and REDOX rate of change of Releach solution, thereby producing an unstable precipitate which tends to re-dissolve, and increases aqueous tin concentration. The precipitation of lead sulphide reductant follows the Fe(III) reduction profile. Excess reductant ( $R_{\text{PbCon/PreCon}} = 1$ ) produces an unstable precipitate which releases and results in higher aqueous tin concentrations. For the maximum reductant addition experiments ( $R_{\text{PbCon/PreCon}} = 1$ ), the rate of tin precipitation is so rapid initially, that the sample taken at one minute into the Releach missed the key change in tin concentration profile. Re-dissolution of the iron precipitate occurred at 10 minutes into the Releach cycle with a REDOX potential (“Eh”) change of 800 to 400 mV. Furthermore, excess reductant does not react completely and a portion departs to residue directly. The excess reductant experiment ( $R_{\text{PbCon/PreCon}} = 1$ ) REDOX change was complete in 10 minutes compared to 60 minutes for the BL case ( $R_{\text{PbCon/PreCon}} = 0.6$ ), and the minimum reductant addition experiment ( $R_{\text{PbCon/PreCon}} = 0.2$ ) never reached Eh equilibrium. The terminal Eh value for the minimum reductant addition case was approximately 700 mV due to insufficient sulphide present for impurity precipitation; the terminal Eh for both the baseline and excess reductant experiments were 380 mV. The terminal tin concentrations at the  $t = 150$  minute mark in the Releach for minimum, BL, and excess reductant cases were 12, 4, and 9 mg/L Sn. Arsenic precipitation was complete for reductant experiments after 45 minutes duration.

There was good correlation between kinetics for tin precipitation rate and arsenic precipitation rate between 350 and 800 mV ( $R^2 = 0.8533$ ), and the arsenic precipitation rate varied between 100 to 5 mg As/min·L and tin varied from 60 to 1 mg Sn/min·L. The precipitation rate of tin increased with increasing reductant. The lead precipitation rate

correlated better with tin precipitation than arsenic precipitation ( $R^2 = 0.8549$  versus  $0.6385$ ) - most likely due to arsenate precipitation with zinc or lead, and not tin. Excess reductant also reduces the rate of PbS dissolution. The tin precipitation kinetics are second order for the minimum and BL reductant experiments, however, a good fit could not be determined for the excess reductant case due to re-dissolution. The kinetic fit  $R^2$  value decreased as the reductant ratio increased, possibly due to arsenate reactions with arsenic, iron, and zinc.

#### As(V) – Fe (III):

As(V) as  $As_2O_5$ ; (BL  $[As]_{(aq)}$  to BL + 10 g/L  $[As]_{(aq)}$ ) affects the final tin solubility in the Reduction process by an increase in total acidity. Increased arsenic concentration increases the total acidity of the solution, thereby increasing the terminal tin concentrations in the presence of aqueous Fe(III). The terminal total acidity increased from 35 to 50 g/L by increasing the arsenic concentration by approximately 8 g/L As (aqueous Fe(III)/As(V) ratio from 4.5 to 0.1). This increase in arsenic concentration relative to Fe(III) increased the terminal tin concentration ( $t = 150$  minutes) from 7 to 50 mg/L Sn. The higher arsenic concentration Releach solution completed initial arsenic precipitation in approximately 20 minutes and then underwent re-dissolution. Comparatively, the BL experiments completed arsenic precipitation in 60 minutes, while the BL + 5 g/L As experiment continued arsenic precipitation during the entire Releach cycle. Tin precipitation kinetics are second order for the BL and BL + 5 g/L As experiments, however, the BL + 10 g/L As experiment was third order.

#### Pure Reagents As(V):

Increasing As(V) concentrations as  $As_2O_5$  without Fe(III) and PbS reductant present in an oxidizing acidic sulphate solution can precipitate aqueous tin readily. Arsenic concentrations above 1 g/L dramatically reduce tin concentrations from 1200 mg/L to less than 100 mg/L. The tin precipitated as a white-grey precipitate, becoming more brown-grey as the initial  $H_2SO_4$  acidity increased from 100 g/L to 220 g/L. The precipitate was not analysed due to lack of time and resources and provides an opportunity for further study.

## 5.2 Proposal of General Overall Tin Precipitation Mechanism

REDOX (Eh): 800 mV to 600 mV

1. Sn (IV) hydrolysis to colloidal  $\text{SnO}_2 \cdot n\text{H}_2\text{O}$
2. Colloidal  $\text{SnO}_2 \cdot n\text{H}_2\text{O}$  to polymerization
3. Co-precipitation or adsorption with lead and iron sulphates or arsenates would coagulate or adsorb acid soluble  $\text{SnSO}_4^{+2}$ .

REDOX (Eh): 600 to 300 mV

4. Sn (IV) hydrolysis to colloidal  $\text{SnO}_2 \cdot n\text{H}_2\text{O}$
5. Colloidal  $\text{SnO}_2 \cdot n\text{H}_2\text{O}$  to polymerization

Note:  $\text{SnSO}_4\text{O}_2$  is thermodynamically feasible in this acidity and REDOX range, but is in question in terms of stability.

## 5.3 Proposal of New Tin Management Strategy for TCML Releach Process

### Shorter Leach Time Reduced Initial Acidity

A shorter leach time of 30 minutes (220 g/L initial  $\text{H}_2\text{SO}_4$ , and 90 °C) is recommended. A longer leach cycle of 45 minutes increases the precipitation of valuable impurities; therefore, there is a greater likelihood of re-dissolution of undesirable impurities.

### Reduced Initial Acidity

Reducing the initial acidity from 220 g/L  $\text{H}_2\text{SO}_4$  by approximately 20 g/L  $\text{H}_2\text{SO}_4$  to 200 g/L  $\text{H}_2\text{SO}_4$  is feasible as higher initial acidity leads to higher terminal tin concentration. The reduced initial acidity will reduce the concentrated acid requirement in the Releach, and this will reduce bulk aqueous  $\text{SO}_4$  loading in the TCML zinc electrolyte circuit.

### Preheat Ge Preconcentrate and Pb Concentrate Reagents

Impurity precipitation is very temperature sensitive, and proceeds rapidly at high temperature. Currently, reagents are at 20 °C and it takes 30 minutes for the reagents to preheat out of a 200 minute Releach cycle.

### Less Sulphide Reductant

Excess lead concentration addition does not entirely effectively with the Ge Preconcentrate leach components. A higher solids density in the leach solution decreases valuable impurities leach efficiency. Currently, 0.6 t Pbcon/t Preconcentrate should be lowered to somewhere between 0.4 and 0.6 t Pbcon/t Preconcentrate to reduce lead concentration operation costs, and reduce downstream residue filtering loading. As well, the total amount of lead concentrate should be reduced when insufficient Ge Preconcentration is not available for the Releach (3 t – 5 t / batch). Excess lead concentrate can increase the tin precipitation rate, and produce an unstable precipitate which undergoes re-dissolution and leads to higher terminal impurity levels.

### Impurities: PO<sub>4</sub><sup>-3</sup>

Where there are downstream process issues from the Releach, a periodic check of the level of P and SiO<sub>2</sub> in the Releach is important. Phosphate incorporation into iron-arsenic precipitates produces an unstable precipitate which can releach. A review of the commercial 2006 Releach Process data found high tin cases (60 to 100 mg/L terminal Sn concentrations) had greater than 1 g/L P concentration. Normally, P is less than 200 mg/L.

### Better Cooling Medium

Currently, approximately 50 % of the Releach 200 minutes cycle time is spent cooling the Releach solution prior to filtration. Better maintenance of existing coils, or indirect cooling medium, or increasing the size of cooling/heating coils can all lead to more effective cooling of the Releach solution, and shorten cycle time.

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**APPENDICES:**

## APPENDIX A PURE REAGENTS: ASSAYS

Table A. 1

Compound		Inventory	Weight	Manufacturer
Lead Sulphide	PbS	1 btl	1 kg	Anachemia
Chalcopyrite	CuFeS <sub>2</sub>	2 btl	50 gm	Alfa Aesar
Copper Sulfide	CuS	1 btl	50 gm	Alfa Aesar
Potassium Iodide (99.0%)	KI	2 btl	650 gm	Anachemia
Zinc Sulphate Heptahydrate	ZnSO <sub>4</sub> ·7H <sub>2</sub> O	9 btl	4.5 kg	Anachemia
Zinc Sulphite dihydrate (98%)	O <sub>3</sub> SZn·2H <sub>2</sub> O	2 btl	5 kg	Alfa Aesar
Ferric Sulfate (72% min)	Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	8 btl	4 kg	Anachemia
Iron Sulfate hepta hydrate	FeSO <sub>4</sub> · 7H <sub>2</sub> O	12 btl	1'2 kg	Anachemia
Sodium Carbonate (99.5%)	Na <sub>2</sub> CO <sub>3</sub>	1 btl	400 gm	Anachemia
Lead Shot	Pb	1 btl	1 kg	
Stannic Oxide (99.9%)	SnO <sub>2</sub>	1 btl	2.0 kg	Spectraum
Stannous Sulfate	SnSO <sub>4</sub>	1 btl	1.5 kg	Spectraum
Stannic Sulfate (99%)	Sn(SO <sub>4</sub> ) <sub>2</sub>	1 btl	1.5 kg	Pfaltz & Bauer
Stannous Chloride (96% min)	SnCl <sub>2</sub>	1 btl	2.5 kg	Spectraum
Stannous Fluoride	SnF <sub>2</sub>	1 btl	500 gm	Alfa Aesar
Stannous Oxide	SnO	1 btl	1.5 kg	Spectraum
Sodium Fluoride	NaF	4 btl	1 kg	Alfa Aesar
Sodium Metasilicate	NaSiO <sub>3</sub>	1 btl	1 kg	Alfa Aesar
Arsenic Pentoxide	As <sub>2</sub> O <sub>5</sub>	10 btl	1 kg	Alfa Aesar
Arsenic Trioxide	As <sub>2</sub> O <sub>3</sub>	5 btl	550 gm	Anachemia

APPENDIX B TCML PROCESS REAGENTS: ASSAYS

Table B. 1

	Pb	Al <sub>2</sub> O <sub>3</sub>	As	Bi	CaO	Cd	Cu	Fe	MgO	Mn	S	Sb	SiO <sub>2</sub>	Sn	Zn
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
PbCon TCML	48.8	0.1	0.0	<0.01	0.6	0.0	0.0	16.5	0.3	<0.01	27.4	0.1	0.2	0.01	4
Ge Preconcentrates TCML	14.6	n/a	1.2	n/a	n/a	n/a	0.1	10.0	0.3	0.4	9.3	n/a	1.6	1.1	14.4

Table C. 1

Subject	Description	Manufacturer	Model No. or Part No.	Description
Electronics				
1a	Balance	Pacific Ind Scale	GX6000	6100 grams X 0.1 grams w/internal calibration
1b	Balance	Pacific Ind Scale	EP6101C	6100 grams X 0.1 grams w/internal calibration
2	BNC to Spade Lug Adaptor	Honeywell	C-05994-90	Allows for connection of pH, ORP & Conductivity probes to respective meters
3	Conductivity Transmitter & Display	EUTECH	C-19505-20	Conductivity Transmitter with display & 4-20 mA OP
4	pH/ORP Transmitter with Display	EUTECH	56717-20	ORP Transmitter with display & 4-20 mA OP
5	pH/ORP Transmitter with Display	EUTECH	56717-20	pH Transmitter with display & 4-20 mA OP
6	Recorder	Honeywell	C-80661-36	Four channel electronic recorder, ACC: 0.1% typical-T/C, Alarm relay contact: SPDT, 1 A, 24 VDC, Inputs: EMF, T/C, RTD, mV & mA. Data storage: 3.5", 1.44 MB floppy disk, Internal buffer: 4MB. Display: 5½" diagonal, Res: 320 x 240 pixels, Power 90-240 vac
7	Recorder Software	Honeywell	C-80660-70	Allows viewing, graphing, printing, storing data and export data files in CVS format to PC
8	Temperature Controller	Coleparmer	C-93285-34	RS-435 terminal & 4-20 mA OP signal, on/off control, +/- 2°F, op T = 0-65C control rating - SPST, 3A at 240 vac, Loop power 24 VDC

Subject	Description	Manufacturer	Model No. or Part No.	Description
9	Temperature Controller	Coleparmer	C-012155-54	RTD - 100 ohms, PID control, control rating - 115 vac, 10 amps
Probes				
10	Conductivity Cells	Coleparmer	C-19500-08	Two electrode cell, $K=10.0\text{cm}^{-1}$ , (up to 5 mS/cm) Cell type - D
11	ORP Double Junction Electrodes	Coleparmer	C-27006-21	Double Junction electrode - Platinum sensor band, 150psi @ 25C
12	pH Double Junction Electrodes	Coleparmer	C-05994-27	Double Junction electrode - Ag/AgCl, 100 ohm ATC
13	Temperature Probes	Coleparmer	C-08500-55	RTD - 100 ohms, PID control, control rating - 115 vac, 10 amps
14	Temperature Probes	Coleparmer	C-08117-70	Type T Temperature probe
15	Temperature Thermometer	Nurnberg	772-3121	Glass'-10 - 110 C
16	Temperature Thermometer	Nurnberg	772-3123	Glass'-20 - 150 C
Mixers (Agitators)				
17	Mixer Programmable	Caframo	C-50800-00	Programmable mixer, Low speed - 20-360 rpm, High speed - 20-1800 rpm
18	Mixer Programmable	Caframo	C-50800-00	Programmable mixer, Low speed - 20-360 rpm, High speed - 20-1800 rpm
19	Mixer Safety Stand	Caframo	C-50001-93	304 Stainless steel rod
20	Heavy Duty Clamp-mixer	Caframo	C-04561-24	304 Stainless steel rod, Zinc-aluminium base with chemical resistant epoxy
21	Mixer Shafts	Caframo	C-04553-57	$\frac{3}{8}$ "D X 18"L stainless steel rod
22	Impellers	Caframo	C-04560-23	A-310 high efficiency axial flow impeller (A-310)
Pumps				

Subject	Description	Manufacturer	Model No. or Part No.	Description
23	Pump Head and Controller	Masterflex	C-07553-80	Variable speed modular drive digital dispensing drive controller - regulates motor speed, on/off switch
24	Pump Head	Masterflex	C-0777200-60	rotation on tubing allows solution to be pumped
25	Power Supply - 24VDC	Labcor	26900-10	24 VDC, 365 mA, 3 <sup>7</sup> / <sub>8</sub> "W x 2 <sup>5</sup> / <sub>8</sub> "H x 5 <sup>7</sup> / <sub>8</sub> "D
26	Power Cord	Labcor	SA-50001-00	Power Cord 110 VAC - 6 feet
Filters				
27	Pressure Filter	KC Welding	n/a	316 Stainless steel
Valves				
28	On/Off Ball Valve	Mass or Kitz	116-5077	316 stainless steel construction
29	Bushings	n/a	104-2454	316 stainless steel (1/2"-1/4")
30	Male Connector	Swaglok	123-4514	316 stainless steel 1/4 NPT - 1/4 Tube
Hose				
31	Multi-Purpose Hose	Swaglok	PB-4-200	Neoprene Rubber (Blue)
Reference Standards				
32	Conductivity – 84	Coleparmer	C-00653-16	Conductivity - 84, ppm KCl - 40.38, ppm NaCl - 38.04, ppm 442 - 50.5
33	Conductivity – 447	Coleparmer	C-00653-47	Conductivity - 447, ppm KCl - 226, ppm NaCl - 215, ppm 442 – 300
34	Conductivity – 1500	Coleparmer	C-00653-15	Conductivity - 1500, ppm KCl - 757, ppm NaCl - 737, ppm 442 – 1050
35	pH - 2.00	Anachemia Science	170-0688	Buffers for meters with 0.01 resolution & with in 0.01 pH at 77°F (25°C)



Subject	Description	Manufacturer	Model No. or Part No.	Description
36	pH - 4.01	Anachemia Science	170-0689	Buffers for meters with 0.01 resolution & with in 0.01 pH at 77°F (25°C)

APPENDIX D      RELEACH and DISSOLUTION TEST PROCEDURES

**Table D. 1: Releach, Dissolution Test Procedures**

	Reduction Releach Procedure:
1	Fill reactor with 3.5 litres of 100 g/L H <sub>2</sub> SO <sub>4</sub> (previously made up with 50/50 reagent grade H <sub>2</sub> SO <sub>4</sub> ).
2	Take an O <sub>2</sub> reading of the appropriate strength H <sub>2</sub> SO <sub>4</sub> solution (40 to 220 g/L H <sub>2</sub> SO <sub>4</sub> ).
3	Standardize ORP probe with standard solution (241mv solution) at start of test.
4	Heat H <sub>2</sub> SO <sub>4</sub> solution to 90 °C, and set speed on mixer to 400 RPM.
5	Take appropriate samples at 90 °C, cool to 25 °C and take an O <sub>2</sub> reading.
6	Slurry Ge Preconcentrate (50/50) from the two sample buckets for a total mass of 1153 grams (wet), with 230 mls of heated demineralized water (at reaction temperature).
7	Add slurried Ge PreConcentrate first, followed by Pb concentrate.
8	Start data logger to record test and record start time.
9	Sample times are 0 minutes (min), 3 minutes, 10 minutes, 30 minutes, 60 minutes, 100 minutes, and 150 minutes.
10	Add Fe powder just prior to 100 minute sample.
11	Filter each sample through a whatman filter (#1), and then again through a Millipore filter. Save solids for assay and S.G measurement.
12	Perform a Fe(II) titration, total Fe titration, and then a total acidity titration on each sample.
13	Determine total Fe by calculation: Fe <sub>total</sub> – Fe(II).
14	Get a final sample, filter, cool and take an O <sub>2</sub> reading.
15	Send all samples to assay office for solids and aqueous analysis.
16	Clean Reactor and sample tubing with demineralised water.

**Table D. 2: Test Procedure for Dissolution**

	Test Procedure for Dissolution / Chemical Reaction Tests
1	Fill reactor with 4.4 litres of 100 g/L H <sub>2</sub> SO <sub>4</sub> (previously made up).
2	Heat to 90 °C, RPM on mixer @ 400 RPM.
3	Standardize ORP probe with standard solution (241mv solution).
4	At required temperature (90 °C) add test reagent grade compounds.
5	Sample @ 10 minute intervals for 2 hours (filter and cool as necessary).
6	Record start time (actual and on data recorder).
7	Record ORP reading at each sample time taken.
8	At test completion empty reactor, rinse with 4 litres tap water, 4 litres DI water, flush with 500 mLs 100 g/L H <sub>2</sub> SO <sub>4</sub> (mixer running)
9	Repeat all tests for duplication.
10	When changing test elements, rinse with 8 litres tap water (2 rinses), then 1 rinse with demineralized water.
11	(4 L) DI water, final 500 mL 100 g/L H <sub>2</sub> SO <sub>4</sub> rinse.
12	Prepare samples for assay office.

**Table E. 1: Free Acid Titration**

	Free Acid Method: (H <sub>2</sub> SO <sub>4</sub> )
1	Buffer and preset a pH meter to a resulting reading of pH 4.0.
2	Pipette a 5 ml aliquot into a 100 or 150 ml beaker.
3	Bulk to 60 or 80 ml with DI water, insert stirring rod and place on a stirring plate.
4	Add KI reagent and stir, and allow to dissolve completely.
5	The iodine color is then removed by adding drop wise a solution of saturated Sodium Thiosulphate. When clear, add one drop in excess.
6	The pH electrode is inserted in the solution and the titration is started by adding 0.51N Sodium Carbonate (Na <sub>2</sub> CO <sub>3</sub> ) until a reading of nearly pH 4.0 on the scale is reached.
7	Note the reading moves rapidly once a reading of pH 3.0 is reached.
8	The titration is complete when a reading of pH 4.0 is reached.
9	$\text{g/L H}_2\text{SO}_4 = \frac{\text{Tit'n} \times (0.025 \times 1000)}{5} = \text{g/L free acid as H}_2\text{SO}_4$

**Table E. 2: Titration for Ferrous Fe**

	Titration for Ferrous Fe(II):
1	Pipette 25 or 50 mls of clear filtrate sample into a clean 250 ml beaker.
2	Dispense 10 mls of 1:1 H <sub>2</sub> SO <sub>4</sub> acid from bottle dispenser into beaker.
3	Bulk to 150 mls with deionized water.
4	Titrate sample with standardized 0.089 N Potassium permanganate (KMnO <sub>4</sub> ) to a permanent faint pink endpoint.
5	Record volume of KMnO <sub>4</sub> used to reach endpoint and compare to chart to convert to g/L Fe(II).

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**Table E. 3: Titration for Total Fe<sub>T</sub>**

	Titration for Total Fe <sub>T</sub> .
1	Pipette 5 mls of sample into 200 ml beaker.
2	Dispense 20 mls of HCl 1:1 acid into beaker and swirl solution.
3	Add stannous chloride by drop until solution clears/
4	Dispense 15 mls of mercuric chloride into beaker/
5	Dispense 15 mls of sulphuric / phosphoric acid solution into beaker.
6	Bulk to 150 mls with water, and add stir bar.
7	Add a few drops Fe indicator.
8	Titrate with potassium dichromate until permanently PURPLE.
9	Read T/Fe off titrator.

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**Table E. 4: Sn(II/IV) Titration Validation Testwork**

	Sn(II/IV) Titration Validation Testwork:
	The purpose of this test work was to develop and validate a reliable Sn(II/IV), and total tin aqueous titration procedure. The procedure would give real time aqueous tin concentrations during the Reduction Releach Process. An iodimetric analysis was used.
	<b><u>Part A.</u></b> Validation of Sn(II) concentration in a pure water and 100 g/L H <sub>2</sub> SO <sub>4</sub> solution.
1	Blank One (deionized H <sub>2</sub> O).
2	Blank Two (100g/L H <sub>2</sub> SO <sub>4</sub> ).
3	Test Solution One (deionized H <sub>2</sub> O + SnCl <sub>2</sub> ·2H <sub>2</sub> O).
4	Test Solution Two (100g/L H <sub>2</sub> SO <sub>4</sub> + SnCl <sub>2</sub> ·2H <sub>2</sub> O).
	<b><u>Part B.</u></b> To determine the effect of different concentrations of SnCl <sub>2</sub> ·2H <sub>2</sub> O in 100g/L H <sub>2</sub> SO <sub>4</sub> solutions.
	<b><u>Part C.</u></b> To determine if impurities such as iron affected the aged tin solutions endpoints.
	<b><u>Part D.</u></b> An alternate procedure (Ronastan EC-1) testing method was evaluated to determine total tin concentrations in solutions. This would give a real time tin reading, as opposed to using ICP analysis.

**Table E. 5: Sn(II/IV) Validation Test Procedure**

	Sn (II/IV) Validation Test Procedure:
1	Prepare a stock solution of 6.75L of 175mL deionized H <sub>2</sub> O: 50 mL HCL.
2	Prepare a stock solution of 4L of 100g/L H <sub>2</sub> SO <sub>4</sub> .
3	Prepare four 1 L solutions, set in a cooling bath to keep temperature below 17 °C
4	Blank 1 - 1 L of deionized H <sub>2</sub> O
5	Blank 2 - 1L of 100 g/L of H <sub>2</sub> SO <sub>4</sub>
6	Test Solution 1 - 1L of deionized H <sub>2</sub> O + 0.19g of SnCl <sub>2</sub> ·2H <sub>2</sub> O
7	Test Solution 2 - 1L of 100 g/L H <sub>2</sub> SO <sub>4</sub> + 0.19g of SnCl <sub>2</sub> ·2H <sub>2</sub> O
8	Set up table with magnetic stirrer set at 6(good mixing without creating a vortex).
9	Set up the Redox, temperature and O <sub>2</sub> probes with clamps.
10	<p><u>Procedure:</u></p> <p><u>Preparation of HCl stock solution (6.75L)</u></p> <ul style="list-style-type: none"> <li>• Mix water and HCl in a ratio of 175 ml H<sub>2</sub>O: 50 ml HCl ratio to make up 6.75 L of stock solution. Let the solution cool to below 17 °C before the Sn titrations. ie 525 ml H<sub>2</sub>O + 150 ml HCl = 675 ml Stock solution.</li> <li>• Prepare 4L of 100 g/L H<sub>2</sub>SO<sub>4</sub>. <ul style="list-style-type: none"> <li>○ 1L of Deionized H<sub>2</sub>O. – Blank 1</li> <li>○ 1L of 100 g H<sub>2</sub>SO<sub>4</sub>/L. - Blank 2</li> </ul> </li> <li>• <u>Carefully measure 0.19 g of SnCl<sub>2</sub>*2H<sub>2</sub>O into :</u> <ul style="list-style-type: none"> <li>○ 1L of Deionized H<sub>2</sub>O. – Blank 1 + SnCl<sub>2</sub>*2H<sub>2</sub>O – Test Solution 1</li> <li>○ 1L of 100 g H<sub>2</sub>SO<sub>4</sub>/L. – Blank 2 + SnCl<sub>2</sub>*2H<sub>2</sub>O – Test Solution 2</li> </ul> </li> </ul> <p>Note: There should be 4 1L solutions (Blank 1, 2, Test Solution 1, Test Solution 2)</p> <ul style="list-style-type: none"> <li>• Measure temperature of the 1L solutions above, the temperature must be below 17 °C for the optimum titration endpoint, if temperature &gt; 17 °C, place in water bath and cool. Check ORP in buffer solution prior to initial ORP measurement to calibrate ORP probe.</li> </ul>



	<ul style="list-style-type: none"> <li>• For each sample, measure and record temperature, ORP, and dissolved O<sub>2</sub>, before Starch/Iodine titration.</li> <li>• <u>Acetic Starch and Iodine titration</u></li> <li>• Have temperature, ORP, and dissolved O<sub>2</sub> probes ready for measurement and record the values at each 0.1 mL increments for the first test.</li> <li>• In 500 mL beaker, place 250 mL of the HCl/DI water mixture. Add 25 mL of solution to be tested (Blank1)</li> <li>• Place beaker with solution on magnetic stir table and set at 6.</li> <li>• Add a few drops of acetic starch and mix well.</li> <li>• Titrate until a persistent dark blue color is obtained in the analyte solution. <ul style="list-style-type: none"> <li>○ Record Temperature, ORP (at endpoint), and dissolved O<sub>2</sub></li> </ul> </li> </ul>
11	Strength of titrant used is 0.001 g/L Sn equivalent.
12	Always used 4 drops of acetic starch.
13	Cool the 250 mL of HCl stock for each titration in a cooling bath to get temperature below 17°C.
14	<p>Calculations: Calculated endpoint.</p> $C_a = V_t * C_t \div V_a$ <p>where:  C<sub>a</sub> = Sn<sup>2+</sup> concentration in analyte (g/L), V<sub>t</sub> = volume of titrant (L), C<sub>t</sub> = concentration of titrant (g/L) and V<sub>a</sub> = volume of analyte (L).</p> <p>The primary standard for the titrant solution is potassium iodate. Excess iodide is added to produce iodine, at a concentration stoichiometric to the concentration of the primary standard. The titrant solution is stabilized by sodium hydroxide. In the titration, stannous is oxidized to stannic by iodine (Sn<sup>+2</sup> + I<sub>2</sub> → Sn<sup>+4</sup> + 2I). A sample containing 0.060 g/L Sn<sup>+2</sup> will require 1.5 mL of titrant.</p>

**Table E. 6: Blank One**

Blank one (deionized H <sub>2</sub> O)				
Burette	mL	Redox	Temp	O <sub>2</sub>
reading	Titrant	mV	°C	mg/L
13.6	0	495	16.8	5.4
	0.1	445	17.8	5.4
	0.2	438	17.8	5.4
	0.3	431	18	5.3
	0.4	428	18	5.4
14	0.5	426	18.1	5.3
	0.6	424	18.2	5.3
	0.7	423	18.2	5.4
	0.8	421	18.2	5.3
	0.9	420	18.3	5.3
	1	419	18.3	5.3
	1.1	418	18.3	5.3
	1.2	417	18.4	5.3
	1.3	416	18.5	5.3
	1.4	416	18.5	5.3
14.9	1.5	415	18.5	5.3
15.4	2	411	18.6	5.3

**Table E. 7: Blank Two**

Blank Two - (100g/L H <sub>2</sub> SO <sub>4</sub> )				
Burette	mL	Redox	temp	O <sub>2</sub>
reading	titrant	mV	°C	mg/L
6.1	0	433	16.2	6.3
	0.1	434	16.3	6.3
	0.2	429	16.3	6.3
6.5	0.3	424	16.4	6.3
	0.4	421	16.4	6.3
	0.5	416	16.5	6.3
	0.6	415	16.5	6.3
	0.7	413	16.5	6.3
	0.8	412	16.5	6.3
7	0.9	410	16.6	6.3
	1	408	16.6	6.3
	1.1	408	16.6	6.3
	1.2	407	16.6	6.3
	1.3	406	16.7	6.3
	1.4	405	16.7	6.3
7.6	1.5	404	16.6	6.3
8.1	2	401	16.9	6.2

**Table E. 8: Test Solution One**

Test Solution One - (deionized H <sub>2</sub> O + 0.19g SnCl <sub>2</sub> ·2H <sub>2</sub> O)				
Burette	mL	ORP	temp	O <sub>2</sub>
reading	Titrant	mV	°C	mg/L
15.4	0	118	17	4.9
	0.1	433	17.3	4.6
	0.2	430	18	4.5
	0.3	427	18	4.5
	0.4	427	18.1	4.4
15.9	0.5	425	18.1	4.4
	0.6	423	18.2	4.4
	0.7	423	18.3	4.4
	0.8	421	18.3	4.4
	0.9	421	18.4	4.4
16.4	1	420	18.5	4.4
	1.1			
	1.2			
	1.3			
	1.4			
	1.5			
16.9	2	415	18.6	4.4

**Table E. 9: Test Solution Two**

Test Solution Two - (100g/L H <sub>2</sub> SO <sub>4</sub> + 0.19g SnCl <sub>2</sub> ·2H <sub>2</sub> O)				
Burette	mL	Redox	temp	O <sub>2</sub>
reading	titrant	mV	°C	mg/L
11.7	0	478	16.2	5.4
	0.1	426	16.4	5.4
	0.2	420	16.5	5.4
	0.3	418	16.6	5.4
	0.4	416	16.7	5.4
12.1	0.5	414	16.8	5.4
	0.6	413	16.9	5.4
	0.7	412	16.9	5.4
	0.8	411	16.9	5.4
	0.9	410	17	5.4
	1	409	17.1	5.4
	1.1	408	17.1	5.4
	1.2	408	17.2	5.4
	1.3	407	17.2	5.4
	1.4	407	17.3	5.3
13.1	1.5	406	17.3	5.3
13.6	2	403	17.4	5.3

**Table E. 10: 200 ppm Sn(II) Time**

200 ppm Sn <sup>2+</sup>			
250 mL Blank 2 + 0.094gSnCl <sub>2</sub> ·2H <sub>2</sub> O			
Time	Redox	Temp	O <sub>2</sub>
secs	mV	°C	mg/L
0	322	17.3	4.3
30	309	17.3	4.3
60	279	17.3	4.3
90	256	17.3	4.3
120	236	17.3	4.3
150	213	17.4	4.3
180	199	17.4	4.3
210	198	17.4	4.9
240	197	17.4	4.8
270	197	17.4	4.7
300	196	17.5	4.5
330	194	17.5	4.2
360	194	17.5	3.9
390	192	17.5	3.6
420	191	17.5	3.2
450	188	17.5	2.7
480	186	17.6	2.1
510	182	17.6	1.6
540	178	17.6	1.2
570	175	17.6	0.8
600	172	17.6	0.6

**Table E. 11: 200 ppm Sn(II)**

200 ppm Sn(II)				
250mL stock HCl solution + 25mL of 200 ppm Sn <sup>2+</sup> + 4 drops of starch				
Burette	Drops	Redox	Temp	O <sub>2</sub>
reading	Added	mV	°C	mg/L
30.00mL	0	76	16.6	4.7
	2	63	16.7	4.3
	2	63	16.7	4.1
	2	69 □	16.7	3.9
		300		
30.3	2	350		3.2

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**Table E. 12: 300 ppm Sn(II) Time**

300 ppm Sn(II)			
(250mL Blank 2 + 0.143gSnCl <sub>2</sub> ·2H <sub>2</sub> O)			
Time	Redox	Temp	O <sub>2</sub>
secs	mV	°C	mg/L
0	300	16.7	5.2
30	210	16.7	5.2
60	188	16.8	5.1
90	186	16.8	5.1
120	185	16.8	5
150	185	16.9	5
180	186	16.9	4.9
210	186	16.9	4.8
240	186	16.9	4.7
270	185	16.9	4.6
300	185	17	4.4
330	185	17	4.3
360	184	17	4.1
390	184	17	3.9
420	183	17.1	3.6
450	182	17.1	3.4
480	181	17.1	3.1
510	180	17.1	2.9
540	179	17.1	2.7
570	177	17.2	2.4
600	175	17.2	2.1



**Table E. 13: 300 ppm Sn(II)**

300 ppm Sn(II)				
250mL stock HCl solution + 25mL of 300 ppm Sn(II) + 4 drops of starch				
Burette	Drops	Redox	Temp	O <sub>2</sub>
reading	Added	mV	°C	mg/L
31.4	0	67	16.9	4.3
	2	54	16.9	4
	2	52	17	3.8
	2	53□	17	3.4
		300		
31.8	2	350		

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**Table E. 14: 400 ppm Sn(II) Time**

400 ppm Sn(II)			
(250mL Blank 2 + 0.193gSnCl <sub>2</sub> ·2H <sub>2</sub> O)			
Time	Redox	Temp	O <sub>2</sub>
secs	mV	°C	mg/L
0	311	15.9	5.3
30	211	15.9	5.3
60	200	16	5.2
90	194	16	5.2
120	191	16	5
150	189	16.1	4.7
180	188	16.1	4.4
210	185	16.1	3.9
240	181	16.2	3.2
270	176	16.2	2.4
300	169	16.2	1.7
330	161	16.3	1.1
360	156	16.3	0.8
390	150	16.3	0.5
420	146	16.3	0.4
450	143	16.4	0.3
480	141	16.4	0.2
510	140	16.4	0.2
540	140	16.5	0.2
570	140	16.5	0.2
600	140	16.5	0.2

**Table E. 15: 400 ppm Sn(II)**

400 ppm Sn(II)				
250mL stock HCl solution + 25mL of 400 ppm Sn(II) + 4 drops of starch				
Burette	Drops	Redox	Temp	O <sub>2</sub>
reading	Added	mV	°C	mg/L
32.2	0	61	15.3	5
	2	47	15.3	4.7
	2	42	15.3	4.6
	2	40	15.4	4.4
	2	39	15.4	4.1
	2	39	15.4	3.8
	2	39	15.5	3.4
	2	41	15.5	3.1
	2	47	15.6	2.5
		300		
33	1	350		

**Table E. 16: 500 ppm Sn(II) Time**

500 ppm Sn(II)			
(250mL Blank 2 + 0.248gSnCl <sub>2</sub> ·2H <sub>2</sub> O)			
Time	Redox	Temp	O <sub>2</sub>
secs	mV	°C	mg/L
0	248	15.6	5.5
30	202	15.6	5.5
60	192	15.6	5.4
90	187	15.6	5.3
120	184	15.7	5.2
150	182	15.7	5.1
180	180	15.7	5
210	179	15.8	4.8
240	177	15.8	4.6
270	176	15,8	4.4
300	175	15.9	4.2
330	174	15.9	3.9
360	173	16	3.7
390	171	16	3.4
420	170	16	3.1
450	169	16.1	2.9
480	167	16.1	2.6
510	166	16.1	2.4
540	164	16.2	2.2
570	162	16.2	2
600	161	16.2	1.8

**Table E. 17: 500 ppm Sn(II)**

500 ppm Sn(II)				
250mL stock HCl solution + 25mL of 500 ppm Sn(II) + 4 drops of starch				
Burette	Drops	Redox	Temp	O <sub>2</sub>
reading	Added	mV	°C	mg/L
11.5	0	54	15.8	4.5
	20	27	16	3.9
	20	25	16.1	3.3
	10	27	16.1	2.9
	2	29	16.2	2.6
	2	32	16.2	2.4
	2	35	16.2	2.2
	2	40	16.3	1.9
	1	46	16.3	1.7
14.3	1	57	16.4	1.3
		300		

**Table E. 18: 700 ppm Sn(II) Time**

700 ppm Sn(II)			
(250mL Blank 2 + 0.332gSnCl <sub>2</sub> ·2H <sub>2</sub> O)			
Time	Redox	Temp	O <sub>2</sub>
secs	mV	°C	mg/L
0	330	15,5	5.4
30	290	15,5	5.4
60	185	15,5	5.3
90	171	15,5	5.2
120	167	15,5	5.1
150	166	15.6	5
180	165	15.6	4.8
210	164	15.6	4.7
240	164	15.7	4.5
270	163	15.7	4.3
300	162	15.7	4.1
330	162	15.7	3.8
360	160	15.8	3.6
390	159	15.8	3.3
420	158	15.8	3
450	157	15.9	2.8
480	155	15.9	2.6
510	154	15.9	2.3
540	152	15.9	2.1
570	150	16	1.9
600	149	16	1.7

**Table E. 19: 700 ppm Sn(II)**

700 ppm Sn(II)				
250mL stock HCl solution + 25mL of 700 ppm Sn(II) + 4 drops of starch				
Burette	Drops	Redox	Temp	O <sub>2</sub>
reading	Added	mV	°C	mg/L
4.7	0	42	14.7	3.7
	20	13	14.8	3.3
	20	10	14.8	3
	14	10	14.9	2.4
	2	12	15	1.8
	2	17	15.1	1.1
	2	18	15.1	1
	2	21	15.2	0.9
	2	24	15.2	0.8
	2	29	15.3	0.7
	2	42	15.3	0.5
8.1	2	61	15.4	0.5
		300		

**Table E. 20: Sn(II/IV), Fe(II) Validation Tests: Part A**

	Sn <sup>2+/4+</sup> Validation Tests Procedure:
1	Cool two 250 ml solutions of Blank 2 (100 g/L H <sub>2</sub> SO <sub>4</sub> ) and two solutions of 250 ml of stock HCl to below 17 °C
2	From one 250 ml of cooled Blank 2, add 0.620g FeSO <sub>4</sub> ·7H <sub>2</sub> O. Set this solution on a magnetic table set at 6 and record ORP, temperature, and O <sub>2</sub> every 30 secs. for 10 min.
3	Take 25 ml of above solution and add to 250 ml of cooled stock HCl. Set this on magnetic stir table set at 6 and add 4 drops of acetic starch.
4	Start titration (using standard titration method we have been using) looking for end point, record burette readings, drops added, Redox, temperature, and O <sub>2</sub> . Repeat steps 2, 3 and 4 using the second cooled 250mL of Blank 2 (100g/L H <sub>2</sub> SO <sub>4</sub> ) and second cooled 250mL of stock HCl but add 0.621g FeSO <sub>4</sub> ·7H <sub>2</sub> O, and 0.235g of SnCl <sub>2</sub> ·2H <sub>2</sub> O to the 250mL of Blank 2 (100g/L H <sub>2</sub> SO <sub>4</sub> ) .



**Table E. 21: 500 ppm Fe(II) Time**

500 ppm Fe(II)			
(250mL Blank 2 + 0.620g FeSO <sub>4</sub> ·7H <sub>2</sub> O)			
Time	Redox	Temp	O <sub>2</sub>
secs	mV	°C	mg/L
0	413	15.8	5.4
30	382	15.7	5.4
60	371	15.7	5.4
90	364	15.7	5.4
120	360	15.7	5.4
150	357	15.8	5.4
180	354	15.8	5.4
210	353	15.8	5.4
240	351	15.8	5.4
270	350	15.8	5.4
300	348	15.8	5.4
330	347	15.8	5.4
360	347	15.9	5.4
390	346	15.9	5.4
420	345	15.9	5.4
450	344	15.9	5.4
480	344	15.9	5.4
510	343	15.9	5.4
540	342	15.9	5.4
570	342	16	5.4
600	342	16	5.4

**Table E. 22: 500 ppm Fe(II)**

500 ppm Fe (II)				
250mL stock HCl solution + 25mL of 500 ppm Fe <sup>2+</sup> + 4 drops of starch				
Burette	Drops	Redox	Temp	O <sub>2</sub>
reading	added	mV	°C	mg/L
30	0	315↓	16.3	5
	2	354	16.3	5.1
	2	372	16.4	5.1
	2	376	16.4	5.1
	2	380	16.4	5.1
30.4	3	381	16.4	5.1
30.7	5	381	16.4	5.1
	3	380	16.4	5.1
31.1	5	378	16.5	5.1
31.7	10	375	16.5	5.1
32.6	20	371	16.5	5.1
37.5		358	16.6	5.1
50		343	16.8	5.1

**Table E. 23: 500 ppm Sn + 500 ppm Fe Time**

500 ppm Sn + 500 ppm Fe			
(250mL Blank 2 + 0.235g SnCl <sub>2</sub> ·2H <sub>2</sub> O + 0.621 g FeSO <sub>4</sub> ·7H <sub>2</sub> O)			
time(secs.)	Redox(mV)	temp.(°C)	O <sub>2</sub> (mg/L)
0	339	14.4	5
30	331	14.4	5
60	303	14.4	5
90	287	14.5	5
120	271	14.5	5
150	254	14.5	5
180	243	14.6	4.9
210	234	14.6	4.9
240	226	14.6	4.9
270	220	14.6	4.9
300	215	14.6	4.9
330	211	14.7	4.9
360	209	14.7	4.9
390	207	14.7	4.9
420	208	14.7	4.9
450	207	14.8	4.8
480	208	14.8	4.8
510	208	14.8	4.8
540	208	14.8	4.8
570	208	14.8	4.8
600	209	14.9	4.8

**Table E. 24: 500 ppm Sn + 500 ppm Fe**

500 ppm Sn + 500 ppm Fe				
250mL stock HCl solution + 25mL of 0.235 g SnCl <sub>2</sub> ·2H <sub>2</sub> O + 0.621g FeSO <sub>4</sub> ·7H <sub>2</sub> O + 4 drops of starch				
Burette	Drops	Redox	Temp	O <sub>2</sub>
reading	Added	mV	°C	mg/L
20	0	338□	14.3	1
	2	385	14.3	0.9
20.15	2	408	14.4	0.9
20.6	10	406	14.4	0.9
	10	400	14.5	1
21.5	10	397	14.5	1
22	2	394	14.6	1
23	20	389	14.6	1
24	22	384	14.7	1.1
25		381	14.8	1.1
26.2		379	14.8	1.2
27		377	14.9	1.2
28		374	14.9	1.3
29		373	15	1.3
30		372	15.1	1.3
31		370	15.3	1.3
40		361	15.3	1.5
50		355	15.5	1.7

**Table E. 25: Block Four: -Sn(II/IV) Fe(II) Validation Tests: Part B**

<b>Block Four: - Sn<sup>+2/+4</sup>, Fe<sup>+2</sup> Validation Tests: Part B Procedure</b>	
1	Cool samples of 100 ppm, 200 ppm, 300 ppm and 400 ppm Sn to below 17°C.
2	Cool samples of 100 ppm, 200 ppm, 300 ppm and 400 ppm Sn to below 17°C.
3	Cool samples of 100 ppm, 200 ppm, 300 ppm and 400 ppm Sn to below 17°C.
4	Cool HCl solution (175mL DI Water : 50mL HCl(conc.)) to below 17° C.
5	Take a 500mL conical flask and add 250mL of the cooled HCl solution then add 25mL of the cooled 100ppm Sn sample and 1g of aluminum and cover the flask with a watch glass.
6	Repeat above step for the 200 ppm, 300 ppm and the 400 ppm Sn samples so that you have 4 conical flasks each with different ppm Sn solution.
7	Take the 4 flasks and place on a heating table and boil solutions to dissolve aluminium, once dissolved boil for 2 more minutes.
8	Take flasks off heating table and cool quickly to room temperature.
9	On each flask (when cooled) do the standard titration we have been doing using 4 drops of acetic starch and a titre of 0.001M of iodine solution (each flask placed on the magnetic stir table set at 6).
10	While doing the titration measure Redox, temp. and O <sub>2</sub> .
11	Sent a 60 mL sample from each of the 100 ppm, 200 ppm, 300 ppm and 400 ppm Sn samples to be assayed along with a 60mL sample of deionized H <sub>2</sub> O.

**Table E. 26: 100 ppm Sn**

100 ppm Sn				
250mL stock HCl solution + 25mL of 100 ppm Sn + 1g aluminium + 4 drops of starch solution (after heating) appears to have residual solids and is cloudy an light grey in colour				
Burette	Drops	Redox	Temp	O <sub>2</sub>
reading	Added	mV	°C	mg/L
0	0	-167	15.6	0.2
	2	-167	15.7	0.2
	4	-154	15.7	0.1
	2	-148	15.8	0.1
	2	-130	15.8	0.1
	2	-128	15.8	0.1
	2	-123	15.8	0.1
	2	-114	15.9	0.1
	2	-109	15.9	0.1
	4	-89	16	0.1
	2	-77	16	0.1
	2	-70	16	0.1
	2	-59	16.1	0.2
	2	-38	16.1	0.2
	2	-17	16.1	0.2
1.7	3	20□	16.3	0.3

**Table E. 27: 200 ppm Sn**

200 ppm Sn				
250mL stock HCl solution + 25mL of 200 ppm Sn + 1g aluminium + 4 drops of starch solution (after heating) appears to have no residual solids and is clear				
Burette	Drops	Redox	Temp	O <sub>2</sub>
reading	Added	mV	°C	mg/L
1.8	0	51	16.7	0.6
	3	57	16.7	0.6
	2	61	16.7	0.5
	20	116	16.8	0.5
	2	290	16.8	0.5
3.2	2	352	16.8	0.6

**Table E. 28: 300 ppm Sn**

300 ppm Sn				
250mL stock HCl solution + 25mL of 300 ppm Sn + 1g aluminium + 4 drops of starch solution (after heating) appears to have some small metal pieces and is clear				
Burette reading	Drops Added	Redox mV	Temp °C	O <sub>2</sub> mg/L
3.2	0			
	3*	31	16.6	0.5
	3	34	16.7	0.4
	10	36	16.7	0.4
	10	50	16.7	0.3
4.6		56	16.7	0.3
	10	137	16.8	0.3
	2	328	16.8	0.4
5.2	1	342	16.9	0.4
*forgot to place ORP and O <sub>2</sub> probes into solution until after first 3 drops added				



**Table E. 29: Table 400 ppm Sn**

400 ppm Sn				
250mL stock HCl solution + 25mL of 400 ppm Sn + 1g aluminum + 4 drops of starch solution (after heating) appears to have some residual solids and is clear				
Burette	Drops	Redox	Temp	O <sub>2</sub>
reading	Added	mV	°C	mg/L
5.2	0	64	16.9	0.5
	9	55	17	0.5
	10	59	17	0.5
	10	70	17	0.5
	10	105	17.1	0.5
	5	318	17.1	0.5
	1	335	17.1	0.6
7.4	1	343	17.1	0.7
Observations: no results from assay samples yet to compare with the titration results (bubbles were coming off the aluminium pieces when it was dissolving)				

## **For PWB Metallization Applications**

### DESCRIPTION

Ronastan EG-1 is an acidic tin plating solution which produces smooth, fine-grained deposits over a wide plating range. Ronastan EG-I deposits can be used as an etch resist in the manufacture of printed circuit boards, where the process shows excellent throwing power and metal distribution, even in high-aspect through holes and microvias.

### PRODUCT PREPARATION AND OPERATION

#### Preparation of 100 Litre Volume

#### Cleaning Procedure for New Bath Installation

Clean the tank to remove any dirt and flush clean with water. Leach with sodium hydroxide (50 g/l) for 8 hours at 40 °C ensuring that the circulation pumps are on. Empty and rinse with water. Fill and circulate with 5-10 % sulphuric acid for a minimum of 4 hours. Empty and rinse with deionized water. The same procedure should also be used for any anode bags, membranes or filter cartridges. If the tank has previously been used with other tin or tin-lead additive systems, discard the bath and clean the tank as above.

If the tank has a heavy coating from the previous solution, the addition of 3 - 10 ml/l of hydrogen peroxide to the sodium hydroxide leaching solution may aid the cleaning process.

## BATH MAKE-UP (100 LITRES VOLUME)

Deionized water	70.0 litres
Sulphuric Acid (SG 1.55, 65%)	18 litres
Stannous Sulphate	4 k g
Ronastan EC-1 M	4 litres
Ronastan EC-1 A	0.3 litres
Deionized water	To final volume

## PROCEDURE

- 1) Add the deionized water followed by the sulphuric acid, slowly with continuous stirring.
- 2) Add the stannous sulphate, stirring well to ensure that the majority of the solid is dissolved.
- 3) Turn of the filter pumps and allow to circulate for 1 hour to allow any undissolved particles to be filtered out.
- 4) Put the anodes into the tanks-preferable in polypropylene anode bags.
- 5) Electrolyse the solution using either laminate boards or preferably corrugated copper foil between 0.1-0.2 A/dm<sup>2</sup> for a minimum of 4 hours.
- 6) Add the Ronastan EGI M followed by Ronastan EC-1 A stirring well between additions.
- 7) Add the remainder of the deionized water to final volume.
- 8) Electrolyse the solution with fresh laminate Panels at 1 A/ dm<sup>2</sup> cathode current density for a minimum of 2 hours with the circulation pumps on.
- 9) The bath is now ready to use.

Notes:

- a) It is very important to add the Ronastan EGI M before the EGIC A, as the EGI A has very low solubility in aqueous solution without the EGI M.
- b) It is normal to see a brown/yellow cloudy precipitate or oiling out on addition of EGI A during make up. This should redissolve on mixing.
- c) The deionized water should be free from chlorides.

## CONTROL LIMITS

### Control Limits

<b>Component</b>	<b>Range</b>	<b>Optimum</b>
Tin(II)	15 - 25 g/L	20 g/L
Sulphuric Acid	160 - 200 g/L	180 g/L
Ronastan EC-	2 - 6 ml/L	3 ml/L
Ronastan EC-	40 - 60 ml/L	50 ml/L
Tin(IV)	0 - 10 g/L	

### Operating Conditions

<b>Parameter</b>	<b>Range</b>	<b>Recommended</b>
Temperature	18-27 °C	22 °C
Cathode Current Density	1.0 - 2.0 A/dm <sup>2</sup>	1.5 A/dm <sup>2</sup>
Anode Current Density	1.0 2.0 A/dm <sup>2</sup>	
Anode to Cathode Ratio	1:1 - 2:1	
Anode to Cathode Distance	20 - 30 cm	
Anodes	Pure tin bar anodes or tin balls in zirconium baskets	
Agitation	Paddle agitation and vibration recommended	
Ventilation	Recommended	
Filtration	Continuously through 1 micron filters	

## YIELD (TYPICALLY)

200-500 ml of Ronastan EG1 A per 1,000 amp/hours.

300-500 ml of Ronastan EGI R per 1,000 amp/hours.

## ANALYSIS

Prior to sampling, the bath volume must be adjusted to operating level with deionized water and thoroughly mixed.

Using Sn(II), Sulphuric Acid, EG1 A and EGI R determinations, make appropriate adjustments according to the Replenishment Schedule. Sn(IV) analysis is recommended as a periodic check on solution life or if plating efficiency has dropped.

## DETERMINATION OF SN(II)

### I. Principle

This is an iodometric titration to determine the Sn(II) concentration in an acid medium.

### II. Reagents

- a) Iodine solution, 0.05M (0.1N) standardised
- b) Hydrochloric acid (300 ml of SG 1.18 acid)
- c) Marble chips
- d) Starch indicator, 1 %: Mix 1g of soluble starch with 10 mL of cold deionised water and pour into 90 ml of hot deionized water (90 – 100 °C); heat at 95 – 100 °C for 1 minute and store in a stoppered bottle

### III. Procedure

- a) Cool a sample of bath to 15 – 25 °C. Pipette 5 ml of cooled sample into a 350 ml conical beaker containing approximately 150 ml of dilute hydrochloric acid and a few marble chips.
- b) Add 1 ml of starch indicator and quickly titrate with the iodine solution (0.05M) to a blue colour end-point.

#### IV. Calculation

$$\frac{\text{Tin(II) (g/l)} = \text{ml of iodine} \times \text{Molarity} \times 118.7}{\text{aliquot (5 ml)}}$$

#### V. Control Limits

Control Limits

<b>Component</b>	<b>Range</b>	<b>Optimum</b>
Tin(II)	15 - 25 g/l	20 g/l

#### VI. Replenishment

To raise tin(II) by 1 g/l, add 2 g/l of stannous sulphate.

### DETERMINATION OF SULPHURIC ACID

#### I. Principle

Sulphuric acid is determined by acid base titration with sodium hydroxide, using methyl orange indicator.

#### II. Reagents

- Sodium hydroxide, 1.00M (1.00N), standardized
- Methyl orange indicator, 0.1 %: Dissolve 0.1g of methyl orange in 100 ml of deionized water

#### III. Procedure

- Cool a sample of bath to 15 – 25 °C. Pipette 5 ml of cooled sample into a 250 ml conical flask and dilute to approximately 100 ml with deionized water.
- Add 5 drops of methyl orange indicator and titrate with sodium hydroxide (1.00M) from a red to a yellow end-point.

#### IV. Calculation

$$\text{Sulphuric Acid (g/l)} = \frac{\text{ml of sodium hydroxide} \times \text{Molarity} \times 49}{\text{aliquot (5 ml)}}$$

#### V. Control Limits

##### Control Limits

Component	Range	Optimum
Sulphuric Acid	160 - 200 g/l	180 g/l

#### VI. Replenishment

To raise sulphuric acid by 10 g/l, add 10 ml/L of sulphuric acid (65Vo w/w, SG 1.55).

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## APPENDIX G TOTAL SN AND SN(IV) - IODOMETRY

### I. Principle

The Sn(IV) is reduced to Sn(II) and the total tin is then found by iodometric titration.

### II. Reagents

- a) Iodine solution, 0.05M (0.1N) standardised
- b) Hydrochloric acid (300 ml/l of SG 1.18 acid)
- c) Marble chips
- d) Starch indicator, 1 %: Mix 1g of soluble starch with 10 ml of cold deionised water and pour into 90 ml of hot deionized water (90 – 100 °C); heat at 95 - 100°C for 1 minute and store in a stoppered bottle
- e) Aluminum sheet (AR grade): Cut into approximately 0.5g pieces

### III. Equipment

- a) 500 ml conical flask
- b) Watch glass

### IV. Procedure

- a) Cool a sample of bath to 15 - 25°C. Pipette 5 ml of cooled sample into a 500 ml conical beaker containing approximately 150 ml of dilute hydrochloric acid.
- b) Add approximately 1 g of aluminum and cover the conical flask with a watch glass.
- c) Boil the solution until all the aluminum has dissolved (about 20 minutes) and then boil for a further 2 minutes.



- d) Add 1 - 2 marble chips, replace the watch glass and cool rapidly to room temperature.
- e) When cool, add 1 ml of starch solution and titrate immediately with 0.05M iodine solution to the blue end point.

#### V. Calculations

$$\frac{\text{Total Sn (g/l)} = \text{ml of iodine} \times \text{Molarity} \times 118.7}{\text{aliquot (5 ml)}}$$

$$\text{Sn(IV) (g/l)} = \text{g/l Total Tin} - \text{g/l Sn(II)}$$

#### VI. Control Limits

Control Limits

<b>Component</b>	<b>Range</b>	<b>Optimum</b>
Sn(IV)	0 - 10 ml/L	

#### VII. Replenishment

The solution should be diluted or replaced when the Sn(IV) reaches 10 ml/l.

## APPENDIX H SPECIATION LEACH

Sample Preparation for Solids Assays for Assay Office

Diagnostic Leach for Fume to Raise In/Ge Concentration – for XRD/SEM (16 Feb 2007)

Procedure for Leaching Oxide Fume to dissolve both Zn and Pb components:

### Stage 1. – Dissolving the Zn

- 1) add 2.5 L of water to 4 L beaker (baffled etc.). Turn on agitator to 400 rpm
- 2) add 500 g of fume
- 3) adjust pH to the 2 to 3 range by adding a 1:1 H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O mixture (~0.5 L)
- 4) leach for 30 minutes
- 5) ensure pH is maintained at <3, and temp stays above 50 °C
- 6) pressure filter the slurry or use #52 Whatman filter and Buchner funnel
- 7) wash the cake with 0.3 L of water (3 x 100 mls)
- 8) determine the moisture in the final cake to estimate dry equivalent cake weight

### Stage 2. – Dissolving the Pb

- a) prepare the ammonium acetate/ammonium chloride solution (4 L)
- b) add 1 L of the solution to a 2.5 L baffled beaker
- c) add the wet solids from Stage 1 (~200 g) to the beaker
- d) agitate slurry and raise temperature to 60 + °C
- e) leach for 60 minutes
- f) pressure filter slurry
- g) wash the residue twice with 0.1 L of water each time
- h) determine the moisture of the final cake and estimate dry cake equivalent weight

If final weight is >25 g, repeat Stages 1 & 2.

Assay Requirements:

- fume for indium(GS01)
- Stage 1 filtrate volume and mg/L indium (each pass)
- Stage 2 filtrate volume and mg/L indium (for each pass)

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**H<sub>2</sub>SO<sub>4</sub> Leach for Ge Preconcentrate – for XRD/SEM**

Oxide Pre Con Acetic Acid Leach June 7, 2007

Check the MSDS for Oxide pre con and for glacial acetic acid.

Make up two litres of 20 % acetic acid. Using a 2 litre graduated cylinder, pour 400 ml of glacial acetic acid slowly into 1600 ml of deionized water in a well ventilated fume hood. Obtain the percent moisture from the Oxide pre con sample. If the sample is around 50 % moisture then take 500 grams and add it to the two litres of 20 % acetic acid in a 3.5 litre baffled Pyrex beaker. Be careful adding the precon to the acetic acid solution because of splashing. Set the agitation around 550 RPM. Mix at 400 RPM using an 8 cm A310 impeller. Make sure all solids are in solution. The Pyrex beaker should be placed on a hot plate. The hot plate should be plugged into a temperature controller with a temperature probe attached to the controller and inserted into the baffled beaker secured by a clamp to the agitator stand. Be careful adding the precon to the acetic acid solution because of splashing. Mix at 400 RPM using an 8 cm A310 impeller.

Bring the temperature up to 60 °C and hold for one hour. Place saran wrap over the mouth of the beaker to contain splashing and reduce evaporation. At the completion of one hour then filter the hot slurry in a 15 centimetre #541 Whatman filter paper in a Buckner funnel. Use thick rubber gloves to avoid being burned. Note filtrate volume and sample. Pass about 50 ml of filtrate through a Millipore filter (0.45 micron) prior to sending away for assay. Return all wet solids after filtration back into the 3.5 litre baffled beaker. Add another 2 litres of 20 % acetic acid and heat to 60 °C. Place saran wrap over the mouth of the beaker to contain splashing and reduce evaporation. Mix at 550 RPM using an 8 cm A310 impeller for one more hour. Filter, note the filtrate volume and also note the wet cake weight. Pass another 50 ml of filtrate through a Millipore filter (0.45 micron) prior to sending away for assay. Air dry the remaining residue. Note the dry weight of the residue and sample prep for assay. Use a mortar and pestle and pass the pulverized solids through a 35 mesh screen. Place all pertinent data on a spread sheet.

- Assay the dry head solids for  
Zn(ASol),Pb,Fe,As,Sn,Cu,Mn,Mg,In,Ge,T/S,SO<sub>4</sub>/S,F,Cl

- Assay the dry residue solids for  
Zn(ASol),Pb,Fe,As,Sn,Cu,Mn,Mg,In,Ge,T/S,SO<sub>4</sub>/S,F,Cl
- Assay filtrate for Zn ,Pb,Fe,As,Sn,Cu,Mn,Mg,In,Ge,T/S,SO<sub>4</sub>/S,F,Cl

There should be one head sample of dried solids, one final air dried residue and two filtrate samples to send for assay.

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Table J. 1: Liquids 1 min

		Time min	ORP mV	Temp oC	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn mg/L	Pb mg/L	S g/L	SO <sub>4</sub> /S g/L	As mg/L	Cl mg/L	F mg/L	MgSO <sub>4</sub> mg/L	Mn mg/L	Cu mg/L	SiO <sub>2</sub> mg/L	Al mg/L	Ca mg/L	Sb mg/L
<b>Baseline</b>	<b>Test #</b>	<b>0</b>	426	90	100	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	0	0		100	0	0	0	0	0	0	0	0	0	0
Baseline	25A	1	493	90.2	37	8.5	5.34	13.84	107.9	33	9	35	36	1100	30	160	1600	610	140	1400	2500	150	220
Baseline	25B	1	482	90.7	36.5	8	3.44	11.84	132	45	17	36	38	1200	30	150	1600	610	130	1500	2400	150	250
Δ As - Baseline Repeat	34C	1	518	88.9	42	7	6.55	13.55	135	86	17	35	38	1000	40	160	1500	620	140	1500	2500	160	280
Baseline	26A	1	501	90.3	40	7.6	6.16	13.76	98.6	66	20	39	40	1700	30	140	1600	590	100	1600	2400	160	290
Baseline	26B	1	514	90.3	44	7.6	5.81	13.41	123.6	84	21	38	40	1500	40	140	1600	620	120	1500	2400	170	310
Δ As - Baseline Repeat	35C	1	507	90.3	38.5	10.2	3.75	13.95	116.7	33	16	36	39	930	40	160	1500	620	130	1400	2500	170	250
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25A	1	493	90.2	37	8.5	5.34	13.84	107.9	33	9	35	36	1100	30	160	1600	610	140	1400	2500	150	220
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25B	1	482	90.7	36.5	8.4	3.44	11.84	132.2	45	17	36	38	1200	30	150	1600	610	130	1500	2400	150	250
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27A	1	493	90.2	86.5	8.6	6.05	14.65	138.2	230	15	52	56	1600	35	130	1600	610	130	1500	2500	210	420
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27B	1	516	90.3	86	10.8	3.48	14.28	118.9	120	19	51	55	1600	40	150	1600	600	120	1500	2400	210	370
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28A	1	435	89.5	5	5.9	0.78	6.66	141.7	3	15	19	21	30	40	140	1700	620	110	1100	1900	110	21
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28B	1	428	90.2	4	5.7	0.4	6.1	122	3	18	19	22	34	40	160	1600	620	100	1100	1900	110	20
Δ Temperature - 90 oC	25A	1	493	90.2	37	8.5	5.34	13.84	107.9	33	9	35	36	1100	30	160	1600	610	140	1400	2500	150	220
Δ Temperature - 90 oC	25B	1	482	90.7	36.5	8.4	3.44	11.84	132.2	45	17	36	38	1200	30	150	1600	610	130	1500	2400	150	250
Δ Temperature - 60 oC	29A	1	519	60.1	35.5	4.1	10.3	14.14	115.1	370	23	35	38	1600	40	150	1600	590	120	1500	2400	160	420
Δ Temperature - 60 oC	29B	1	523	60.4	43	4.5	9.41	13.91	110.1	380	26	36	38	1700	30	150	1600	620	130	1500	2500	150	440
Δ Temperature - 30 oC	30A	1	513	35.8	18	1.6	8.45	10.05	121.8	210	28	24	25	1100	40	130	1600	600	120	1200	2000	120	230
Δ Temperature - 30 oC	30B	1	535	33.4	39	1.6	11.46	13.06	120.7	420	24	32	33	2000	40	130	1700	630	110	1500	2400	180	440
Δ PbCon - 0.6 Ratio	25A	1	493	90.2	37	8.5	5.34	13.84	107.9	33	9	35	36	1100	30	160	1600	610	140	1400	2500	150	220
Δ PbCon - 0.6 Ratio	25B	1	482	90.7	36.5	8.4	3.44	11.84	132.2	45	17	36	38	1200	30	150	1600	610	130	1500	2400	150	250
Δ PbCon - 1 Ratio	31A	1	523	90.2	37	12.3	2.58	14.88	166.1	23	16	36	39	1200	30	160	1600	600	120	1500	2400	220	240
Δ PbCon - 0.2 Ratio	31B	1	573	89.5	64.5	3.6	10.65	14.25	63.1	220	21	39	45	1200	30	150	1600	620	140	1500	2500	150	390
Δ PbS - 0.6 Ratio	32A	1	496	90.5	51.5	10.3	3.95	14.25	130.9	77	14	40	43	1300	50	150	1600	620	100	1400	2500	100	280
Δ PbS - 0.35 Ratio	32B	1	443	90.7	10	6.8	2.62	9.42	100.1	10	18	23	25	250	40	150	1600	610	80	1400	2300	96	46
Δ PbS - 0.12 Ratio	32C	1	640	89.9	38	1.7	11.28	12.98	53.4	110	26	32	34	1400	10	150	1600	590	110	1500	2400	100	220
Δ PbS - 0.6 Ratio	33A	1	n/a	89.6	39.5	12.8	1.72	14.52	129.8	29	15	37	39	1200	70	150	1600	620	69	1500	2500	95	200
Δ PbS - 0.35 Ratio	33B	1	519	90.5	55	8.3	6.68	14.98	85.2	100	26	41	42	1200	55	150	1600	630	110	1500	2500	120	310
Δ PbS - 0.12 Ratio	33C	1	581	88.9	63.5	3.7	11.38	15.08	59.2	290	27	40	43	1500	40	140	1600	640	120	1500	2500	120	390
Δ As + 10 g/L	34A	1	498	90	45	7.3	6.14	13.44	87	55	18	35	38	7700	40	170	1600	630	150	1500	2600	150	270
Δ As + 5 g/L	34B	1	509	90	42	7.3	6.15	13.45	53	49	19	34	36	4500	40	150	1500	600	130	1400	2400	140	250
Δ As + 10 g/L	35A	1	464	90.6	47.5	10	4.25	14.25	115.4	48	15	34	38	8400	30	150	1600	620	120	1500	2500	180	250
Δ As + 5 g/L	35B	1	480	89.4	42	9.2	4.43	13.63	98	48	16	35	36	4600	40	160	1600	630	130	1500	2500	170	250

Table J. 2: Solids 1 min

		Time min	ORP mV	Temp oC	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn wt%	Pb wt%	S wt%	SO <sub>4</sub> /S w%	As w%	Cl w%	F w%	MgSO <sub>4</sub> w%	Mn w%	Cu w%	SiO <sub>2</sub> w%	Fe w%	Zn w%	MgO w%
Baseline	Test #	0	426	90	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Baseline	25A	1	493	90.2	37	8.5	5.34	13.84	107.9	1.4	46	17	4.3	0.78	0	0.011	0	0.03	0.05	3.3	4.6	9.4	0.02
Baseline	25B	1	482	90.7	36.5	8	3.44	11.84	132	1.2	47	17	4.5	0.58	0	0.01	0	0.02	0.04	3.4	4.7	9.8	0.02
Δ As - Baseline Repeat	34C	1	518	88.9	42	7	6.55	13.55	135	1.1	46	16	3.4	0.47	0.01	0.009	0	0.03	0.04	3.3	4.6	9.4	0.02
Baseline	26A	1	501	90.3	40	7.6	6.16	13.76	98.6	1.6	45	16	4.4	0.79	0	0.012	0	0.02	0.04	3.2	4.5	8.8	0.03
Baseline	26B	1	514	90.3	44	7.6	5.81	13.41	123.6	1.3	48	17	3.3	0.58	0.01	0.01	0	0.02	0.04	3.4	4.7	9.7	0.02
Δ As - Baseline Repeat	35C	1	507	90.3	38.5	10.2	3.75	13.95	116.7	1.3	46	16	3	0.63	0.01	0.02	0	0.03	0.05	3.2	4.5	8.8	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25A	1	493	90.2	37	8.5	5.34	13.84	107.9	1.4	46	17	4.3	0.78	0	0.011	0	0.03	0.05	3.3	4.6	9.4	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25B	1	482	90.7	36.5	8.4	3.44	11.84	132.2	1.2	47	17	4.5	0.58	0	0.01	0	0.02	0.04	3.4	4.7	9.8	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27A	1	493	90.2	86.5	8.6	6.05	14.65	138.2	1	45	17	2.9	0.38	0.01	0.006	0	0.02	0.04	3.2	4.3	9.3	0.03
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27B	1	516	90.3	86	10.8	3.48	14.28	118.9	1.2	44	17	3.4	0.48	0.01	0.004	0	0.02	0.04	3.2	4.2	9	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28A	1	435	89.5	5	5.9	0.78	6.66	141.7	1.1	37.4	14	4.9	1.3	0	0.026	0	0.04	0.05	3	9.2	8.9	0.04
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28B	1	428	90.2	4	5.7	0.4	6.1	122	1.3	37.7	14	5.1	1.4	0.01	0.025	0	0.04	0.05	3	9.5	8.7	0.04
Δ Temperature - 90 oC	25A	1	493	90.2	37	8.5	5.34	13.84	107.9	1.4	46	17	4.3	0.78	0	0.011	0	0.03	0.05	3.3	4.6	9.4	0.02
Δ Temperature - 90 oC	25B	1	482	90.7	36.5	8.4	3.44	11.84	132.2	1.2	47	17	4.5	0.58	0	0.01	0	0.02	0.04	3.4	4.7	9.8	0.02
Δ Temperature - 60 oC	29A	1	519	60.1	35.5	4.1	10.3	14.14	115.1	1.1	48	17	4.8	0.29	0.01	0.012	0	0.02	0.05	3.2	4.4	10.2	0.02
Δ Temperature - 60 oC	29B	1	523	60.4	43	4.5	9.41	13.91	110.1	1.1	48	17	3.5	0.28	0.01	0.014	0	0.02	0.05	3.3	4.3	10.2	0.02
Δ Temperature - 30 oC	30A	1	513	35.8	18	1.6	8.45	10.05	121.8	1.2	43	15	0.045	0.73	0.01	0.026	0	0.04	0.05	3.2	6.8	9.9	0.03
Δ Temperature - 30 oC	30B	1	535	33.4	39	1.6	11.46	13.06	120.7	0.79	46	17	0.043	0.31	0.01	0.016	0	0.04	0.05	3.1	4.7	10.3	0.04
Δ PbCon - 0.6 Ratio	25A	1	493	90.2	37	8.5	5.34	13.84	107.9	1.4	46	17	4.3	0.78	0	0.011	0	0.03	0.05	3.3	4.6	9.4	0.02
Δ PbCon - 0.6 Ratio	25B	1	482	90.7	36.5	8.4	3.44	11.84	132.2	1.2	47	17	4.5	0.58	0	0.01	0	0.02	0.04	3.4	4.7	9.8	0.02
Δ PbCon - 1 Ratio	31A	1	523	90.2	37	12.3	2.58	14.88	166.1	0.89	46	18	3.1	0.52	0	0.01	0	0.02	0.05	3.5	4.7	9.7	0.03
Δ PbCon - 0.2 Ratio	31B	1	573	89.5	64.5	3.6	10.65	14.25	63.1	2.1	45	13	8.1	0.63	0.01	0.006	0	0.04	0.05	2.3	3	7.1	0.04
Δ PbS - 0.6 Ratio	32A	1	496	90.5	51.5	10.3	3.95	14.25	130.9	1.1	63	13	5.8	0.46	0.01	0.004	0.006	0.02	0.04	0.53	0.71	1.8	0.02
Δ PbS - 0.35 Ratio	32B	1	443	90.7	10	6.8	2.62	9.42	100.1	1.7	45	11	7.5	1.5	0	0.015	0	0.04	0.06	0.95	6.1	3.3	0.04
Δ PbS - 0.12 Ratio	32C	1	640	89.9	38	1.7	11.28	12.98	53.4	2.7	44	9.3	7.8	1.4	0	0.013	0	0.05	0.05	1.2	3.3	4.4	0.03
Δ PbS - 0.6 Ratio	33A	1	not taken	89.6	39.5	12.8	1.72	14.52	129.8	1.2	60	12	6.5	0.65	0.01	0.006	0	0.03	0.06	0.58	1.5	1.9	0.02
Δ PbS - 0.35 Ratio	33B	1	519	90.5	55	8.3	6.68	14.98	85.2	1.7	57	11	6	0.71	0.01	0.005	0	0.04	0.06	0.97	1.7	2.6	0.03
Δ PbS - 0.12 Ratio	33C	1	581	88.9	63.5	3.7	11.38	15.08	59.2	1.7	53	10	6.6	0.53	0.01	0.008	0	0.05	0.07	1	1.9	3	0.03
Δ As + 10 g/L	34A	1	498	90	45	7.3	6.14	13.44	87	1.7	43	15	5	2	0.01	0.01	0	0.03	0.04	3	4.2	8.1	0.02
Δ As + 5 g/L	34B	1	509	90	42	7.3	6.15	13.45	53	2.6	41	11	4.9	2.3	0.01	0.009	0	0.03	0.04	3	3.4	5.9	0.03
Δ As + 10 g/L	35A	1	464	90.6	47.5	10	4.25	14.25	115.4	1.2	43	16	3.7	1.6	0.01	0.006	0	0.03	0.06	3.1	4.7	8.7	0.02
Δ As + 5 g/L	35B	1	480	89.4	42	9.2	4.43	13.63	98	1.4	45	16	3.9	1.3	0	0.011	0	0.03	0.05	3.2	4.5	8.8	0.03

Table J. 3: Liquids 3 min

		Time min	ORP mV	Temp oC	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn mg/L	Pb mg/L	S g/L	SO <sub>4</sub> /S g/L	As mg/L	Cl mg/L	F mg/L	MgSO <sub>4</sub> mg/L	Mn mg/L	Cu mg/L	SiO <sub>2</sub> mg/L	Al mg/L	Ca mg/L	Sb mg/L
<b>Baseline</b>	<b>Test #</b>	<b>0</b>	426	90	100	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	0	0		100	0	0	0	0	0	0	0	0	0	0
Baseline	25A	3	433	90.1	30	11.3	2.29	13.69	138.9	14	10	34	36	960	30	160	1600	620	140	1400	2500	190	180
Baseline	25B	3	437	90.2	37.5	9.9	3.54	13.44	121.8	21	17	36	38	1100	30	150	1600	610	130	1400	2400	140	220
Δ As - Baseline Repeat	34C	3	467	90	36.5	8.9	4.24	13.14	134.8	25	17	35	38	890	40	150	1500	610	140	1400	2500	160	220
Baseline	26A	3	471	90.5	42	9.6	4.05	13.65	113	31	23	38	40	1600	40	140	1600	590	110	1500	2400	150	240
Baseline	26B	3	542	90.2	42.5	10	3.32	13.32	123.6	29	17	38	40	1300	35	140	1600	610	120	1500	2400	170	240
Δ As - Baseline Repeat	35C	3	441	90	33	11.9	1.98	13.88	117.9	13	19	36	38	840	30	160	1500	610	130	1400	2400	170	190
Δ H2SO4 - 100 g/L	25A	3	433	90.1	30	11.3	2.29	13.69	138.9	14	10	34	36	960	30	160	1600	620	140	1400	2500	190	180
Δ H2SO4 - 100 g/L	25B	3	437	90.2	37.5	9.9	3.54	13.44	121.8	21	17	36	38	1100	30	150	1600	610	130	1400	2400	140	220
Δ H2SO4 - 160 g/L	27A	3	470	90.4	79	11.4	2.97	14.37	124.9	43	14	51	55	1400	30	130	1600	600	130	1400	2400	210	310
Δ H2SO4 - 160 g/L	27B	3	475	90.3	78	11	2.95	13.95	120.2	45	19	50	54	1500	40	140	1600	590	120	1400	2300	210	310
Δ H2SO4 - 40 g/L	28A	3	336	90.4	0.5	7.5	0.05	7.55	143.2	1	17	20	19	12	40	150	1700	620	71	1200	1900	110	16
Δ H2SO4 - 40 g/L	28B	3	333	90.4	2	6.9	0.26	7.16	136	1	17	20	21	12	30	130	1700	620	67	1100	1900	110	15
Δ Temperature - 90 oC	25A	3	433	90.1	30	11.3	2.29	13.69	138.9	14	10	34	36	960	30	160	1600	620	140	1400	2500	190	180
Δ Temperature - 90 oC	25B	3	437	90.2	37.5	9.9	3.54	13.44	121.8	21	17	36	38	1100	30	150	1600	610	130	1400	2400	140	220
Δ Temperature - 60 oC	29A	3	476	60	40	5.8	8.18	13.98	122.6	250	27	35	37	1400	40	150	1600	600	120	1400	2400	160	360
Δ Temperature - 60 oC	29B	3	478	60.2	42.5	6.3	7.29	13.59	137.8	250	29	35	37	1400	40	150	1600	620	130	1500	2400	160	370
Δ Temperature - 30 oC	30A	3	488	36.1	15.5	3.3	6.34	9.64	120.3	160	39	23	24	920	40	130	1600	600	120	1200	2000	120	190
Δ Temperature - 30 oC	30B	3	513	33.9	29	3.1	9.23	12.33	119.2	360	28	30	32	1800	30	140	1500	570	100	1400	2200	170	400
Δ PbCon - 0.6 Ratio	25A	3	433	90.1	30	11.3	2.29	13.69	138.9	14	10	34	36	960	30	160	1600	620	140	1400	2500	190	180
Δ PbCon - 0.6 Ratio	25B	3	437	90.2	37.5	9.9	3.54	13.44	121.8	21	17	36	38	1100	30	150	1600	610	130	1400	2400	140	220
Δ PbCon - 1 Ratio	31A	3	384	90	34.5	13.7	0.68	14.38	181	10	14	35	39	1200	30	160	1600	590	85	1500	2400	260	200
Δ PbCon - 0.2 Ratio	31B	3	532	90.2	62.5	3.8	10.01	13.81	66.2	100	18	39	45	1000	30	150	1500	620	140	1400	2400	150	330
Δ PbS - 0.6 Ratio	32A	3	426	90.3	46	13.1	1.04	14.14	137.6	12	12	39	41	1100	40	150	1600	610	64	1400	2500	97	190
Δ PbS - 0.35 Ratio	32B	3	408	90.2	8	7.5	2.07	9.57	93.7	4	21	22	24	140	40	150	1600	620	63	1400	2300	96	35
Δ PbS - 0.12 Ratio	32C	3	517	90.3	36	2.9	9.9	12.8	57.5	52	21	30	33	1300	40	140	1600	590	110	1500	2400	110	170
Δ PbS - 0.6 Ratio	33A	3	not taken	92	34	14.5	0	14.44	110.4	9	15	36	38	1200	70	140	1600	600	37	1400	2400	91	150
Δ PbS - 0.35 Ratio	33B	3	457	90.1	47.5	11.6	3.18	14.78	88.1	29	18	40	42	1100	50	140	1600	630	110	1400	2500	110	240
Δ PbS - 0.12 Ratio	33C	3	522	90.8	59.5	6.1	8.75	14.85	57.8	81	23	39	43	1200	45	130	1500	620	130	1400	2400	120	300
Δ As + 10 g/L	34A	3	441	89.9	44.5	8.5	4.63	13.13	95.9	41	18	34	39	8200	40	160	1500	620	150	1400	2500	170	230
Δ As + 5 g/L	34B	3	459	89.9	40	8.8	4.49	13.29	133.6	37	18	34	38	4500	40	140	1500	600	130	1400	2400	160	230
Δ As + 10 g/L	35A	3	416	90.4	45.5	10.7	3.63	14.33	116.3	39	17	34	38	8300	40	150	1500	610	110	1400	2400	170	230
Δ As + 5 g/L	35B	3	424	90.4	38.5	11.9	2.05	13.95	122	23	18	34	36	4400	40	160	1500	620	120	1400	2400	170	190



**Table J. 4: Solids 3 min**

		Time min	ORP m/V	Temp oC	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn wt%	Pb wt%	S wt%	SO <sub>4</sub> /S w%	As w%	Cl w%	F w%	MgSO <sub>4</sub> w%	Mn w%	Cu w%	SiO <sub>2</sub> w%	Fe w%	Zn w%	MgO w%
<b>Baseline</b>	<b>Test #</b>	<b>0</b>	426	90	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Baseline	25A	3	433	90.1	30	11.3	2.29	13.69	138.9	1.3	45	17	4.5	0.74	0	0.01	0	0.02	0.04	3.5	4.7	8.9	0.02
Baseline	25B	3	437	90.2	37.5	9.9	3.54	13.44	121.8	1.2	46	17	4.4	0.65	0	0.01	0	0.02	0.04	3.4	4.7	9.4	0.02
Δ As - Baseline Repeat	34C	3	467	90	36.5	8.9	4.24	13.14	134.8	1.1	45	16	3.2	0.53	0.01	0.009	0	0.02	0.04	3.2	4.6	8.9	0.03
Baseline	26A	3	471	90.5	42	9.6	4.05	13.65	113	1.4	46	17	2.6	0.75	0.01	0.011	0	0.03	0.04	3.3	4.9	9	0.02
Baseline	26B	3	542	90.2	42.5	10	3.32	13.32	123.6	1.3	47	17	3.3	0.67	0	0.009	0	0.03	0.04	3.4	4.7	9	0.03
Δ As - Baseline Repeat	35C	3	441	90	33	11.9	1.98	13.88	117.9	1.3	46	16	3.7	0.67	0.01	0.019	0	0.03	0.05	3.3	4.5	8.6	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25A	3	433	90.1	30	11.3	2.29	13.69	138.9	1.3	45	17	4.5	0.74	0	0.01	0	0.02	0.04	3.5	4.6	8.9	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25B	3	437	90.2	37.5	9.9	3.54	13.44	121.8	1.2	46	17	4.4	0.65	0	0.01	0	0.02	0.04	3.4	4.7	9.4	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27A	3	470	90.4	79	11.4	2.97	14.37	124.9	1.2	44	17	2.7	0.55	0	0.006	0	0.03	0.04	3.3	4.3	8.6	0.03
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27B	3	475	90.3	78	11	2.95	13.95	120.2	1.2	43	17	3.7	0.56	0.01	0.004	0	0.03	0.04	3.3	4.4	8.7	0.03
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28A	3	336	90.4	0.5	7.5	0.05	7.55	143.2	1.2	38.6	15	4.6	1.3	0.01	0.024	0	0.04	0.07	3.1	8.9	8.9	0.04
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28B	3	333	90.4	2	6.9	0.26	7.16	136	1.2	38.9	15	4.8	1.3	0.01	0.022	0	0.04	0.07	3.1	8.8	9	0.04
Δ Temperature - 90 oC	25A	3	433	90.1	30	11.3	2.29	13.69	138.9	1.3	45	17	4.5	0.74	0	0.01	0	0.02	0.04	3.5	4.6	8.9	0.02
Δ Temperature - 90 oC	25B	3	437	90.2	37.5	9.9	3.54	13.44	121.8	1.2	46	17	4.4	0.65	0	0.01	0	0.02	0.04	3.4	4.7	9.4	0.02
Δ Temperature - 60 oC	29A	3	476	60	40	5.8	8.18	13.98	122.6	1.1	47	17	3.3	0.42	0.01	0.013	0	0.02	0.05	3.3	4.5	10	0.02
Δ Temperature - 60 oC	29B	3	478	60.2	42.5	6.3	7.29	13.59	137.8	1.1	49	17	4.1	0.4	0.01	0.013	0	0.02	0.05	3.2	4.5	10.1	0.03
Δ Temperature - 30 oC	30A	3	488	36.1	15.5	3.3	6.34	9.64	120.3	1.3	42	15	0.045	0.86	0.04	0.025	0	0.03	0.05	3.3	7.1	9.8	0.03
Δ Temperature - 30 oC	30B	3	513	33.9	29	3.1	9.23	12.33	119.2	0.87	47	17	0.043	0.32	0.01	0.014	0	0.03	0.05	3.4	4.7	10.5	0.03
Δ PbCon - 0.6 Ratio	25A	3	433	90.1	30	11.3	2.29	13.69	138.9	1.3	45	17	4.5	0.74	0	0.01	0	0.02	0.04	3.5	4.6	8.9	0.02
Δ PbCon - 0.6 Ratio	25B	3	437	90.2	37.5	9.9	3.54	13.44	121.8	1.2	46	17	4.4	0.65	0	0.01	0	0.02	0.04	3.4	4.7	9.4	0.02
Δ PbCon - 1 Ratio	31A	3	384	90	34.5	13.7	0.68	14.38	181	0.82	46	18	2.7	0.47	0	0.007	0	0.02	0.06	3.5	4.7	9.6	0.03
Δ PbCon - 0.2 Ratio	31B	3	532	90.2	62.5	3.8	10.01	13.81	66.2	2.1	44	13	4.5	0.77	0.01	0.006	0	0.03	0.05	2.4	3.2	6.7	0.04
Δ PbS - 0.6 Ratio	32A	3	426	90.3	46	13.1	1.04	14.14	137.6	1.2	62	13	6	0.5	0	0.004	0	0.02	0.06	0.54	0.7	1.8	0.02
Δ PbS - 0.35 Ratio	32B	3	408	90.2	8	7.5	2.07	9.57	93.7	1.8	44	11	7.9	1.7	0.01	0.016	0	0.05	0.07	0.96	6.5	3.5	0.04
Δ PbS - 0.12 Ratio	32C	3	517	90.3	36	2.9	9.9	12.8	57.5	2.6	44	9.6	7.9	1.4	0	0.012	0	0.04	0.05	1.2	3.3	4.1	0.02
Δ PbS - 0.6 Ratio	33A	3	not taken	92	34	14.5	0	14.44	110.4	1.4	56	12	5.8	0.75	0.01	0.006	0	0.03	0.07	0.64	1.3	2.2	0.02
Δ PbS - 0.35 Ratio	33B	3	457	90.1	47.5	11.6	3.18	14.78	88.1	1.7	54	11	6.7	0.78	0.01	0.004	0	0.04	0.05	0.92	1.4	2.5	0.03
Δ PbS - 0.12 Ratio	33C	3	522	90.8	59.5	6.1	8.75	14.85	57.8	2.1	51	10	6.7	0.85	0	0.008	0	0.04	0.05	1.1	1.7	3.1	0.03
Δ As + 10 g/L	34A	3	441	89.9	44.5	8.5	4.63	13.13	95.9	1.6	44	16	4.5	2.1	0	0.011	0	0.03	0.04	3.2	4.4	8.1	0.03
Δ As + 5 g/L	34B	3	459	89.9	40	8.8	4.49	13.29	133.6	1.1	47	17	3	1	0	0.008	0	0.02	0.04	3.2	4.6	9	0.02
Δ As + 10 g/L	35A	3	416	90.4	45.5	10.7	3.63	14.33	116.3	1.2	45	16	3.5	1.6	0.01	0.008	0	0.03	0.05	3.1	4.7	8.6	0.02
Δ As + 5 g/L	35B	3	424	90.4	38.5	11.9	2.05	13.95	122	1.2	44	16	3.3	1.2	0	0.012	0	0.03	0.05	3.1	4.5	8.6	0.03

**Table J. 5: Liquids 10 min**

		Time min	ORP m/V	Temp oC	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn mg/L	Pb mg/L	S g/L	SO <sub>4</sub> /S g/L	As mg/L	Cl mg/L	F mg/L	MgSO <sub>4</sub> mg/L	Mn mg/L	Cu mg/L	SiO <sub>2</sub> mg/L	Al mg/L	Ca mg/L	Sb mg/L
<b>Baseline</b>	<b>Test #</b>	<b>0</b>	426	90	100	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	0	0		100	0	0	0	0	0	0	0	0	0	0
Baseline	25A	10	365	90.2	28	13.7	0.3	14	149	6	10	33	34	910	20	160	1500	600	130	1400	2400	220	140
Baseline	25B	10	406	90.3	33	12.9	2.74	15.64	123.3	8	14	36	38	1000	30	150	1600	620	130	1400	2400	170	170
Δ As - Baseline Repeat	34C	10	419	90.2	33	11.9	1.48	13.38	123.2	8	15	33	37	820	45	160	1600	620	140	1400	2500	180	180
Baseline	26A	10	407	90.6	37	13	0.56	13.56	113	14	15	38	40	1500	30	140	1600	580	100	1500	2400	200	190
Baseline	26B	10	421	90.2	38.5	12.7	0.7	13.4	124.6	12	15	37	41	1300	35	150	1600	600	110	1400	2400	200	200
Δ As - Baseline Repeat	35C	10	375	90.3	31	14.3	0	13.31	116.2	5	16	35	39	840	40	160	1500	610	130	1300	2500	190	160
Δ H2SO4 - 100 g/L	25A	10	365	90.2	28	13.7	0.3	14	149	6	10	33	34	910	20	160	1500	600	130	1400	2400	220	140
Δ H2SO4 - 100 g/L	25B	10	406	90.3	33	12.9	2.74	15.64	123.3	8	14	36	38	1000	30	150	1600	620	130	1400	2400	170	170
Δ H2SO4 - 160 g/L	27A	10	398	90	74.5	14	0.59	14.59	126	15	14	50	54	1400	45	130	1600	600	120	1300	2400	220	260
Δ H2SO4 - 160 g/L	27B	10	409	90.2	74	13.5	0	13.23	123	16	15	50	53	1500	45	140	1600	600	110	1300	2300	210	260
Δ H2SO4 - 40 g/L	28A	10	272	90.5	0	7.7	0.75	8.45	145.1	1	22	19	20	10	40	140	1700	630	1	1200	1700	120	13
Δ H2SO4 - 40 g/L	28B	10	265	90.3	1	8	0.12	8.12	140.8	1	14	19	21	10	40	140	1700	630	1	1100	1700	110	13
Δ Temperature - 90 oC	25A	10	365	90.2	28	13.7	0.3	14	149	6	10	33	34	910	20	160	1500	600	130	1400	2400	220	140
Δ Temperature - 90 oC	25B	10	406	90.3	33	12.9	2.74	15.64	123.3	8	14	36	38	1000	30	150	1600	620	130	1400	2400	170	170
Δ Temperature - 60 oC	29A	10	454	59.9	34	7.3	6.25	13.55	122.4	110	28	34	36	1200	40	140	1600	590	120	1400	2400	170	270
Δ Temperature - 60 oC	29B	10	456	60	38	8.1	5.82	13.92	121.6	110	29	34	36	1200	40	150	1600	620	130	1500	2500	170	290
Δ Temperature - 30 oC	30A	10	464	29.7	13.5	3.9	5.48	9.38	125.4	120	37	23	24	780	40	130	1600	600	120	1200	2000	120	160
Δ Temperature - 30 oC	30B	10	492	30.4	29	4.5	7.78	12.28	114.5	330	24	28	31	1700	40	130	1500	550	100	1400	2100	170	370
Δ PbCon - 0.6 Ratio	25A	10	365	90.2	28	13.7	0.3	14	149	6	10	33	34	910	20	160	1500	600	130	1400	2400	220	140
Δ PbCon - 0.6 Ratio	25B	10	406	90.3	33	12.9	2.74	15.64	123.3	8	14	36	38	1000	30	150	1600	620	130	1400	2400	170	170
Δ PbCon - 1 Ratio	31A	10	158	90.3	33.5	14.4	0.66	15.06	171.3	10	12	35	38	1300	40	160	1600	600	1	1500	2400	280	210
Δ PbCon - 0.2 Ratio	31B	10	514	90.3	61	5.1	8.75	13.85	68.5	62	19	38	45	980	40	160	1600	640	150	1400	2500	160	300
Δ PbS - 0.6 Ratio	32A	10	237	89.9	44	14.3	0.48	14.78	136.3	10	11	39	42	1200	50	150	1600	610	1	1300	2500	100	160
Δ PbS - 0.35 Ratio	32B	10	361	90.2	6.5	8.7	1.21	9.91	101.7	1	14	21	24	69	40	150	1600	610	41	1400	2300	95	28
Δ PbS - 0.12 Ratio	32C	10	511	90.2	36	3.2	9.65	12.85	56.3	45	18	31	34	1300	40	140	1600	600	110	1500	2400	110	160
Δ PbS - 0.6 Ratio	33A	10	not taken	92.3	33	16	0	15.01	118.9	7	12	35	38	1300	70	140	1600	600	1	1400	2400	96	150
Δ PbS - 0.35 Ratio	33B	10	441	90.2	46	11.9	3.26	15.16	83	16	14	39	42	1100	55	140	1600	630	110	1400	2500	120	210
Δ PbS - 0.12 Ratio	33C	10	516	91	59.5	6.3	8.49	14.79	58.7	55	16	40	44	1200	40	140	1600	650	130	1400	2500	130	280
Δ As + 10 g/L	34A	10	404	90.1	44	10.8	1.96	12.76	100	27	16	34	37	8600	40	170	1500	630	150	1400	2600	190	200
Δ As + 5 g/L	34B	10	420	90.3	39	11	2.56	13.56	136.6	20	20	34	39	4600	30	150	1600	620	140	1400	2500	170	190
Δ As + 10 g/L	35A	10	367	90.3	44	13.4	1.26	14.66	117.1	29	17	34	36	9200	40	150	1600	640	120	1500	2500	200	200
Δ As + 5 g/L	35B	10	373	90.3	39	14	0.36	14.36	120.9	14	14	34	37	4700	40	160	1600	630	130	1400	2500	190	160

Table J. 6: Solids 10 min

		Time min	ORP mV	Temp 0C	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn wt%	Pb wt%	S wt%	SO <sub>4</sub> /S w%	As w%	Cl w%	F w%	MgSO <sub>4</sub> w%	Mn w%	Cu w%	SiO <sub>2</sub> w%	Fe w%	Zn w%	MgO w%
<b>Baseline</b>	<b>Test #</b>	<b>0</b>	426	90	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Baseline	25A	10	365	90.2	28	13.7	0.3	14	149	1.1	47	18	4.4	0.65	0	0.06	0	0.02	0.05	3.3	4.6	8.4	0.02
Baseline	25B	10	406	90.3	33	12.9	2.74	15.64	123.3	1.2	47	17	4.6	0.71	0	0.007	0	0.02	0.04	3.3	4.7	8.3	0.02
Δ As - Baseline Repeat	34C	10	419	90.2	33	11.9	1.48	13.38	123.2	1.2	44	16	3.1	0.62	0	0.007	0	0.02	0.04	3.2	4.5	8	0.02
Baseline	26A	10	407	90.6	37	13	0.56	13.56	113	1.4	46	17	3	0.76	0	0.008	0	0.02	0.04	3.4	4.8	8.2	0.02
Baseline	26B	10	421	90.2	38.5	12.7	0.7	13.4	124.6	1.3	47	18	3.8	0.69	0.01	0.007	0	0.03	0.04	3.4	4.6	8.3	0.03
Δ As - Baseline Repeat	35C	10	375	90.3	31	14.3	0	13.31	116.2	1.3	46	17	4.2	0.67	0.01	0.012	0	0.03	0.05	3.4	4.5	8.2	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25A	10	365	90.2	28	13.7	0.3	14	149	1.1	47	18	4.4	0.65	0	0.06	0	0.02	0.05	3.3	4.6	8.4	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25B	10	406	90.3	33	12.9	2.74	15.64	123.3	1.2	47	17	4.6	0.71	0	0.007	0	0.02	0.04	3.3	4.7	8.3	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27A	10	398	90	74.5	14	0.59	14.59	126	1.2	44	18	3.6	0.54	0.01	0.006	0	0.03	0.04	3.3	4.3	8	0.03
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27B	10	409	90.2	74	13.5	0	13.23	123	1.2	43	18	4.7	0.57	0.01	0.007	0	0.03	0.04	3.3	4.3	8.1	0.03
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28A	10	272	90.5	0	7.7	0.75	8.45	145.1	1.1	38.8	15	4.9	1.3	0.01	0.025	0	0.04	0.1	3	8.1	8.9	0.04
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28B	10	265	90.3	1	8	0.12	8.12	140.8	1.1	39.2	15	5.8	1.2	0	0.024	0	0.04	0.09	3.1	7.9	9	0.04
Δ Temperature - 90 oC	25A	10	365	90.2	28	13.7	0.3	14	149	1.1	47	18	4.4	0.65	0	0.06	0	0.02	0.05	3.3	4.6	8.4	0.02
Δ Temperature - 90 oC	25B	10	406	90.3	33	12.9	2.74	15.64	123.3	1.2	47	17	4.6	0.71	0	0.007	0	0.02	0.04	3.3	4.7	8.3	0.02
Δ Temperature - 60 oC	29A	10	454	59.9	34	7.3	6.25	13.55	122.4	1.2	46	17	3.3	0.59	0.01	0.012	0	0.02	0.04	3.3	4.5	9.6	0.02
Δ Temperature - 60 oC	29B	10	456	60	38	8.1	5.82	13.92	121.6	1.2	47	17	4.4	0.59	0.01	0.011	0	0.02	0.04	3.3	4.5	9.6	0.02
Δ Temperature - 30 oC	30A	10	464	29.7	13.5	3.9	5.48	9.38	125.4	1.2	42	16	0.043	0.91	0.01	0.024	0	0.03	0.05	3.2	7	9.8	0.03
Δ Temperature - 30 oC	30B	10	492	30.4	29	4.5	7.78	12.28	114.5	1	49	17	0.049	0.36	0.01	0.012	0	0.02	0.05	3.3	4.7	10.6	0.03
Δ PbCon - 0.6 Ratio	25A	10	365	90.2	28	13.7	0.3	14	149	1.1	47	18	4.4	0.65	0	0.06	0	0.02	0.05	3.3	4.6	8.4	0.02
Δ PbCon - 0.6 Ratio	25B	10	406	90.3	33	12.9	2.74	15.64	123.3	1.2	47	17	4.6	0.71	0	0.007	0	0.02	0.04	3.3	4.7	8.3	0.02
Δ PbCon - 1 Ratio	31A	10	158	90.3	33.5	14.4	0.66	15.06	171.3	0.86	46	19	2	0.43	0	0.007	0	0.02	0.1	3.6	4.6	9.6	0.03
Δ PbCon - 0.2 Ratio	31B	10	514	90.3	61	5.1	8.75	13.85	68.5	2.1	44	13	5.8	0.82	0.01	0.005	0	0.03	0.04	2.5	3.2	6.1	0.04
Δ PbS - 0.6 Ratio	32A	10	237	89.9	44	14.3	0.48	14.78	136.3	1.2	59	13	5.4	0.48	0	0.004	0	0.02	0.09	0.59	0.57	1.8	0.02
Δ PbS - 0.35 Ratio	32B	10	361	90.2	6.5	8.7	1.21	9.91	101.7	1.6	44	11	7.4	1.7	0	0.017	0	0.04	0.07	0.89	5.7	3.2	0.03
Δ PbS - 0.12 Ratio	32C	10	511	90.2	36	3.2	9.65	12.85	56.3	2.7	44	10	7.3	1.6	0	0.011	0	0.04	0.05	1.2	3.5	4.2	0.02
Δ PbS - 0.6 Ratio	33A	10	not taken	92.3	33	16	0	15.01	118.9	1.3	57	12	5.9	0.63	0.01	0.006	0	0.03	0.1	0.63	0.84	2.1	0.02
Δ PbS - 0.35 Ratio	33B	10	441	90.2	46	11.9	3.26	15.16	83	1.8	52	11	6.6	0.88	0	0.004	0	0.03	0.05	0.97	1.4	2.6	0.03
Δ PbS - 0.12 Ratio	33C	10	516	91	59.5	6.3	8.49	14.79	58.7	2.2	51	9.9	6.7	0.95	0.01	0.008	0	0.04	0.05	1.2	1.8	3.3	0.03
Δ As + 10 g/L	34A	10	404	90.1	44	10.8	1.96	12.76	100	1.6	44	16	4.7	1.8	0	0.011	0	0.03	0.04	3.4	4.5	7.6	0.03
Δ As + 5 g/L	34B	10	420	90.3	39	11	2.56	13.56	136.6	1.1	46	17	2.9	1	0.01	0.008	0	0.02	0.04	3.3	4.6	8.2	0.03
Δ As + 10 g/L	35A	10	367	90.3	44	13.4	1.26	14.66	117.1	1.2	46	17	3.7	1.3	0.01	0.011	0	0.03	0.05	3.3	4.8	8.6	0.02
Δ As + 5 g/L	35B	10	373	90.3	39	14	0.36	14.36	120.9	1.1	44	16	3.8	1	0	0.01	0	0.03	0.05	3.2	4.5	8.4	0.03

**Table J. 7: Liquids 30 min**

		Time min	ORP m/V	Temp oC	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn mg/L	Pb mg/L	S g/L	SO <sub>4</sub> /S g/L	As mg/L	Cl mg/L	F mg/L	MgSO <sub>4</sub> mg/L	Mn mg/L	Cu mg/L	SiO <sub>2</sub> mg/L	Al mg/L	Ca mg/L	Sb mg/L
<b>Baseline</b>	<b>Test #</b>	<b>0</b>	426	90	100	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	0	0		100	0	0	0	0	0	0	0	0	0	0
Baseline	25A	30	283	90.3	25.6	14.6	0.3	14.9	125.3	4	13	34	35	1100	30	160	1600	610	1	1400	2500	210	190
Baseline	25B	30	223	90.1	31	15	0	14.51	119	8	15	35	38	1200	40	150	1600	620	1	1400	2400	210	200
Δ As - Baseline Repeat	34C	30	277	90.4	30	13.9	0	13.9	138.9	4	13	34	37	960	40	160	1500	620	6	1300	2500	220	190
Baseline	26A	30	60	90.3	35.5	14.6	0	14.36	106.8	9	13	38	39	1700	40	150	1600	600	1	1500	2400	220	220
Baseline	26B	30	172	90.3	38.5	14.2	0	14.09	123.5	7	13	38	39	1400	40	150	1600	610	1	1400	2400	210	210
Δ As - Baseline Repeat	35C	30	153	90.1	28.5	15.2	0	14.71	120.7	4	21	35	38	990	45	160	1500	610	1	1300	2500	220	230
Δ H2SO4 - 100 g/L	25A	30	283	90.3	25.6	14.6	0.3	14.9	125.3	4	13	34	35	1100	30	160	1600	610	1	1400	2500	210	190
Δ H2SO4 - 100 g/L	25B	30	223	90.1	31	14.8	0	14.51	118.6	8	15	35	38	1200	40	150	1600	620	1	1400	2400	210	200
Δ H2SO4 - 160 g/L	27A	30	195	90.3	77.5	15	0.13	15.13	126.9	11	12	51	54	1400	40	150	1600	600	1	1100	2500	220	230
Δ H2SO4 - 160 g/L	27B	30	199	90.1	76.5	15	0	13.95	124.5	11	12	51	53	1600	40	150	1600	610	1	1200	2400	220	240
Δ H2SO4 - 40 g/L	28A	30	176	90.3	0	9.2	0.55	9.75	143.1	1	11	18	20	12	40	140	1600	620	1	1000	1200	120	11
Δ H2SO4 - 40 g/L	28B	30	161	90.1	0	9.1	0	8.54	136.1	1	10	18	17	10	40	120	1500	580	1	920	1100	110	10
Δ Temperature - 90 oC	25A	30	283	90.3	25.6	14.6	0.3	14.9	125.3	4	13	34	35	1100	30	160	1600	610	1	1400	2500	210	190
Δ Temperature - 90 oC	25B	30	223	90.1	31	14.8	0	14.51	118.6	8	15	35	38	1200	40	150	1600	620	1	1400	2400	210	200
Δ Temperature - 60 oC	29A	30	429	59.8	31	9.7	4.83	14.53	121.3	28	17	33	36	1000	40	150	1600	600	130	1400	2400	200	210
Δ Temperature - 60 oC	29B	30	424	59.9	28	10.8	2.79	13.59	123.2	26	17	34	37	960	40	160	1600	600	130	1300	2400	210	200
Δ Temperature - 30 oC	30A	30	440	30.2	9	5.1	4.2	9.3	135.6	61	30	22	24	570	35	140	1500	590	120	1200	2000	120	130
Δ Temperature - 30 oC	30B	30	461	30.6	28	5.3	6.78	12.08	115.3	310	27	29	30	1600	40	130	1500	560	100	1400	2200	180	360
Δ PbCon - 0.6 Ratio	25A	30	283	90.3	25.6	14.6	0.3	14.9	125.3	4	13	34	35	1100	30	160	1600	610	1	1400	2500	210	190
Δ PbCon - 0.6 Ratio	25B	30	223	90.1	31	14.8	0	14.51	118.6	8	15	35	38	1200	40	150	1600	620	1	1400	2400	210	200
Δ PbCon - 1 Ratio	31A	30	148	90.2	32	14.8	0.73	15.53	171.3	5	12	34	38	1400	30	160	1600	600	1	1400	2400	280	170
Δ PbCon - 0.2 Ratio	31B	30	493	90	53.5	7.1	6.64	13.74	67.1	36	17	38	44	920	40	150	1600	630	150	1300	2400	170	270
Δ PbS - 0.6 Ratio	32A	30	179	90.2	45.5	14.8	0.26	15.06	125.4	6	9	39	42	1200	50	150	1600	610	1	1200	2500	110	130
Δ PbS - 0.35 Ratio	32B	30	312	90.1	4.5	10.3	0.49	10.79	96.2	1	10	21	24	59	20	150	1600	610	13	1400	2300	99	22
Δ PbS - 0.12 Ratio	32C	30	507	90.2	36	3.6	9.06	12.66	55.5	35	16	31	34	1200	40	140	1600	600	110	1500	2500	110	140
Δ PbS - 0.6 Ratio	33A	30	196	91.8	32	16.5	0	15.36	108.3	7	12	36	37	1400	70	140	1600	610	1	1300	2400	110	140
Δ PbS - 0.35 Ratio	33B	30	432	90.3	46	12.9	2.43	15.33	84.7	11	13	40	41	1000	55	140	1600	640	120	1300	2500	120	180
Δ PbS - 0.12 Ratio	33C	30	513	90	58.5	6.7	8.19	14.89	54.3	43	14	40	43	1100	40	140	1600	640	130	1300	2500	130	260
Δ As + 10 g/L	34A	30	338	90.1	40.5	13.5	0.1	13.6	105.4	24	16	33	37	8800	40	170	1500	610	130	1400	2500	210	190
Δ As + 5 g/L	34B	30	297	90.2	37	13.8	0.27	14.07	139.7	16	13	34	38	4900	40	160	1500	610	61	1400	2400	210	210
Δ As + 10 g/L	35A	30	268	89.9	42	15	0.4	15.4	117.9	31	15	33	37	9000	35	160	1500	610	7	1400	2400	210	240
Δ As + 5 g/L	35B	30	152	90.2	36.5	15.4	0	15.17	120.6	16	12	34	37	4900	40	160	1600	630	1	1400	2500	220	230

Table J. 8: Solids 30 min

		Time min	ORP m/V	Temp oC	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn wt%	Pb wt%	S wt%	SO <sub>4</sub> /S w%	As w%	Cl w%	F w%	MgSO <sub>4</sub> w%	Mn w%	Cu w%	SiO <sub>2</sub> w%	Fe w%	Zn w%	MgO w%
<b>Baseline</b>	<b>Test #</b>	<b>0</b>	426	90	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Baseline	25A	30	283	90.3	25.6	14.6	0.3	14.9	125.3	1.3	46	17	4.5	0.61	0	0.005	0	0.02	0.12	3.4	4.2	8	0.02
Baseline	25B	30	223	90.1	31	15	0	14.51	119	1.4	46	17	4.6	0.63	0	0.006	0	0.02	0.12	3.4	4.2	7.9	0.02
Δ As - Baseline Repeat	34C	30	277	90.4	30	13.9	0	13.9	138.9	1.1	46	16	4.2	0.47	0	0.005	0	0.02	0.11	3.1	4.1	7.4	0.02
Baseline	26A	30	60	90.3	35.5	14.6	0	14.36	106.8	1.5	45	17	3.4	0.69	0	0.007	0	0.02	0.11	3.5	4.3	7.6	0.02
Baseline	26B	30	172	90.3	38.5	14.2	0	14.09	123.5	1.3	47	18	4.3	0.6	0	0.006	0	0.02	0.11	3.5	4.2	8	0.02
Δ As - Baseline Repeat	35C	30	153	90.1	28.5	15.2	0	14.71	120.7	1.3	47	17	3.7	0.53	0	0.015	0	0.02	0.12	3.4	4.1	8.1	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25A	30	283	90.3	25.6	14.6	0.3	14.9	125.3	1.3	46	17	4.5	0.61	0	0.005	0	0.02	0.12	3.4	4.6	8	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25B	30	223	90.1	31	14.8	0	14.51	118.6	1.4	46	17	4.6	0.63	0	0.006	0	0.02	0.12	3.4	4.7	7.9	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27A	30	195	90.3	77.5	15	0.13	15.13	126.9	1.3	45	18	3.4	0.54	0.01	0.006	0	0.02	0.11	3.5	4	7.8	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27B	30	199	90.1	76.5	15	0	13.95	124.5	1.3	43	18	4.5	0.57	0.01	0.007	0	0.02	0.1	3.7	3.9	7.7	0.03
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28A	30	176	90.3	0	9.2	0.55	9.75	143.1	1.1	38.1	15	5.3	1.3	0	0.03	0	0.04	0.1	3.1	7.4	8.9	0.04
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28B	30	161	90.1	0	9.1	0	8.54	136.1	1.1	37.6	15	5.5	1.2	0	0.028	0	0.04	0.1	3.1	7.1	9	0.04
Δ Temperature - 90 oC	25A	30	283	90.3	25.6	14.6	0.3	14.9	125.3	1.3	46	17	4.5	0.61	0	0.005	0	0.02	0.12	3.4	4.6	8	0.02
Δ Temperature - 90 oC	25B	30	223	90.1	31	14.8	0	14.51	118.6	1.4	46	17	4.6	0.63	0	0.006	0	0.02	0.12	3.4	4.7	7.9	0.02
Δ Temperature - 60 oC	29A	30	429	59.8	31	9.7	4.83	14.53	121.3	1.3	44	17	3.6	0.71	0.01	0.009	0	0.03	0.04	3.2	4.5	9	0.03
Δ Temperature - 60 oC	29B	30	424	59.9	28	10.8	2.79	13.59	123.2	1.3	46	17	4.7	0.7	0.01	0.009	0	0.03	0.04	3.3	4.5	9.1	0.03
Δ Temperature - 30 oC	30A	30	440	30.2	9	5.1	4.2	9.3	135.6	1.2	42	16	0.047	0.97	0.01	0.022	0	0.03	0.05	3.2	7	9.6	0.03
Δ Temperature - 30 oC	30B	30	461	30.6	28	5.3	6.78	12.08	115.3	1.1	48	17	0.052	0.41	0.01	0.012	0	0.02	0.05	3.4	4.8	10.5	0.03
Δ PbCon - 0.6 Ratio	25A	30	283	90.3	25.6	14.6	0.3	14.9	125.3	1.3	46	17	4.5	0.61	0	0.005	0	0.02	0.12	3.4	4.6	8	0.02
Δ PbCon - 0.6 Ratio	25B	30	223	90.1	31	14.8	0	14.51	118.6	1.4	46	17	4.6	0.63	0	0.006	0	0.02	0.12	3.4	4.7	7.9	0.02
Δ PbCon - 1 Ratio	31A	30	148	90.2	32	14.8	0.73	15.53	171.3	0.83	45	18	3.2	0.41	0	0.007	0	0.02	0.1	3.5	4.5	9.4	0.03
Δ PbCon - 0.2 Ratio	31B	30	493	90	53.5	7.1	6.64	13.74	67.1	2.3	45	14	5.7	0.96	0	0.006	0	0.03	0.04	2.8	3.3	5.4	0.04
Δ PbS - 0.6 Ratio	32A	30	179	90.2	45.5	14.8	0.26	15.06	125.4	1.2	58	13	5.6	0.49	0	0.004	0	0.02	0.09	0.66	0.53	1.8	0.02
Δ PbS - 0.35 Ratio	32B	30	312	90.1	4.5	10.3	0.49	10.79	96.2	1.7	43	10	7.9	1.7	0	0.015	0	0.04	0.08	0.9	5	3.2	0.02
Δ PbS - 0.12 Ratio	32C	30	507	90.2	36	3.6	9.06	12.66	55.5	2.9	45	9.7	8	1.6	0	0.01	0	0.04	0.05	1.2	3.5	4.1	0.03
Δ PbS - 0.6 Ratio	33A	30	196	91.8	32	16.5	0	15.36	108.3	1.5	56	12	6.4	0.64	0.01	0.004	0	0.02	0.1	0.7	0.7	2.1	0.02
Δ PbS - 0.35 Ratio	33B	30	432	90.3	46	12.9	2.43	15.33	84.7	1.7	51	11	5.9	0.86	0	0.005	0	0.03	0.04	0.98	1.4	2.5	0.03
Δ PbS - 0.12 Ratio	33C	30	513	90	58.5	6.7	8.19	14.89	54.3	2.4	50	9.9	6.9	1	0	0.008	0	0.04	0.04	1.3	1.8	3.3	0.03
Δ As + 10 g/L	34A	30	338	90.1	40.5	13.5	0.1	13.6	105.4	1.5	43	17	4.7	1.5	0	0.01	0	0.03	0.05	3.3	4.3	7.2	0.03
Δ As + 5 g/L	34B	30	297	90.2	37	13.8	0.27	14.07	139.7	1.1	47	17	3.1	0.77	0.01	0.006	0	0.02	0.08	3.2	4.3	7.8	0.02
Δ As + 10 g/L	35A	30	268	89.9	42	15	0.4	15.4	117.9	1.2	45	17	4	1.1	0.01	0.01	0	0.03	0.12	3.3	4.3	8.3	0.02
Δ As + 5 g/L	35B	30	152	90.2	36.5	15.4	0	15.17	120.6	1.2	46	16	3.2	0.86	0.01	0.009	0	0.03	0.12	3.3	4.1	8.2	0.02

**Table J. 9: Liquids 60 min**

		Time min	ORP m/V	Temp 0C	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn mg/L	Pb mg/L	S g/L	SO <sub>4</sub> /S g/L	As mg/L	Cl mg/L	F mg/L	MgSO <sub>4</sub> mg/L	Mn mg/L	Cu mg/L	SiO <sub>2</sub> mg/L	Al mg/L	Ca mg/L	Sb mg/L
<b>Baseline</b>	<b>Test #</b>	<b>0</b>	426	90	100	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	0	0		100	0	0	0	0	0	0	0	0	0	0
Baseline	25A	60	163	90.2	25	15	0.3	15.3	120.9	3	14	34	35	1100	40	160	1600	610	1	1300	2500	210	170
Baseline	25B	60	93	90.4	30.5	15	0	14.92	126	6	14	36	38	1300	40	150	1600	620	1	1300	2500	220	190
Δ As - Baseline Repeat	34C	60	144	90	27.5	14.1	0	13.58	120.1	3	13	33	38	1000	40	160	1600	620	1	1300	2500	220	180
Baseline	26A	60	(-77) / 211	90.6	36	14.8	0	14.53	108.5	8	13	37	40	1700	40	140	1600	590	1	1400	2400	220	200
Baseline	26B	60	162	90.1	40	14.3	0	14.19	112.5	6	12	37	40	1500	40	140	1600	610	1	1300	2400	220	190
Δ As - Baseline Repeat	35C	60	141	90	27.5	15.3	0	14.93	125.7	3	14	35	39	1000	45	160	1500	610	1	1200	2500	220	220
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25A	60	163	90.2	25	15	0.3	15.3	120.9	3	14	34	35	1100	40	160	1600	610	1	1300	2500	210	170
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25B	60	93	90.4	30.5	15.2	0	14.92	126	6	14	36	38	1300	40	150	1600	620	1	1300	2500	220	190
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27A	60	192	90	74	14.8	0	14.74	121.8	8	11	50	55	1400	40	150	1600	610	1	950	2500	230	200
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27B	60	192	90.3	72.5	14.7	0	14.85	112.3	8	12	50	54	1600	40	150	1600	610	1	1000	2400	230	210
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28A	60	142	90.4	0	9.8	0.61	10.41	136.7	1	11	18	20	12	40	130	1700	650	1	900	960	120	8
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28B	60	137	90.3	0	9.9	0	9.44	140	1	11	19	20	11	40	140	1600	620	1	830	920	120	9
Δ Temperature - 90 oC	25A	60	163	90.2	25	15	0.3	15.3	120.9	3	14	34	35	1100	40	160	1600	610	1	1300	2500	210	170
Δ Temperature - 90 oC	25B	60	93	90.4	30.5	15.2	0	14.92	126	6	14	36	38	1300	40	150	1600	620	1	1300	2500	220	190
Δ Temperature - 60 oC	29A	60	378	61	32	11.6	1.94	13.54	122.7	9	15	34	36	1000	40	150	1600	620	130	1300	2500	230	170
Δ Temperature - 60 oC	29B	60	378	60	30	12.6	0.92	13.22	108.3	8	13	33	36	930	50	150	1600	610	130	1300	2400	220	170
Δ Temperature - 30 oC	30A	60	424	30.3	6.5	6.2	2.89	9.09	135.6	26	21	22	23	390	40	140	1500	590	120	1200	2100	130	98
Δ Temperature - 30 oC	30B	60	447	30.5	27	6.5	5.89	12.39	117.5	250	27	30	31	1500	30	140	1500	580	110	1500	2300	190	330
Δ PbCon - 0.6 Ratio	25A	60	163	90.2	25	15	0.3	15.3	120.9	3	14	34	35	1100	40	160	1600	610	1	1300	2500	210	170
Δ PbCon - 0.6 Ratio	25B	60	93	90.4	30.5	15.2	0	14.92	126	6	14	36	38	1300	40	150	1600	620	1	1300	2500	220	190
Δ PbCon - 1 Ratio	31A	60	147	90.3	30.5	15.5	0	15.29	186.9	7	11	34	38	1400	40	160	1600	600	1	1300	2400	280	160
Δ PbCon - 0.2 Ratio	31B	60	475	89.9	53.5	8.6	4.72	13.32	58.7	25	13	39	45	890	30	160	1600	640	150	1200	2500	170	250
Δ PbS - 0.6 Ratio	32A	60	177	90.2	41	15.6	0	14.21	109.5	8	10	39	41	1200	50	160	1600	620	1	1200	2500	120	140
Δ PbS - 0.35 Ratio	32B	60	294	90.2	4	10.5	0	10.29	95.9	< 1	9	21	24	71	10	140	1500	600	6	1300	2200	100	20
Δ PbS - 0.12 Ratio	32C	60	503	90.3	35.5	3.6	8.9	12.5	57.2	33	15	30	31	1200	40	140	1600	600	110	1400	2400	110	130
Δ PbS - 0.6 Ratio	33A	60	189	90.3	31.5	16.6	0	15.84	112.3	7	13	35	38	1400	70	140	1600	610	1	1300	2400	110	140
Δ PbS - 0.35 Ratio	33B	60	430	90	45	13.2	1.78	14.98	88.4	10	11	40	41	1000	55	140	1600	650	130	1200	2500	120	170
Δ PbS - 0.12 Ratio	33C	60	512	90.2	58	6.6	8.16	14.76	52	39	13	39	43	1100	40	130	1600	640	130	1200	2500	130	250
Δ As + 10 g/L	34A	60	144	90.4	39	14.2	0.04	14.24	106.6	33	15	33	37	9000	40	170	1500	620	1	1400	2500	220	270
Δ As + 5 g/L	34B	60	140	90.1	35	14.5	0	14.2	139.2	12	14	34	37	5200	40	160	1600	640	1	1400	###	220	240
Δ As + 10 g/L	35A	60	141	90.6	40.5	16	0	14.79	117.2	25	15	36	38	9400	30	160	1700	680	1	1400	2500	220	260
Δ As + 5 g/L	35B	60	142	90.1	35	15.5	0	15.22	121.9	10	13	33	37	5000	40	170	1600	640	1	1400	2500	220	220

**Table J.10: Solids 60 min**

		Time min	ORP mV	Temp oC	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn wt%	Pb wt%	S wt%	SO <sub>4</sub> /S w%	As w%	Cl w%	F w%	MgSO <sub>4</sub> w%	Mn w%	Cu w%	SiO <sub>2</sub> w%	Fe w%	Zn w%	MgO w%
<b>Baseline</b>	<b>Test #</b>	<b>0</b>	426	90	100	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Baseline	25A	60	163	90.2	25	15	0.3	15.3	120.9	1.3	46	18	4.7	0.61	0.61	0.005	0	0.02	0.12	3.5	4.1	8	0.02
Baseline	25B	60	93	90.4	30.5	15	0	14.92	126	1.2	46	17	5.1	0.57	0	0.004	0	0.03	0.12	3.4	4.1	7.7	0.02
Δ As - Baseline Repeat	34C	60	144	90	27.5	14.1	0	13.58	120.1	1.3	45	17	4.4	0.52	0.01	0.006	0	0.02	0.13	3.4	4	7.7	0.02
Baseline	26A	60	<sup>(-77) /</sup> 211	90.6	36	14.8	0	14.53	108.5	1.4	45	18	3.7	0.65	0	0.007	0	0.02	0.11	3.6	4.3	7.8	0.03
Baseline	26B	60	162	90.1	40	14.3	0	14.19	112.5	1.3	46	18	3.2	0.6	0	0.006	0	0.02	0.11	3.6	4.2	7.9	0.02
Δ As - Baseline Repeat	35C	60	141	90	27.5	15.3	0	14.93	125.7	1.2	47	17	3.4	0.49	0	0.011	0	0.02	0.12	3.4	4.1	8	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25A	60	163	90.2	25	15	0.3	15.3	120.9	1.3	46	18	4.7	0.61	0.61	0.005	0	0.02	0.12	3.5	4.6	8	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25B	60	93	90.4	30.5	15.2	0	14.92	126	1.2	46	17	5.1	0.57	0	0.004	0	0.03	0.12	3.4	4.7	7.7	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27A	60	192	90	74	14.8	0	14.74	121.8	1.3	45	18	3.7	0.54	0.01	0.006	0	0.02	0.11	3.7	3.9	7.7	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27B	60	192	90.3	72.5	14.7	0	14.85	112.3	1.2	43	17	4.5	0.55	0	0.007	0	0.02	0.1	3.5	4	7.8	0.03
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28A	60	142	90.4	0	9.8	0.61	10.41	136.7	1.2	37.7	15	5.8	1.3	0	0.032	0	0.04	0.09	3.2	7	8.8	0.04
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28B	60	137	90.3	0	9.9	0	9.44	140	1.1	37.1	15	6	1.2	0.01	0.033	0	0.05	0.1	3.2	6.6	8.9	0.04
Δ Temperature - 90 oC	25A	60	163	90.2	25	15	0.3	15.3	120.9	1.3	46	18	4.7	0.61	0.61	0.005	0	0.02	0.12	3.5	4.6	8	0.02
Δ Temperature - 90 oC	25B	60	93	90.4	30.5	15.2	0	14.92	126	1.2	46	17	5.1	0.57	0	0.004	0	0.03	0.12	3.4	4.7	7.7	0.02
Δ Temperature - 60 oC	29A	60	378	61	32	11.6	1.94	13.54	122.7	1.3	45	17	3.7	0.71	0.01	0.009	0	0.02	0.04	3.3	4.4	8.7	0.03
Δ Temperature - 60 oC	29B	60	378	60	30	12.6	0.92	13.22	108.3	1.4	44	18	4.7	0.79	0.01	0.008	0	0.03	0.04	3.5	4.5	8.8	0.03
Δ Temperature - 30 oC	30A	60	424	30.3	6.5	6.2	2.89	9.09	135.6	1.1	42	16	0.05	1	0.01	0.021	0	0.03	0.05	3.1	6.8	9.5	0.03
Δ Temperature - 30 oC	30B	60	447	30.5	27	6.5	5.89	12.39	117.5	1.2	47	17	0.056	0.51	0.01	0.012	0	0.02	0.05	3.4	4.8	10.2	0.03
Δ PbCon - 0.6 Ratio	25A	60	163	90.2	25	15	0.3	15.3	120.9	1.3	46	18	4.7	0.61	0.61	0.005	0	0.02	0.12	3.5	4.6	8	0.02
Δ PbCon - 0.6 Ratio	25B	60	93	90.4	30.5	15.2	0	14.92	126	1.2	46	17	5.1	0.57	0	0.004	0	0.03	0.12	3.4	4.7	7.7	0.02
Δ PbCon - 1 Ratio	31A	60	147	90.3	30.5	15.5	0	15.29	186.9	0.82	45	18	3	0.38	0	0.006	0	0.02	0.1	3.5	4.4	9.3	0.03
Δ PbCon - 0.2 Ratio	31B	60	475	89.9	53.5	8.6	4.72	13.32	58.7	2.5	42	14	6.1	1	0	0.006	0	0.04	0.04	2.9	3.2	4.6	0.04
Δ PbS - 0.6 Ratio	32A	60	177	90.2	41	15.6	0	14.21	109.5	1.4	55	13	5.1	0.51	0	0.004	0	0.02	0.1	0.79	0.52	2	0.02
Δ PbS - 0.35 Ratio	32B	60	294	90.2	4	10.5	0	10.29	95.9	1.6	44	10	7.8	1.6	0	0.014	0	0.04	0.08	0.9	4.3	3	0.03
Δ PbS - 0.12 Ratio	32C	60	503	90.3	35.5	3.6	8.9	12.5	57.2	2.8	45	9.4	8.1	1.7	0.01	0.011	0	0.04	0.05	1.3	3.8	4.2	0.03
Δ PbS - 0.6 Ratio	33A	60	189	90.3	31.5	16.6	0	15.84	112.3	1.3	55	12	6.9	0.58	0.01	0.003	0	0.02	0.1	0.7	0.61	1.9	0.02
Δ PbS - 0.35 Ratio	33B	60	430	90	45	13.2	1.78	14.98	88.4	1.7	52	10	6	0.85	0	0.006	0	0.03	0.04	1	1.4	2.4	0.02
Δ PbS - 0.12 Ratio	33C	60	512	90.2	58	6.6	8.16	14.76	52	2.3	49	9.5	6.7	1	0	0.008	0	0.04	0.04	1.4	1.8	3.1	0.03
Δ As + 10 g/L	34A	60	144	90.4	39	14.2	0.04	14.24	106.6	1.4	44	17	4	1.3	0.01	0.007	0	0.03	0.13	3.5	4	7.2	0.03
Δ As + 5 g/L	34B	60	140	90.1	35	14.5	0	14.2	139.2	1.1	47	17	3.1	0.72	0.01	0.006	0	0.02	0.12	3.3	4.1	7.7	0.02
Δ As + 10 g/L	35A	60	141	90.6	40.5	16	0	14.79	117.2	1.2	46	17	3.9	1.1	0.01	0.013	0	0.03	0.13	3.4	4.2	8.3	0.02
Δ As + 5 g/L	35B	60	142	90.1	35	15.5	0	15.22	121.9	1.2	45	16	3.4	0.85	0.01	0.008	0	0.03	0.13	3.3	4	8.1	0.02

**Table J.11: Liquids 100 min**

		Time min	ORP m/V	Temp oC	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn mg/L	Pb mg/L	S g/L	SO <sub>4</sub> /S g/L	As mg/L	Cl mg/L	F mg/L	MgSO <sub>4</sub> mg/L	Mn mg/L	Cu mg/L	SiO <sub>2</sub> mg/L	Al mg/L	Ca mg/L	Sb mg/L
<b>Baseline</b>	<b>Test #</b>	<b>0</b>	426	90	100	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	0	0		100	0	0	0	0	0	0	0	0	0	0
Baseline	25A	100	133	90.3	23.5	15.3	0.3	15	120	2	13	33	35	1100	46	160	1600	610	1	1200	2500	220	150
Baseline	25B	100	79	91	31	15	0	14.77	120	6	13	36	37	1300	30	150	1600	610	1	1200	2400	210	170
Δ As - Baseline Repeat	34C	100	135	90.2	28	14.6	0	14.36	136.4	3	12	34	38	1000	40	160	1600	640	1	1200	2500	230	160
Baseline	26A	100	143	90.8	35	15.2	0	14.76	113.3	8	13	38	40	1700	40	150	1700	590	1	1300	2400	230	180
Baseline	26B	100	162	90.2	35.5	14.5	0	14.27	123	6	12	37	41	1500	40	140	1600	610	1	1200	2400	220	170
Δ As - Baseline Repeat	35C	100	144	90.1	27.5	16	0	15.25	125.3	3	14	35	38	1000	45	170	1500	620	1	1100	2500	220	200
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25A	100	133	90.3	23.5	15.3	0.3	15	120	2	13	33	35	1100	46	160	1600	610	1	1200	2500	220	150
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25B	100	79	91	31	15.2	0	14.77	119.5	6	13	36	37	1300	30	150	1600	610	1	1200	2400	210	170
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27A	100	194	90.4	85.5	15.4	0	15.31	124	8	9	50	55	1400	40	160	1600	620	1	740	2500	240	170
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27B	100	191	90.4	74.5	15.5	0	14.96	119.9	9	12	51	53	1600	50	150	1700	620	1	920	2400	240	190
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28A	100	147	90.5	0	9.9	1.23	10.13	143.1	1	10	18	18	10	40	120	1600	600	1	740	790	120	6
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28B	100	130	90.4	0	11.6	0	9.72	134	1	11	18	19	10	40	130	1600	620	1	720	730	120	8
Δ Temperature - 90 oC	25A	100	133	90.3	23.5	15.3	0.3	15	120	2	13	33	35	1100	46	160	1600	610	1	1200	2500	220	150
Δ Temperature - 90 oC	25B	100	79	91	31	15.2	0	14.77	119.5	6	13	36	37	1300	30	150	1600	610	1	1200	2400	210	170
Δ Temperature - 60 oC	29A	100	296	60.2	29	13.6	0.13	13.73	118.9	8	11	34	36	1100	40	160	1600	620	100	1300	2400	220	180
Δ Temperature - 60 oC	29B	100	287	59.9	28	13.4	0.47	13.87	120.8	5	12	33	37	1000	40	160	1500	600	95	1200	2300	220	180
Δ Temperature - 30 oC	30A	100	412	30.1	6	7.3	1.77	9.07	141.8	11	17	21	22	260	45	140	1500	580	120	1200	2000	130	83
Δ Temperature - 30 oC	30B	100	437	30.1	25	7.4	5.26	12.66	120.8	160	25	30	31	1300	30	140	1600	580	110	1500	2300	210	280
Δ PbCon - 0.6 Ratio	25A	100	133	90.3	23.5	15.3	0.3	15	120	2	13	33	35	1100	46	160	1600	610	1	1200	2500	220	150
Δ PbCon - 0.6 Ratio	25B	100	79	91	31	15.2	0	14.77	119.5	6	13	36	37	1300	30	150	1600	610	1	1200	2400	210	170
Δ PbCon - 1 Ratio	31A	100	147	89.9	31.5	16.3	0	15.56	179.5	5	12	34	37	1500	40	160	1600	610	1	1200	2500	290	190
Δ PbCon - 0.2 Ratio	31B	100	460	90	50.5	10.1	3.88	13.98	71.3	17	14	39	45	870	40	160	1600	640	160	1100	2500	170	230
Δ PbS - 0.6 Ratio	32A	100	188	90	42	15.6	0	15.07	119.2	9	9	39	41	1300	50	150	1600	620	1	1100	2500	130	150
Δ PbS - 0.35 Ratio	32B	100	282	90.2	3.5	10.7	0.15	10.85	104.9	1	10	21	23	74	40	140	1600	610	3	1300	2300	100	18
Δ PbS - 0.12 Ratio	32C	100	502	90.4	35	3.7	8.93	12.63	59	29	15	31	35	1200	40	140	1600	600	110	1400	2400	120	120
Δ PbS - 0.6 Ratio	33A	100	192	90.2	30.5	171	0	15.84	111	4	12	35	38	1400	70	140	1600	610	1	1200	2400	120	140
Δ PbS - 0.35 Ratio	33B	100	428	90.2	43.5	13.3	1.96	15.26	72.1	8	11	40	42	1000	60	140	1600	640	120	1200	2500	130	170
Δ PbS - 0.12 Ratio	33C	100	512	90.1	58.5	6.8	8.11	14.91	56	38	10	40	44	1100	40	140	1600	630	130	1200	2500	130	240
Δ As + 10 g/L	34A	100	147	89.9	38	14.9	0	14.23	125.2	23	14	34	37	9100	40	170	1600	630	1	1300	2600	230	260
Δ As + 5 g/L	34B	100	139	90.2	35	14.7	0	14.58	143.7	9	12	34	36	5100	40	160	1600	620	1	1400	2500	220	210
Δ As + 10 g/L	35A	100	144	90	39	16.1	0	15.66	119.7	19	13	33	38	8900	35	160	1500	610	1	1300	2400	220	240
Δ As + 5 g/L	35B	100	150	90	35	16.4	0	15.43	125.7	9	13	34	36	4900	45	160	1600	640	1	1300	2500	220	200



Table J.12: Solids 100 min

		Time min	ORP m/V	Temp oC	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn wt%	Pb wt%	S wt%	SO <sub>4</sub> /S w%	As w%	Cl w%	F w%	MgSO <sub>4</sub> w%	Mn w%	Cu w%	SiO <sub>2</sub> w%	Fe w%	Zn w%	MgO w%
<b>Baseline</b>	<b>Test #</b>	<b>0</b>	426	90	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Baseline	25A	100	133	90.3	23.5	15.3	0.3	15	120	1.3	46	17	4.3	0.6	0	0.005	0	0.02	0.13	3.6	4.1	7.8	0.02
Baseline	25B	100	79	91	31	15	0	14.77	120	1.3	46	18	4.5	0.59	0.01	0.008	0	0.02	0.12	3.5	4	7.7	0.02
Δ As - Baseline Repeat	34C	100	135	90.2	28	14.6	0	14.36	136.4	1.2	48	17	4.2	0.48	0	0.006	0	0.02	0.13	3.4	4.1	7.6	0.02
Baseline	26A	100	143	90.8	35	15.2	0	14.76	113.3	1.4	45	18	2.9	0.63	0	0.006	0	0.02	0.11	3.7	4.2	7.5	0.04
Baseline	26B	100	162	90.2	35.5	14.5	0	14.27	123	1.3	46	18	3.6	0.57	0	0.006	0	0.02	0.11	3.6	4.1	7.8	0.02
Δ As - Baseline Repeat	35C	100	144	90.1	27.5	16	0	15.25	125.3	1.3	47	17	3.9	0.5	0	0.008	0	0.02	0.12	3.5	4	8.1	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25A	100	133	90.3	23.5	15.3	0.3	15	120	1.3	46	17	4.3	0.6	0	0.005	0	0.02	0.13	3.6	4.6	7.8	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25B	100	79	91	31	15.2	0	14.77	119.5	1.3	46	18	4.5	0.59	0.01	0.008	0	0.02	0.12	3.5	4.7	7.7	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27A	100	194	90.4	85.5	15.4	0	15.31	124	1.1	42	18	4.9	0.51	0	0.006	0	0.03	0.1	3.5	3.9	7.5	0.03
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27B	100	191	90.4	74.5	15.5	0	14.96	119.9	1.3	43	17	4.6	0.55	0	0.007	0	0.02	0.1	3.7	3.8	7.6	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28A	100	147	90.5	0	9.9	1.23	10.13	143.1	1.1	38.4	15	5.3	1.3	0	0.026	0	0.04	0.1	3.3	6.7	8.9	0.04
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28B	100	130	90.4	0	11.6	0	9.72	134	1.2	36.7	15	5.9	1.3	0.01	0.035	0	0.04	0.1	3.3	6.6	8.9	0.04
Δ Temperature - 90 oC	25A	100	133	90.3	23.5	15.3	0.3	15	120	1.3	46	17	4.3	0.6	0	0.005	0	0.02	0.13	3.6	4.6	7.8	0.02
Δ Temperature - 90 oC	25B	100	79	91	31	15.2	0	14.77	119.5	1.3	46	18	4.5	0.59	0.01	0.008	0	0.02	0.12	3.5	4.7	7.7	0.02
Δ Temperature - 60 oC	29A	100	296	60.2	29	13.6	0.13	13.73	118.9	1.3	44	18	3.3	0.67	0.01	0.008	0	0.03	0.06	3.4	4.2	8.5	0.03
Δ Temperature - 60 oC	29B	100	287	59.9	28	13.4	0.47	13.87	120.8	1.3	44	18	5.1	0.63	0.01	0.006	0	0.02	0.06	3.3	4.1	8.4	0.02
Δ Temperature - 30 oC	30A	100	412	30.1	6	7.3	1.77	9.07	141.8	1.1	42	16	0.051	1.1	0.01	0.02	0	0.03	0.05	3.1	6.7	9.3	0.03
Δ Temperature - 30 oC	30B	100	437	30.1	25	7.4	5.26	12.66	120.8	1.2	49	18	0.059	0.64	0.01	0.012	0	0.02	0.04	3.5	5	10.3	0.03
Δ PbCon - 0.6 Ratio	25A	100	133	90.3	23.5	15.3	0.3	15	120	1.3	46	17	4.3	0.6	0	0.005	0	0.02	0.13	3.6	4.6	7.8	0.02
Δ PbCon - 0.6 Ratio	25B	100	79	91	31	15.2	0	14.77	119.5	1.3	46	18	4.5	0.59	0.01	0.008	0	0.02	0.12	3.5	4.7	7.7	0.02
Δ PbCon - 1 Ratio	31A	100	147	89.9	31.5	16.3	0	15.56	179.5	0.85	46	19	3.5	0.36	0	0.007	0	0.02	0.1	3.6	4.5	9.4	0.03
Δ PbCon - 0.2 Ratio	31B	100	460	90	50.5	10.1	3.88	13.98	71.3	2.2	45	14	6.7	0.96	0.01	0.007	0	0.04	0.04	2.9	3.1	3.9	0.04
Δ PbS - 0.6 Ratio	32A	100	188	90	42	15.6	0	15.07	119.2	1.3	55	13	5.7	0.44	0	0.004	0	0.02	0.1	0.76	0.49	1.8	0.02
Δ PbS - 0.35 Ratio	32B	100	282	90.2	3.5	10.7	0.15	10.85	104.9	1.5	47	11	7.8	1.6	0	0.014	0	0.04	0.09	0.88	4	2.9	0.02
Δ PbS - 0.12 Ratio	32C	100	502	90.4	35	3.7	8.93	12.63	59	2.7	44	9	8.1	1.6	0	0.011	0	0.04	0.04	1.2	3.7	4.1	0.03
Δ PbS - 0.6 Ratio	33A	100	192	90.2	30.5	17.1	0	15.84	111	1.4	57	12	7.2	0.59	0.01	0.004	0	0.02	0.1	0.77	0.59	2	0.02
Δ PbS - 0.35 Ratio	33B	100	428	90.2	43.5	13.3	1.96	15.26	72.1	1.9	48	9.8	5.9	0.98	0	0.007	0	0.04	0.04	1.1	1.4	2.7	0.03
Δ PbS - 0.12 Ratio	33C	100	512	90.1	58.5	6.8	8.11	14.91	56	2.4	48	9.3	6.3	1.1	0	0.007	0	0.04	0.04	1.5	2	3.3	0.03
Δ As + 10 g/L	34A	100	147	89.9	38	14.9	0	14.23	125.2	1.2	44	17	3.6	1.2	0.01	0.006	0	0.03	0.13	3.3	3.9	7.2	0.02
Δ As + 5 g/L	34B	100	139	90.2	35	14.7	0	14.58	143.7	1.1	47	17	3.1	0.71	0.01	0.006	0	0.02	0.12	3.2	4.1	7.7	0.02
Δ As + 10 g/L	35A	100	144	90	39	16.1	0	15.66	119.7	1.3	47	17	4.1	1.1	0.01	0.012	0	0.03	0.13	3.4	4.2	8.3	0.02
Δ As + 5 g/L	35B	100	150	90	35	16.4	0	15.43	125.7	1.2	46	17	3.9	0.82	0	0.008	0	0.02	0.13	3.4	4	8.1	0.02

**Table J.13: Liquids 150 min**

		Time min	ORP m/V	Temp oC	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn mg/L	Pb mg/L	S g/L	SO <sub>4</sub> /S g/L	As mg/L	Cl mg/L	F mg/L	MgSO <sub>4</sub> mg/L	Mn mg/L	Cu mg/L	SiO <sub>2</sub> mg/L	Al mg/L	Ca mg/L	Sb mg/L
<b>Baseline</b>	<b>Test #</b>	<b>0</b>	426	90	100	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	0	0		100	0	0	0	0	0	0	0	0	0	0
Baseline	25A	150	140	89.6	23.5	15.6	0.3	15.3	124.6	2	13	34	35	1200	45	160	1600	620	1	1200	2500	220	140
Baseline	25B	150	97	90.1	30.5	15.6	0	15.3	135	6	13	37	37	1300	40	160	1600	630	1	1200	2500	220	160
Δ As - Baseline Repeat	34C	150	145	90.2	27.5	15.0	0	14.41	133.2	3	13	34	37	1100	40	170	1600	640	1	1100	2600	230	150
Baseline	26A	150	138	90.3	34.5	16.0	0	15.4	121.2	7	13	37	39	1600	40	150	1600	600	1	1300	2400	230	140
Baseline	26B	150	152	90.3	34	18.2	0	15.09	121.6	6	13	37	41	1400	40	140	1600	620	1	1200	2400	220	130
Δ As - Baseline Repeat	35C	150	139	89.9	26.5	15.8	0	14.74	124.8	3	15	35	38	1100	40	160	1500	630	1	1100	2500	230	190
Δ H2SO4 - 100 g/L	25A	150	140	89.6	23.5	15.6	0.3	15.3	124.6	2	13	34	35	1200	45	160	1600	620	1	1200	2500	220	140
Δ H2SO4 - 100 g/L	25B	150	97	90.1	30.5	15.6	0	15.3	134.5	6	13	37	37	1300	40	160	1600	630	1	1200	2500	220	160
Δ H2SO4 - 160 g/L	27A	150	195	90.3	77.5	15.5	0	15.39	133	8	10	54	59	1500	40	170	1700	670	1	590	2700	260	170
Δ H2SO4 - 160 g/L	27B	150	192	90.5	73	15.8	0	15.02	105.5	8	10	51	54	1600	40	150	1700	620	1	740	2400	240	170
Δ H2SO4 - 40 g/L	28A	150	129	90.4	0	10	0.76	10.76	140.4	1	11	18	16	9	40	110	1700	620	1	690	650	120	7
Δ H2SO4 - 40 g/L	28B	150	121	90.1	0	10.3	0	10.22	143.7	1	10	19	21	9	40	120	1700	630	1	660	600	120	8
Δ Temperature - 90 oC	25A	150	140	89.6	23.5	15.6	0.3	15.3	124.6	2	13	34	35	1200	45	160	1600	620	1	1200	2500	220	140
Δ Temperature - 90 oC	25B	150	97	90.1	30.5	15.6	0	15.3	134.5	6	13	37	37	1300	40	160	1600	630	1	1200	2500	220	160
Δ Temperature - 60 oC	29A	150	280	60	33.5	13.6	0.24	13.84	129.9	7	10	33	36	1100	40	160	1500	590	61	1200	2300	220	180
Δ Temperature - 60 oC	29B	150	280	61	30	13.4	0.42	13.82	121.5	4	11	33	35	1100	40	150	1500	600	63	1200	2300	220	180
Δ Temperature - 30 oC	30A	150	401	29.9	4.5	8	1.04	9.04	165.9	6	14	22	21	170	40	140	1500	590	120	1200	2100	130	77
Δ Temperature - 30 oC	30B	150	429	29.9	23	8.4	3.86	12.26	124.1	110	19	29	31	1200	30	140	1500	580	110	1400	2300	210	250
Δ PbCon - 0.6 Ratio	25A	150	140	89.6	23.5	15.6	0.3	15.3	124.6	2	13	34	35	1200	45	160	1600	620	1	1200	2500	220	140
Δ PbCon - 0.6 Ratio	25B	150	97	90.1	30.5	15.6	0	15.3	134.5	6	13	37	37	1300	40	160	1600	630	1	1200	2500	220	160
Δ PbCon - 1 Ratio	31A	150	146	90.1	28.5	17	0	15.92	181.3	9	13	33	38	1600	40	170	1600	610	1	1200	2400	300	230
Δ PbCon - 0.2 Ratio	31B	150	445	89.6	50	11.4	2.93	14.33	71	12	12	40	45	850	40	160	1600	640	160	1100	2500	180	210
Δ PbS - 0.6 Ratio	32A	150	196	90.1	41	16.3	0	14.74	124.4	12	10	38	41	1300	10	150	1600	620	1	1100	2500	130	140
Δ PbS - 0.35 Ratio	32B	150	280	90	3	10.6	0.85	11.45	105.6	1	9	22	19	70	30	140	1600	610	3	1300	2200	110	17
Δ PbS - 0.12 Ratio	32C	150	503	90.3	35	3.7	8.67	12.37	68.5	27	15	31	34	1200	45	140	1600	610	120	1400	2500	120	110
Δ PbS - 0.6 Ratio	33A	150	198	90.4	30	17.1	0	15.72	120.7	6	12	35	38	1400	75	140	1600	620	1	1200	2500	130	140
Δ PbS - 0.35 Ratio	33B	150	428	89.9	45	13.4	1.89	15.29	93.8	8	14	40	42	1000	55	150	1600	640	130	1100	2500	130	160
Δ PbS - 0.12 Ratio	33C	150	511	90.1	59.5	7.4	7.47	14.87	56.9	37	11	40	44	1100	40	140	1600	640	140	1100	2500	140	240
Δ As + 10 g/L	34A	150	141	90.1	36	15.3	0	14.53	140	18	14	33	37	9000	40	170	1600	630	1	1300	2600	230	240
Δ As + 5 g/L	34B	150	138	90.1	33	16.9	0	14.55	132.6	7	13	34	37	5100	40	160	1600	620	1	1300	2400	220	190
Δ As + 10 g/L	35A	150	147	90.1	38.5	16.4	0	15.87	126.6	17	14	33	37	9200	40	160	1600	630	1	1300	2400	220	240
Δ As + 5 g/L	35B	150	150	90.2	35	16.8	0	15.27	132.6	7	13	34	35	4900	45	170	1600	640	1	1300	2500	230	190

Table J.14: Solids 150 min

		Time min	ORP mV	Temp oC	H <sub>2</sub> SO <sub>4</sub> g/L	Fe 2+	Fe 3+	Fe T	Solids g/L	Sn wt%	Pb wt%	S wt%	SO <sub>4</sub> /S w%	As w%	Cl w%	F w%	MgSO <sub>4</sub> w%	Mn w%	Cu w%	SiO <sub>2</sub> w%	Fe w%	Zn w%	MgO w%
<b>Baseline</b>	<b>Test #</b>	<b>0</b>	426	90	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Baseline	25A	150	140	89.6	23.5	15.6	0.3	15.3	124.6	1.3	46	18	5	0.57	0	0.005	0	0.02	0.12	3.6	4	7.8	0.02
Baseline	25B	150	97	90.1	30.5	15.6	0	15.3	135	1.2	47	18	4.7	0.54	0	0.008	0	0.02	0.12	3.4	4	7.7	0.02
Δ As - Baseline Repeat	34C	150	145	90.2	27.5	15.0	0	14.41	133.2	1.2	45	17	4.6	0.48	0.01	0.008	0	0.02	0.13	3.5	4	7.7	0.02
Baseline	26A	150	138	90.3	34.5	16.0	0	15.4	121.2	1.3	46	18	3.6	0.66	0.01	0.006	0	0.02	0.11	3.6	4.5	7.4	0.02
Baseline	26B	150	152	90.3	34	18.2	0	15.09	121.6	1.3	46	18	3.2	0.63	0	0.007	0	0.03	0.12	3.6	4.5	7.7	0.02
Δ As - Baseline Repeat	35C	150	139	89.9	26.5	15.8	0	14.74	124.8	1.2	46	17	4.1	0.5	0	0.007	0	0.02	0.12	3.5	3.9	7.9	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25A	150	140	89.6	23.5	15.6	0.3	15.3	124.6	1.3	46	18	5	0.57	0	0.005	0	0.02	0.12	3.6	4.6	7.8	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 100 g/L	25B	150	97	90.1	30.5	15.6	0	15.3	134.5	1.2	47	18	4.7	0.54	0	0.008	0	0.02	0.12	3.4	4.7	7.7	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27A	150	195	90.3	77.5	15.5	0	15.39	133	1.1	44	18	4.8	0.49	0	0.007	0	0.03	0.11	3.7	3.7	7.5	0.02
Δ H <sub>2</sub> SO <sub>4</sub> - 160 g/L	27B	150	192	90.5	73	15.8	0	15.02	105.5	1.2	42	17	4.7	0.54	0	0.007	0	0.03	0.1	3.6	3.8	7.6	0.03
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28A	150	129	90.4	0	10	0.76	10.76	140.4	1.2	36.7	15	5.4	1.3	0	0.038	0	0.04	0.09	3.3	6.6	8.7	0.04
Δ H <sub>2</sub> SO <sub>4</sub> - 40 g/L	28B	150	121	90.1	0	10.3	0	10.22	143.7	1.1	38	16	6	1.2	0.01	0.038	0	0.04	0.1	3.3	6.3	9	0.04
Δ Temperature - 90 oC	25A	150	140	89.6	23.5	15.6	0.3	15.3	124.6	1.3	46	18	5	0.57	0	0.005	0	0.02	0.12	3.6	4.6	7.8	0.02
Δ Temperature - 90 oC	25B	150	97	90.1	30.5	15.6	0	15.3	134.5	1.2	47	18	4.7	0.54	0	0.008	0	0.02	0.12	3.4	4.7	7.7	0.02
Δ Temperature - 60 oC	29A	150	280	60	33.5	13.6	0.24	13.84	129.9	1.2	46	18	3.9	0.59	0.01	0.008	0	0.02	0.08	3.3	4.1	8.4	0.02
Δ Temperature - 60 oC	29B	150	280	61	30	13.4	0.42	13.82	121.5	1.3	46	18	5.2	0.6	0.01	0.007	0	0.02	0.08	3.4	4.1	8.5	0.02
Δ Temperature - 30 oC	30A	150	401	29.9	4.5	8	1.04	9.04	165.9	0.88	44	16	0.05	0.99	0.01	0.02	0	0.03	0.05	2.9	6.3	9.2	0.03
Δ Temperature - 30 oC	30B	150	429	29.9	23	8.4	3.86	12.26	124.1	1.3	47	18	0.064	0.73	0.01	0.011	0	0.02	0.04	3.5	4.9	9.9	0.03
Δ PbCon - 0.6 Ratio	25A	150	140	89.6	23.5	15.6	0.3	15.3	124.6	1.3	46	18	5	0.57	0	0.005	0	0.02	0.12	3.6	4.6	7.8	0.02
Δ PbCon - 0.6 Ratio	25B	150	97	90.1	30.5	15.6	0	15.3	134.5	1.2	47	18	4.7	0.54	0	0.008	0	0.02	0.12	3.4	4.7	7.7	0.02
Δ PbCon - 1 Ratio	31A	150	146	90.1	28.5	17	0	15.92	181.3	0.85	44	19	4.3	0.3	0	0.006	0	0.02	0.1	3.7	4.4	9.4	0.03
Δ PbCon - 0.2 Ratio	31B	150	445	89.6	50	11.4	2.93	14.33	71	2.1	44	14	6.7	0.92	0	0.009	0	0.03	0.04	2.9	3.1	3.4	0.04
Δ PbS - 0.6 Ratio	32A	150	196	90.1	41	16.3	0	14.74	124.4	1.2	57	13	6.4	0.43	0	0.003	0	0.02	0.09	0.82	0.43	1.6	0.02
Δ PbS - 0.35 Ratio	32B	150	280	90	3	10.6	0.85	11.45	105.6	1.5	47	10	7.9	1.6	0	0.014	0	0.04	0.09	0.91	4	2.9	0.02
Δ PbS - 0.12 Ratio	32C	150	503	90.3	35	3.7	8.67	12.37	68.5	2.4	47	9.4	8.3	1.4	0	0.01	0	0.04	0.05	1.3	3.6	3.5	0.03
Δ PbS - 0.6 Ratio	33A	150	198	90.4	30	17.1	0	15.72	120.7	1.3	56	12	6.8	0.5	0.01	0.003	0	0.02	0.09	0.73	0.55	1.8	0.02
Δ PbS - 0.35 Ratio	33B	150	428	89.9	45	13.4	1.89	15.29	93.8	1.5	52	9.9	5.7	0.75	0	0.006	0	0.03	0.03	0.99	1.3	2.2	0.02
Δ PbS - 0.12 Ratio	33C	150	511	90.1	59.5	7.4	7.47	14.87	56.9	2.1	47	9.3	6.9	0.93	0	0.007	0	0.04	0.06	1.5	2	3	0.03
Δ As + 10 g/L	34A	150	141	90.1	36	15.3	0	14.53	140	1.1	45	17	3.7	1.2	0.01	0.006	0	0.03	0.12	3.2	3.9	7.2	0.02
Δ As + 5 g/L	34B	150	138	90.1	33	16.9	0	14.55	132.6	1.2	46	17	4.2	0.76	0.01	0.007	0	0.02	0.12	3.3	4	7.6	0.02
Δ As + 10 g/L	35A	150	147	90.1	38.5	16.4	0	15.87	126.6	1.2	47	17	4.1	1.1	0	0.014	0	0.03	0.13	3.4	4.2	8.3	0.02
Δ As + 5 g/L	35B	150	150	90.2	35	16.8	0	15.27	132.6	1.1	45	17	3.7	0.79	0	0.019	0	0.02	0.12	3.3	3.9	8	0.02

APPENDIX K REDUCTION RELEACH TESTWORK

Table K. 1: Dissolution Results Test 39A

Date: Jan. 22 / 08										Test # 39A	
Experiment Description: Dissolution Sn(SO <sub>4</sub> ) <sub>2</sub> / As <sub>2</sub> O <sub>5</sub>											
Time	ORP mV	Temp °C	H <sub>2</sub> SO <sub>4</sub> g/L	Comments / Observations	Sample Type	Sample Date	Lot/ Time	Comment	Sn mg/L	As mg/L	
0 min	233	90.1	100.5	slow filtering	DC99	20080122	8000	Dissolution Test 39A	280	47	
1 hour	239	90.2	100.5	slow filtering	DC99	20080122	8001	Dissolution Test 39A	130	72	
2 hour	191	89.5	100	slow filtering	DC99	20080122	8002	Dissolution Test 39A	62	81	
3 hour	174	89.2	100.5	better	DC99	20080122	8003	Dissolution Test 39A	35	90	
4 hour	184	89.9	100.5	better	DC99	20080122	8004	Dissolution Test 39A	19	92	
				<b>Sn(SO<sub>4</sub>)<sub>2</sub></b>	<b>As<sub>2</sub>O<sub>5</sub></b>						
Initial Weights				20.1 gms	2.2 gms						

Table K. 2: Dissolution Results Test 39B

Date: Jan. 22 / 08										Test # 39B	
Experiment Description: Dissolution Sn(SO <sub>4</sub> ) <sub>2</sub> / As <sub>2</sub> O <sub>5</sub>											
Time	ORP mV	Temp °C	H <sub>2</sub> SO <sub>4</sub> g/L	Comments / Observations	Sample Type	Sample Date	Lot/ Time	Comment	Sn mg/L	As mg/L	
0 min	234	89.9	100	slow filtering	DC99	20080122	8005	Dissolution Test 39B	310	56	
1 hour	143	89.6	99.5	slow filtering	DC99	20080122	8006	Dissolution Test 39B	23	58	
2 hour	149	90.1	99.5	slow filtering	DC99	20080122	8007	Dissolution Test 39B	5	64	
3 hour	167	89.9	100.5	better	DC99	20080122	8008	Dissolution Test 39B	3	64	
4 hour	189	90.3	100.5	better	DC99	20080122	8009	Dissolution Test 39B	< 1	64	
				<b>Sn(SO<sub>4</sub>)<sub>2</sub></b>	<b>As<sub>2</sub>O<sub>5</sub></b>						
Initial Weights				20.01 gms	2.03 gms						

**Table K. 3: Dissolution Results Test 40A**

Date: Jan. 24 / 08										Test # 40A	
Experiment Description: Dissolution SnSO <sub>4</sub> / As <sub>2</sub> O <sub>5</sub> / ZnSO <sub>4</sub>											
Time	ORP m/V	Temp °C	H <sub>2</sub> SO <sub>4</sub> g/L	Comments / Observations	Sample Type	Sample Date	Lot/ Time	Comment	As g/L	Zn g/L	Sn mg/L
0 min	327	90.1	92.5	good filtering	DC99	20080124	8016	Dissol Test #40A	3	34	41
1 hour	280	89.8	91	good filtering	DC99	20080124	8017	Dissol Test #40A	2.9	34	13
2 hour	268	89.9	89.5	good filtering	DC99	20080124	8018	Dissol Test #40A	2.9	34	9
3 hour	266	89.8	90.5	good filtering	DC99	20080124	8019	Dissol Test #40A	2.9	35	6
4 hour	271	90.2	91.5	good filtering	DC99	20080124	8020	Dissol Test #40A	2.9	35	4
Initial Weights					<b>SnSO<sub>4</sub></b>	<b>As<sub>2</sub>O<sub>5</sub></b>		<b>ZnSO<sub>4</sub></b>			
					2.08	20.03		550.2			

**Table K. 4: Dissolution Results Test 40B**

Date: Jan. 24 / 08										Test # 40B	
Experiment Description: Dissolution SnSO <sub>4</sub> / As <sub>2</sub> O <sub>5</sub> / ZnSO <sub>4</sub>											
Time	ORP m/V	Temp °C	H <sub>2</sub> SO <sub>4</sub> g/L	Comments / Observations	Sample Type	Sample Date	Lot/ Time	Comment	As g/L	Zn g/L	Sn mg/L
0 min	326	90	90.5	good filtering	DC99	20080124	8021	Dissol Test #40B	3	35	42
1 hour	340	90.2	89.5	good filtering	DC99	20080124	8022	Dissol Test #40B	2.9	35	7
2 hour	373	90.3	90.5	good filtering	DC99	20080124	8023	Dissol Test #40B	2.9	35	3
3 hour	389	90	91	good filtering	DC99	20080124	8024	Dissol Test #40B	2.9	35	3
4 hour	394	89.4	90	good filtering	DC99	20080124	8025	Dissol Test #40B	2.9	35	3
Initial Weights					<b>SnSO<sub>4</sub></b>	<b>As<sub>2</sub>O<sub>5</sub></b>					
					2 gms	20.01 gms					

**Table K. 5: Dissolution Results Test 41A**

Date: Feb. 21 / 08										Test # 41A	
Experiment Description: Dissolution SnSO <sub>4</sub> / As <sub>2</sub> O <sub>5</sub>											
Time	ORP mV	Temp °C	H <sub>2</sub> SO <sub>4</sub> g/L	Comments / Observations	Sample Type	Sample Date	Lot/ Time	Comment	Sn mg/L	As mg/L	
0 min	247	90.1	103.5	good	DC99	20080222	8036	Test 41A 0 min	2500	230	
1 hour	106	89.9	104	good	DC99	20080222	8037	Test 41A 1 hr	2800	190	
2 hour	111	90.9	104.5	good	DC99	20080222	8038	Test 41A 2 hr	2100	180	
3 hour	118	89.8	103.5	good	DC99	20080222	8039	Test 41A 3 hr	1700	180	
4 hour	121	89.7	103	good	DC99	20080222	8040	Test 41A 4 hr	1200	170	
Initial Weights					SnSO <sub>4</sub> 2.0 gms			As <sub>2</sub> O <sub>5</sub> 20.1 gms			

**Table K. 6: Dissolution Results Test 41B**

Date: Feb. 21 / 08										Test # 41B	
Experiment Description: Dissolution SnSO <sub>4</sub> / As <sub>2</sub> O <sub>5</sub>											
Time	ORP mV	Temp °C	H <sub>2</sub> SO <sub>4</sub> g/L	Comments / Observations	Sample Type	Sample Date	Lot/ Time	Comment	Sn mg/L	As mg/L	
0 min	227	90.1	103	good	DC99	20080222	8041	Test 41B 0 min	2900	200	
1 hour	249	89.7	102	good	DC99	20080222	8042	Test 41B 1 hr	2900	240	
2 hour	244	89.6	102	good	DC99	20080222	8043	Test 41B 2 hr	2700	200	
3 hour	244	90.4	103	good	DC99	20080222	8044	Test 41B 3 hr	2700	180	
4 hour	214	90.1	103	good	DC99	20080222	8045	Test 41B 4 hr	2300	170	
Initial Weights					SnSO <sub>4</sub> 2.05 gms			As <sub>2</sub> O <sub>5</sub> 20.02 gms			

**Table K. 7: Dissolution Results Test 42A**

Date: Mar 15 / 08											Test # 42A
Experiment Description: Dissolution SnSO <sub>4</sub> / As <sub>2</sub> O <sub>5</sub>											
Time	ORP mV	Temp °C	H <sub>2</sub> SO <sub>4</sub> g/L	Comments / Observations	Sample Type	Sample Date	Lot/ Time	Comment	Sn mg/L	As mg/L	
0 min	280	89.9	100	good	DC99	20080316	8000	Test 42A 0 min	63	3.4	
1 hour	317	90	99.5	good	DC99	20080316	8001	Test 42A 1 hr	61	3.2	
2 hour	326	89.9	100	good	DC99	20080316	8002	Test 42A 2 hr	54	3.3	
3 hour	330	90.1	100	good	DC99	20080316	8003	Test 42A 3 hr	50	3.3	
4 hour	333	90.2	101.5	good	DC99	20080316	8004	Test 42A 4 hr	52	3.3	
Initial Weights				SnSO <sub>4</sub> 2.08 gms	As <sub>2</sub> O <sub>5</sub> 20.09 gms	H <sub>2</sub> SO <sub>4</sub> g/L 100 g/L					

**Table K. 8: Dissolution Results Test 42B**

Date: Mar 15 / 08											Test # 42B
Experiment Description: Dissolution SnSO <sub>4</sub> / As <sub>2</sub> O <sub>5</sub>											
Time	ORP mV	Temp °C	H <sub>2</sub> SO <sub>4</sub> g/L	Comments / Observations	Sample Type	Sample Date	Lot/ Time	Comment	Sn mg/L	As mg/L	
0 min	355	89.9	100	New ORP Probe	DC99	20080316	8005	Test 42B 0 min	63	3.3	
1 hour	348	90	100.5	good	DC99	20080316	8006	Test 42B 1 hr	61	3.3	
2 hour	377	90	100	good	DC99	20080316	8007	Test 42B 2 hr	51	3.2	
3 hour	377	89.9	100.5	good	DC99	20080316	8008	Test 42B 3 hr	54	3.2	
4 hour	385	90.2	100.5	good	DC99	20080316	8009	Test 42B 4 hr	49	3.2	
Initial Weights				SnSO <sub>4</sub> 2.01 gms	As <sub>2</sub> O <sub>5</sub> 20.07gms	H <sub>2</sub> SO <sub>4</sub> g/L 100 g/L					

**Table K. 9: Dissolution Results Test 42C**

Date: Mar 16 / 08											Test # 42C
Experiment Description: Dissolution SnSO <sub>4</sub> / As <sub>2</sub> O <sub>5</sub>											
Time	ORP mV	Temp °C	H <sub>2</sub> SO <sub>4</sub> g/L	Comments / Observations	Sample Type	Sample Date	Lot/ Time	Comment	Sn mg/L	As mg/L	
0 min	231	90.5	219	good	DC99	20080316	8010	Test 42C 0 min	86	3.4	
1 hour	347	90.8	219.5	good	DC99	20080316	8011	Test 42C 1 hr	110	3.3	
2 hour	298	90.6	220	good	DC99	20080316	8012	Test 42C 2 hr	110	3.3	
3 hour	253	90.3	219	good	DC99	20080316	8013	Test 42C 3 hr	95	3.2	
4 hour	235	89.9	219	good	DC99	20080316	8014	Test 42C 4 hr	86	3.2	
Initial Weights				<b>SnSO<sub>4</sub></b> 2.04 gms	<b>As<sub>2</sub>O<sub>5</sub></b> 20.09 gms	<b>H<sub>2</sub>SO<sub>4</sub> g/L</b> 220 g/L					

**Table K.10: Dissolution Results Test 42D**

Date: Mar 16 / 08											Test # 42D
Experiment Description: Dissolution SnSO <sub>4</sub> / As <sub>2</sub> O <sub>5</sub>											
Time	ORP mV	Temp °C	H <sub>2</sub> SO <sub>4</sub> g/L	Comments / Observations	Sample Type	Sample Date	Lot/ Time	Comment	Sn mg/L	As mg/L	
0 min	239	90.5	218	good	DC99	20080316	8015	Test 42D 0 min	3.4	170	
1 hour	156	90.3	221	good	DC99	20080316	8016	Test 42D 1 hr	3.3	140	
2 hour	152	90.4	221	good	DC99	20080316	8017	Test 42D 2 hr	3.3	130	
3 hour	154	90.8	219	good	DC99	20080316	8018	Test 42D 3 hr	3.3	110	
4 hour	158	90.3	220	good	DC99	20080316	8019	Test 42D 4 hr	3.5	100	
Initial Weights				<b>SnSO<sub>4</sub></b> 2.05 gms	<b>As<sub>2</sub>O<sub>5</sub></b> 20.06 gms	<b>H<sub>2</sub>SO<sub>4</sub> g/L</b> 220 g/L					



APPENDIX L PURE COMPONENT TESTS

Table L. 1: SnSO<sub>4</sub> - A

SnSO <sub>4</sub> - A								
Sample Type	Sample Date	Lot/Time	Comment	Time (minutes)	Sn <sup>2+</sup> mg/L	Sn mg/L	F/Acid g/L	SO <sub>4</sub> mg/L
ZC98	20060615	8000	T#1A 10 min	10	10	120	103	97000
ZC98	20060615	8001	T#1A 20 min	20	10	110	104	96000
ZC98	20060615	8002	T#1A 30 min	30	5	110	104	97000
ZC98	20060615	8003	T#1A 40 min	40	10	110	105	98000
ZC98	20060615	8004	T#1A 50 min	50	5	110	106	99000
ZC98	20060615	8005	T#1A 60 min	60	10	110	105	98000
ZC98	20060615	8006	T#1A 70 min	70	15	110	107	100000
ZC98	20060615	8007	T#1A 80 min	80	10	110	108	100000
ZC98	20060615	8008	T#1A 90 min	90	15	110	108	100000
ZC98	20060615	8009	T#1A 100 min	100	10	110	109	100000
ZC98	20060615	8010	T#1A 110 min	110	10	120	110	110000
ZC98	20060615	8011	T#1A 120 min	120	10	120	109	100000

**Table L. 2: SnSO<sub>4</sub> – B**

SnSO <sub>4</sub> - B								
Sample Type	Sample Date	Lot/Time	Comment	Time (minutes)	Sn <sup>2+</sup> mg/L	Sn mg/L	F/Acid g/L	SO <sub>4</sub> mg/L
ZC98	20060615	8012	T#1B 10 min	10	5	120	102	97000
ZC98	20060615	8013	T#1B 20 min	20	5	120	102	97000
ZC98	20060615	8014	T#1B 30 min	30	5	120	103	99000
ZC98	20060615	8015	T#1B 40 min	40	5	120	104	100000
ZC98	20060615	8016	T#1B 50 min	50	5	120	104	98000
ZC98	20060615	8017	T#1B 60 min	60	5	120	105	90000
ZC98	20060615	8018	T#1B 70 min	70	< 5	120	103	97000
ZC98	20060615	8019	T#1B 80 min	80	< 5	120	106	98000
ZC98	20060615	8020	T#1B 90 min	90	< 5	120	107	100000
ZC98	20060615	8021	T#1B 100 min	100	< 5	120	107	100000
ZC98	20060615	8022	T#1B 110 min	110	< 5	130	108	100000
ZC98	20060615	8023	T#1B 120 min	120	5	130	109	100000

**Table L. 3: As<sub>2</sub>O<sub>3</sub> – A**

As <sub>2</sub> O <sub>3</sub> - A							
Sample Type	Sample Date	Lot/Time	Comment	Time (minutes)	As mg/L	SO <sub>4</sub> mg/L	F/Acid g/L
ZC98	20060621	8120	T #6A 10 min	10	1900	100000	101
ZC98	20060621	8121	T #6A 20 min	20	1900	100000	102
ZC98	20060621	8122	T #6A 30 min	30	1900	110000	103
ZC98	20060621	8123	T #6A 40 min	40	1900	110000	103
ZC98	20060621	8124	T #6A 50 min	50	1900	110000	104
ZC98	20060621	8125	T #6A 60 min	60	2000	110000	104
ZC98	20060621	8126	T #6A 70 min	70	1900	110000	108
ZC98	20060621	8127	T #6A 80 min	80	2000	110000	108
ZC98	20060621	8128	T #6A 90 min	90	2000	110000	108
ZC98	20060621	8129	T #6A 100 min	100	2000	110000	110
ZC98	20060621	8130	T #6A 110 min	110	2100	110000	111
ZC98	20060621	8131	T #6A 120 min	120	2200	110000	110

**Table L. 4: As<sub>2</sub>O<sub>3</sub> – B**

As <sub>2</sub> O <sub>3</sub> - B							
Sample Type	Sample Date	Lot/Time	Comment	Time (minutes)	As mg/L	SO <sub>4</sub> mg/L	F/Acid g/L
ZC98	20060621	8132	T #6B 10 min	10	2000	100000	108
ZC98	20060621	8133	T #6B 20 min	20	2000	100000	110
ZC98	20060621	8134	T #6B 30 min	30	2000	100000	106
ZC98	20060621	8135	T #6B 40 min	40	2000	100000	106
ZC98	20060621	8136	T #6B 50 min	50	2100	110000	108
ZC98	20060621	8137	T #6B 60 min	60	2100	110000	108
ZC98	20060621	8138	T #6B 70 min	70	2100	110000	105
ZC98	20060621	8139	T #6B 80 min	80	2100	110000	105
ZC98	20060621	8140	T #6B 90 min	90	2200	110000	106
ZC98	20060621	8141	T #6B 100 min	100	2200	110000	106
ZC98	20060621	8142	T #6B 110 min	110	2100	110000	108
ZC98	20060621	8143	T #6B 120 min	120	2200	110000	109

APPENDIX M STABILITY CONSTANTS I (Brubaker, 1955)

Table M. 1: Stability Constants I

$\text{H}_2\text{SO}_4$	$S \times 10^4$	$(S - S_0) \times 10_4$	$\text{SO}_4^-$	$\mu$	$\gamma_{\pm}$	$\gamma_{22}$	$\gamma_{22} (\text{cor.})$	$a_{\text{H}_2\text{O}}$
0.9605	9.08	8.50	0.201	1.483	0.124	0.074	0.103	0.958
0.9221	7.77	7.19	0.25	1.422	0.126	0.076	0.106	0.959
0.8837	6.92	6.34	0.24	1.364	0.127	0.077	0.107	0.960
0.8645	6.03	5.45	0.234	1.333	0.128	0.078	0.108	0.962
0.8452	5.05	4.67	0.229	1.303	0.128	0.079	0.108	0.963
0.8068	4.4	3.82	0.218	1.243	0.130	0.081	0.110	0.965
0.7684	3.85	3.27	0.207	1.182	0.132	0.083	0.112	0.966
0.7298	3.1	2.52	0.196	1.122	0.134	0.085	0.114	0.968
0.7146	2.95	2.37	0.192	1.099	0.134	0.086	0.115	0.969
0.6723	2.39	1.81	0.180	1.032	0.137	0.089	0.118	0.970
0.6339	1.88	1.30	0.170	0.974	0.139	0.092	0.120	0.972
0.5763	1.30	0.720	0.154	0.884	0.142	0.098	0.125	0.968
0.4995	1.09	0.510	0.133	0.766	0.147	0.107	0.131	0.978
0.4803	0.938	0.358	0.127	0.734	0.149	0.100	0.133	0.979
0.3842	0.648	0.068	0.100	0.584	0.159	0.126	0.146	0.983
0.2882	0.580							
0.1921	0.580							
0.9605	7.72	7.41	0.324	1.609	0.140	0.069	0.107	0.960
0.8837	5.73	5.42	0.301	1.486	0.144	0.073	0.113	0.967
0.8645	4.58	4.27	0.297	1.459	0.144	0.075	0.114	0.968
0.8452	4.44	4.13	0.388	1.421	0.146	0.076	0.116	0.969
0.7684	2.88	2.57	0.260	1.288	0.150	0.079	0.120	0.971
0.7298	2.50	2.19	0.247	1.224	0.152	0.082	0.122	0.973
0.6723	1.83	1.52	0.226	1.124	0.156	0.085	0.126	0.975
0.5763	0.970	0.658	0.192	0.960	0.161	0.093	0.133	0.979
0.4995	0.915	0.603	0.164	0.828	0.167	0.101	0.139	0.982
0.4803	0.714	0.402	0.158	0.796	0.168	0.104	0.141	0.983
0.3842	0.312							
0.2882	0.312							

Note:  $\gamma_{22} = \gamma_{\text{SnOSO}_4\text{SO}_4}$   $\gamma_{\pm} = \gamma_{\text{H}_2\text{SO}_4}$

## APPENDIX N STABILITY CONSTANTS II (Stirrup, 1977)

Table N. 1: Stability Constants II

Reaction			<i>K</i>
$3\text{Sn}^{2+}$	$+4\text{H}_2\text{O}$	$\leftrightarrow \text{Sn}_3(\text{OH})_4^{2+} + 4\text{H}^+$	$1.69 \times 10^{-7} \text{ }^a$
$\text{Sn}^{2+}$	$+ \text{H}_2\text{O}$	$\leftrightarrow \text{SnOH}^+ + \text{H}^+$	$1.26 \times 10^{-4} \text{ }^a$
$2\text{Sn}^{2+}$	$+2\text{H}_2\text{O}$	$\leftrightarrow \text{Sn}_2(\text{OH})_2^{2+} + 2\text{H}^+$	$3.98 \times 10^{-5} \text{ }^a$
$\text{Sn}^{2+}$	$+ \text{Cl}^-$	$\leftrightarrow \text{SnCl}^+$	$14 \text{ }^a$
$\text{Sn}^{2+}$	$+2\text{Cl}^-$	$\leftrightarrow \text{SnCl}_2$	$50 \text{ }^a$
$\text{Sn}^{2+}$	$+3\text{Cl}^-$	$\leftrightarrow \text{SnCl}_3^-$	$48 \text{ }^a$
$\text{Sn}^{2+}$	$+4\text{Cl}^-$	$\leftrightarrow \text{SnCl}_4^{2-}$	$10 \text{ }^a$
$\text{Sn}^{2+}$	$+ \text{Br}^-$	$\leftrightarrow \text{SnBr}^+$	$5.38 \text{ }^a$
$\text{Sn}^{2+}$	$+2\text{Br}^-$	$\leftrightarrow \text{SnBr}_2$	$13.9 \text{ }^a$
$\text{Sn}^{2+}$	$+3\text{Br}^-$	$\leftrightarrow \text{SnBr}_3^-$	$22.1 \text{ }^a$
$\text{Sn}^{2+}$	$+ \text{F}^-$	$\leftrightarrow \text{SnF}^+$	$1.1 \times 10^4 \text{ }^b$
$\text{Sn}^{2+}$	$+2\text{F}^-$	$\leftrightarrow \text{SnF}_2$	$5.9 \times 10^6 \text{ }^b$
$\text{Sn}^{2+}$	$+3\text{F}^-$	$\leftrightarrow \text{SnF}_3^-$	$2.8 \times 10^9 \text{ }^b$
$\text{SnCl}_2$	$+2\text{Cl}^-$	$\leftrightarrow \text{SnCl}_4^{2-}$	$2.16 \times 10^2 \text{ }^a$
$\text{SnCl}_4$	$+2\text{Cl}^-$	$\leftrightarrow \text{SnCl}_6^{2-}$	$6.15 \times 10^5 \text{ }^a$
$\text{Sn}^{2+}$	$+2\text{SO}_4^{2-}$	$\leftrightarrow \text{Sn}(\text{SO}_4)_2$	$1.4 \times 10^{-2} \text{ }^a$
$\text{SnO}_2(\text{aq.})$	$+2\text{H}_2\text{SO}_4$	$\leftrightarrow (\text{SnSO}_4)^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	$5 \times 10^{-2} \text{ }^c$
a, at 25 °C	b, at 30 °C	c, average of d.c. and a.c. values	

Table O. 1: Thermodynamics of Tin I

Electrode	$E^0$ (V)	$(\delta E^0/\delta T)_{th}(V K^{-1})$	$(\delta E^0/\delta T)_{isoth}(V K^{-1})$	$\Delta G^0$ KJ/mol	$\Delta H^0$ KJ/mol	S (J/K)
$Sn^{2+} + 2e = Sn$	-0.136	$-2.8 \times 10^{-4}$	$5.89 \times 10^{-4}$	-27.2	-22.6	-63.6
$Sn^{2+} + 2e = Sn(Hg)$	-					
$Sn^{4+} + 2e = Sn^{2+}$	0.1396					
$Sn = Sn^{2+} + 2e$	-0.154			27.87	2.84	(-) 27.61

University of Cape

Table P. 1: Thermodynamics of Tin II

System	$k^0 = (\text{cm s}^{-1})$	$i \frac{0}{0} (\text{A cm}^{-2})$	$i_0 (\text{A cm}^{-2})$	$\alpha_A$	$\alpha_K$
Sn/Sn <sup>2+</sup> /HClO <sub>4</sub>		2			
Sn(Hg)/Sn <sup>2+</sup> /1M NaClO <sub>4</sub>	0.9 ± 0.1				0.60 ± 0.05
Sn(Hg)/Sn <sup>2+</sup> /2M HClO <sub>4</sub> /camphor (sat.)				0.70 <sub>0/1</sub>	1.42 <sub>0/1</sub>
				1.25 <sub>1/2</sub>	0.44 <sub>1/2</sub>
Sn/1M Sn(II)/1M HCl			0.1456	1.09	
Sn(Hg)/Sn(II)/1M HCl/0.1M N <sub>2</sub> H <sub>2+</sub> ·2HCl	1.53 × 10 <sup>-3</sup>	0.294		1.13	0.62
Sn/Sn(II)/HCl ( <i>I</i> = 1.1)		0.38		1.44	0.60
Sn/0.4M SnSO <sub>4</sub> /1M H <sub>2</sub> SO <sub>4</sub>			0.11		
Sn/SnSO <sub>4</sub> /1M H <sub>2</sub> SO <sub>4</sub>					0.56
Sn(Hg)/Sn(II)/0.5M H <sub>2</sub> SO <sub>4</sub>	0.61 × 10 <sup>-3</sup>	0.118		1.10	0.88
Sn(Hg)/Sn(II)/1M H <sub>2</sub> SO <sub>4</sub>	10 <sup>-3</sup>			1.17	0.76
C/0.104M SnCl <sub>2</sub> /0.081M SnCl <sub>4</sub> /4M HCl			7 × 10 <sup>-3</sup> <sub>2/3</sub>	0.43 <sub>2/3</sub>	
			8 × 10 <sup>-6</sup> <sub>3/4</sub>	0.41 <sub>3/4</sub>	
Hg/10 <sup>-3</sup> M SnCl <sub>2</sub> /10 <sup>-3</sup> M SnCl <sub>4</sub> /2M acetate buffer	3.16 × 10 <sup>-9</sup>		10 <sup>-14</sup>		

APPENDIX Q ACTIVITY OF  $\text{SnOSO}_4\text{SO}_4$  (Brubaker, 1955)

Table Q. 1: Activity of  $\text{SnOSO}_4\text{SO}_4$

	30°	18°		30°	18°
( $\text{H}_2\text{SO}_4$ )	$-a_{22}$	$-a_{22}$	( $\text{H}_2\text{SO}_4$ )	$-a_{22}$	$-a_{22}$
0.9605	0.098	0.118	0.7146	0.113	...
0.9221	0.101	...	0.6723	0.118	0.153
0.8837	0.140	0.127	0.6339	0.119	...
0.8645	0.105	0.126	0.5763	0.119	0.160
0.8452	0.105	0.129	0.4995	0.115	0.160
0.8068	0.108	...	0.4803	0.114	0.169
0.7684	0.111	0.140	0.3842	0.109	0.167
0.7298	0.115	0.141			



$$K = \frac{a_{(\text{SnSO}_4)(\text{SO}_4)} a^2_{\text{H}_2\text{O}}}{a^2_{\text{H}_2\text{SO}_4}} = \frac{(\text{SnSO}_4^{+2})(\text{SO}_4^{-2}) \gamma^2_{22} a^2_{\text{H}_2\text{O}}}{16(\text{H}_2\text{SO}_4)^6 \gamma^6_{\pm}}$$

$$F = (\text{SnSO}_4)(\text{SO}_4) \gamma^2_{22} a^2_{\text{H}_2\text{O}} = (S - S_0)(\text{SO}_4) \gamma^2_{22} a^2_{\text{H}_2\text{O}}$$

$$\frac{1}{16} a^2_{\text{H}_2\text{SO}_4} = (\text{H}_2\text{SO}_4)^6 \gamma^6_{\pm}$$



*General Approaches to Quantifying Aqueous Systems Solubility*

**ESTIMATING ACTIVITY COEFFICIENTS**

**Ionic Interactions**

Equilibrium concentrations aqueous solutions are often discussed in terms of activities. The forces and interaction between ions in solution extend further than that of uncharged non-polar solutions and ideal laws do not apply. The chemical electrostatic interactions of ions in solution are a function of their size and charge.

**Debye-Hückel**

The Debye- Hückel theory was proposed in 1923. Debye-Hückel assumes that ions are point charges in a continuous constant ionic medium of dielectric constant equal to that of water. A theoretical form that the activity coefficient should be obeyed in dilute solutions ( $<0.001$  mol/L). Essentially, the ions in dilute solutions have an activity that is smaller than its concentration, and activity coefficients are set to unity, and the activity equals the concentration.

A major assumption with this theory is the assumption that the total concentration of ions in the background electrolyte are constant and kept constant, and do not react with the ions of interest. Concentrations greater than (0.1 M) have other factors which influence activity. Several factors which have been identified which can affect the activity of an ion are ion size (ion-size parameter), charge (salting out parameter), and charge interaction (interaction parameter), and ion pairing (ion pairing constant).

**Ion Size; (Ion-size Parameter)**

- This parameter accounts for the size of the cation or anion which affects what other ions can be present in a given solution volume

### Size and Charge (charged, and uncharged) Salting Out Parameter;

- The salting out parameter accounts for ions hydration ability at higher concentrations.

### Charge Interaction; (Interaction Parameter)

- The parameter which accounts for anions and cations of like charge can be forced closer together at higher concentrations

### Ion-Pairing; (Ion pairing constant)

- The similarity between charges of anion and cations. This factor is accounted for by the ion-pairing constant.

The major law which applies to dilute solutions for a completely dissociated electrolyte is the “limiting law”;

$$-\log \gamma_{\pm} = Az_+z_-\sqrt{I} \quad \text{Eqn 1}$$

- $\gamma_{\pm}$  is the geometric mean activity coefficient of the two ions.
- $A$  is a constant which is a function of absolute temperature  $T$ , and the dielectric constant  $\epsilon$  of the solvent:
- $z_+$  and  $z_-$  are the charges on the two ions.
- The Ionic Strength (I) is:

$$I = \frac{1}{2} \sum_1 C_1 z_1^2 \quad \text{Eqn 2}$$

$C_1$  in mol/L represents the total concentration of every ion,  $z_i$  charge  $z_1$ . For example, the ionic strength of  $C$  molar LiF is

$$I = \frac{1}{2} ([\text{Li}^+] + [\text{F}^-]) = C \quad \text{Eqn 3}$$

And the ionic strength of  $C$  molar  $\text{SnSO}_4$  is

$$I = \frac{1}{2}\{[\text{Sn}^{2+}](4) + [\text{SO}_4^{2-}](4)\} = 4C \quad \text{Eqn 4}$$

Only electrically neutral combinations of these single-ion activities can be measured experimentally (Butler, 1998). Any equilibrium expression can be written using electrically neutral combinations of single-ion activity coefficients: (Butler, 1998):

$$K_a^\circ \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = [\text{H}^+] \gamma_+ [\text{A}^-] \gamma_- \quad \text{Eqn 5}$$

$$\frac{K_a^\circ \gamma_o}{\gamma_+ \gamma_-} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \text{Eqn 6}$$

### Ion-Size Parameter

The ion size parameter is required because the limiting law predicts much smaller activity coefficients than are observed at intermediate concentrations. Additional terms in the equations are included when approximations are made, which gives the extended Debye-Hückel law. For a single ion of charge  $z$ :

$$-\log \gamma_z = Az^2 \frac{\sqrt{I}}{1 + Ba\sqrt{I}} \quad \text{Eqn 7}$$

Here  $A$  is the same constant as in equation [7],  $a$  is an adjustable parameter, measured in  $\text{\AA}$  ( $10^{-10}$  m), which corresponds roughly to the effective size of a hydrated ion, and  $B$  is a function of the temperature ( $T$ ) and dielectric constant ( $\epsilon$ ):

For a binary electrolyte:

$$-\log \gamma_{\pm} = A|z_+ z_-| \frac{\sqrt{I}}{1 + Ba\sqrt{I}} \quad \text{Eqn 8}$$

For a single 1-1 salt such as LiCl, with concentration  $m$  in mol/kg, the Debye-Hückel equation becomes:

$$-\log \gamma_{\pm} = A \frac{\sqrt{m}}{1 + Ba\sqrt{m}} \quad \text{Eqn 9}$$

A published a list of values for the ion-size parameter  $a$  for 130 selected ions was tabulated by Kielland in 1937 (Butler, 1998). Kielland's list was determined from experimental data on binary solutions and used to estimate multi-component system activities. Another scientist proposed for ions in which the hydrated ion size was unknown, that  $a$  be taken to be  $1/B = 3.0 \text{ \AA}$  at  $25 \text{ }^{\circ}\text{C}$ , resulting in modification to equation [16].

$$\log \gamma_{\pm} = Az_{+}z_{-} \frac{\sqrt{I}}{1 + \sqrt{I}} \quad \text{Eqn 10}$$

**The Davies Equation (> 0.1 M) (Butler, 1998)**

Because the extended Debye-Hückel equation does not fit experimental activity coefficient data accurately above 0.1 M, Guggenheim suggested the following empirical method:

$$\log \gamma_{\pm} = Az_{+}z_{-} \frac{\sqrt{I}}{1 + \sqrt{I}} + bI + cI^2 + dI^3 + \dots \quad \text{Eqn 11}$$

Davies studied the first coefficient  $b$  for a number of 1-1 and 1-2 electrolytes, and proposed an equation without any adjustable parameters:

$$-\log \gamma_{\pm} = Az_{+}z_{-} \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad \text{Eqn 12}$$

or for single ions:

$$-\log \gamma_{\pm} = Az^2 \left( \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad \text{Eqn 13}$$

### Pitzer Ion Interaction Approach (Butler, 1998)

For strong electrolyte solutions near saturated concentrations, in 1973, Pitzer expanded the Debye-Huckel theory to account for the ionic strength dependence. This approach uses 12 parameters, three of which are adjustable. A major assumption is that the electrolytes do not form complexes.

$m$  = molality

$z_M$  = charge of cation = 1 for univalent-univalent electrolyte

$z_x$  = charge of anion = 1 for univalent-univalent electrolyte

**Table R. 1: Estimated Error in  $\gamma_{\pm}$  (Butler, 1998)**

Ionic strength, Molal	Standard deviation of $\log \gamma_{\pm}$ ( $\sigma$ )	Corresponding error for $\gamma_{\pm}$ (95% confidence limit)
0.1	0.014	$\pm 7\%$
0.2	0.025	$\pm 12\%$
0.5	0.053	$\pm 28\%$
1	0.093	$\pm 54\%$
2	0.162	$\pm 111\%$

$\nu_M$  = moles of cation per mole of salt = 1 for univalent-univalent electrolyte

$\nu_x$  = moles of anion per mole of salt = 1 for univalent-univalent electrolyte

$A_{\Phi} = 0.3915$  for 25 °C, universal parameter

$b = 1.2$ , universal parameter

$\alpha = 2.0$ , universal parameter

$\beta(0) = \text{electrolyte parameter}^{12}$

$\beta(1) = \text{electrolyte parameter}^{12}$

$C_{MX}^\Phi = \text{electrolyte parameter}^{12}$

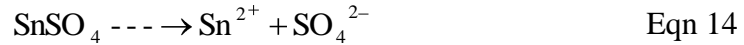
$I = \text{ionic strength} = m$  for univalent-univalent electrolyte

Three of these parameters are adjustable parameters evaluated through a least-squares regression on data such as the Robinson and Stokes data. The next step involves calculations (Butler, 1998):

- $x = \alpha\sqrt{I}$
- $g_{\epsilon} = 2[1 - (1+x)\exp(-x)]/x^2$
- $C_{MX}^\gamma = 1.5C_{MX}^\Phi$
- $B_{MX} = \beta_{MX}^0 + \beta_{MX}^1 g_{\epsilon}$
- $B_{MX}^\Phi = \beta_{MX}^0 + \beta_{MX}^1 \exp(-x)$
- $B_{MX}^\gamma = B_{MX} + B_{MX}^\Phi$
- $f^\gamma = -A_\phi[\sqrt{I}/(1+b\sqrt{I}) + (2/b)\ln(1+b\sqrt{I})]$
- $\ln\gamma_{\pm} = |z_M z_X| f^\gamma + m(2\nu_M \nu_X / \nu_M + \nu_X) B_{MX}^\gamma + m^2 [2^3 \sqrt{\nu_M \nu_X} / \nu_M + \nu_X] C_{MX}^\gamma$
- $\log \gamma_{\pm} = \frac{\ln \gamma_{\pm}}{\ln(10)}$

### Heterogeneous Mass Transfer and Chemical Kinetics

When a salt  $\text{SnSO}_4$  dissolves in water, the dissolution is fast and then slows down near as saturation is approached. We can write the chemical equation as:



The mass transfer rate is:

$$J = k_T^{\text{Sn}^{2+}} ([\text{Sn}^{2+}]_s - [\text{Sn}^{2+}]_b) \quad \text{Eqn 15}$$

$$= K_T^{\text{SO}_4^{2-}} ([\text{SO}_4^{2-}]_s - [\text{SO}_4^{2-}]_b) \quad \text{Eqn 16}$$

$K_T^i$  is the mass transfer coefficient of species  $i$  (in  $\text{m}\cdot\text{sec}^{-1}$ )

$[i]_s$  and  $[i]_b$  are the concentration of species  $i$  on the mineral particle surface and bulk solution.

The value of the mass transfer coefficient  $K_T^i$  for particles freely suspended in a liquid environment has been presented by Harriott, and his fitted equation for the Stoke's Law region is (Peters, 1985):

$$K_T^i = (D_i/2r) \times [(2 + B(\mu/(\rho \times D))^{1/3}) \times (4g\rho_1 \times (\rho_s - \rho_1)/9\mu^2) \times r^{2/3}] \quad \text{Eqn 17}$$

Where  $D_i$  is the diffusion coefficient of  $i$  ( $\text{m}^2 \text{sec}^{-1}$ )

$r^i$  is the "Stokes" radius of the particle ( $\text{m}$ )

$\mu$  is the solution viscosity (Newton sec.  $\text{m}^{-2}$ )

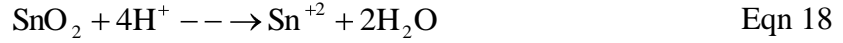
$\rho_1$  is the solution density ( $\text{Kg m}^{-3}$ )

$\rho$  is the solid particle density ( $\text{Kg m}^{-3}$ )

$g$  is the gravitational constant ( $9.81 \text{ m}\cdot\text{sec}^{-2}$ ) and

$B$  is an adjustable parameter, with a value of about 0.6 for free settling

As the solution becomes more saturated the solubility decreases, the leaching rate decreases for the dissolution of a SnO<sub>2</sub> particle in H<sub>2</sub>SO<sub>4</sub>, we have the chemistry:



The H<sup>+</sup> ions transfer to the SnO<sub>2</sub> surface, and Sn<sup>2+</sup> ions leave the surface.

$$J_{\text{Sn}^{2+}} = K_T^{\text{Sn}^{2+}} ([\text{Sn}^{2+}]_s - [\text{Sn}^{2+}]_b) \quad \text{Eqn 19}$$

$$J_{\text{H}^+} = K_T^{\text{H}^+} ([\text{H}^+]_b - [\text{H}^+]_s) \quad \text{Eqn 20}$$

These two flux equations are tied together by a steady state condition.

$$J_i = -D_i(dC/dx)_x + \mu_i C_i(d\Phi/dx)_x \quad \text{Eqn 21}$$

where i is the appropriate ion (H<sup>+</sup>, Sn<sup>2+</sup>, or SO<sub>4</sub><sup>-2</sup>); μ<sub>i</sub> is the mobility of the ion, and Φ is the electrical potential near a leaching ZnO surface; the subscript x is the (variable) distance from the surface. The flux of SO<sub>4</sub><sup>-2</sup> ions is zero in the steady – state. When dΦ/dx = 0, the large difference between D<sub>H<sup>+</sup></sub> and D<sub>Sn<sup>2+</sup></sub> leads to J<sub>H<sup>+</sup></sub> + 2J<sub>Sn<sup>2+</sup></sub> << 0, and as the H<sup>+</sup> ions rush to the SnO<sub>2</sub> surface by diffusion, the surface develops an excess positive charge that creates an unsteady – state flux of all three ions. During the unsteady – state, charge neutrality requires that

$$J_{\text{H}^+} + 2J_{\text{Sn}^{2+}} + 2J_{\text{SO}_4^{2-}} = 0 \quad \text{Eqn 22}$$

in which case sulphate ions become concentrated at the surface, along with tin ions. The end of this unsteady – state case occurs when

$$J_{\text{SO}_4^{2-}} = 0; \text{ therefore } d[\text{SO}_4^{2-}]/dx = (2F[\text{SO}_4^{2-}]/RT)d\Phi/dx \quad \text{Eqn 23}$$



When  $[H^+]_s$  and  $[Sn^{2+}]_s$  are tied together by the equilibrium:

$$[H^+]_s^4 / [Sn^{2+}]_s = K_s \quad \text{Eqn 24}$$

The rate of change for a particle radius:

$$-(dr/dt) = K_T^i [C_s^i - C_b^i] V_m^i \quad \text{Eqn 25}$$

$C_s^i - C_b^i$  is the concentration difference between the solid surface and the solution for the species  $i$ .

$V_m^i$  is the molar volume of the solid per mole of the transported species  $i$ .

### Chemical Rate Control in Leaching (Peters, 1985)

Many laboratory studies of leaching systems indicate that surface chemical reactions are often rate-controlling in leaching. The usual criterion for this conclusion is that

- a) the reaction rate is proportional to reactive mineral surface area,
- b) there is no dependence of reaction rate on agitation, provided there is enough agitation to keep particles in suspension,
- c) the reaction rate is highly temperature dependent, and
- d) there is usually no dependence of reaction rate on solution concentration of products.

Minerals that leach uniformly:

$$dC_i / dt = K_L A_s = -1/\nu * dW/dt \quad \text{Eqn 26}$$

$K_L$  is the heterogeneous rate constant, moles<sup>-2</sup> sec<sup>-1</sup>.

$A_s$  is the particle surface area per m<sup>3</sup> solution and  $\nu$  is a stoichiometry factor.

$W$ , the weight of unleached solid particles per  $m^3$  solution, is given by

$$W_i = \sum_i \rho_n f_s r_i^3 \quad \text{Eqn 27}$$

where the subscript  $i$  represents a particle set of essentially constant radius  $r_i$  and  $f_s$  is the shape factor for particles\*. (\*Note:  $f_s = (4/3)\pi$  for spheres)

$$dW_i / dt = 3\rho_n f_s r_i^2 [dr_i / dt] \quad \text{Eqn 28}$$

$$\text{and } -dr_i / dt = k_1,$$

$$= 3(\rho_n f_s)^{1/3} W_i^{2/3} k_1 \quad \text{Eqn 29}$$

The differential equation is:

$$dW_i / W_i^{2/3} = 3(\rho_n f_s)^{1/3} k_1 dt \quad \text{Eqn 30}$$

Integrating between the limits  $W_i^0$  at  $t = 0$  and  $W_i$  at  $t$ , and dividing by  $(W_i^0)^{1/3}$  becomes

$$1 - (W_i / W_i^0)^{1/3} = (\rho_n f_s / W_i^0)^{1/3} k_1 t \quad \text{Eqn 31}$$

Finally, we can substitute  $W_i = v(C_i^{\max} - C_i)$  and  $W_i^0 = vC_i^{\max}$  on the left and  $W_i^0 = \rho_n f_s (r_i^0)^3$  on the right to obtain:

$$1 - [1 - (C_i / C_i^{\max})]^{1/3} = k_1 t / r_i^0 \quad \text{Eqn 32}$$

### Activation Energies and Temperature Dependence of Leaching (Peters, 1985)

The chemical rate-control usually has a large temperature dependence (compared to mass-transfer rate-control). The Arrhenius Equation in logarithmic form:

$$d(\log k_1) / d(1/K) = E_a / 2.303R \quad \text{Eqn 33}$$

However, this equation is strictly true only for a true rate constant, rather than a rate measurement

T is the absolute temperature K

R is the universal gas constant, (8.3144 J.mole<sup>-1</sup>K<sup>-1</sup>)

E<sub>a</sub> is the Arrhenius activation energy, in joules/mole.

E<sub>a</sub> Chemical rate control is from 20 to 80 or more kJ/mole. For a mass-transfer process in an aqueous solution, the values are typically between 10 kJ/mol to 20 kJ/mol.

### **Shrinking Core Kinetics** (Peters, 1985)

If a particle leaches in such a way that the solute depleted shell is a porous residue of similar morphology to the original. Both reagents and reaction products to diffuse through this shell. The diffusion coefficient is smaller than it is in the liquid boundary layer, but is related to the latter by the relationship:

$$D^r = D_i \xi / \tau \quad \text{Eqn 34}$$

ξ is the fractional porosity of the solid

τ is the average tortuosity of the pores.

It is convenient to identify τ with the radius change of the core, rather than the thickness of the shell, i.e.  $\alpha\tau = \lambda/(r_o-r)$  where λ is the pore length. The leaching is then related to the rate of disappearance of core volume, i.e.

$$J_i = v dV_c / dt \quad \text{Eqn 35}$$

v is the moles of solute per unit volume

$$V_c = f_v r_c^3 \quad \text{Eqn 36}$$

The shape factor,  $f_v$ , is  $4\pi/3$  for spheres.

The flux  $J_i$  is moles per second

The flux for the particle as a whole is constrained by the diffusional resistance of the porous reaction product, with the relationship:

$$J_i = D_1^r (dC_i / dr)_r (4\pi r^2) \quad \text{Eqn 37}$$

The total flux of species  $i$  passes through the shell between  $r = r_c$  and  $r = r_o$ , and is actually independent of  $r$ . At any time, equation [46] can be rearranged so that

$$J_i dr / r^2 = -4\pi D_1^r dC_i \quad \text{Eqn 38}$$

This is the flux through any differential radius  $dr$  as well as the flux through the entire shell. Because the flux is independent of  $r$  and  $C$ , both sides of equation [47] can be integrated. The boundary conditions are:  $C_i = C_c$  when  $r = r_c$  and  $C_i = C_o$  when  $r = r_o$ :

$$J_i - \int_{r_c}^{r_o} r^{-2} dr = -4\pi D_1^r \int_{C_c}^{C_o} dC_i \quad \text{Eqn 39}$$

$$-J_i (r_o^{-1} - r_c^{-1}) = -4\pi D_1^r (C_o - C_c) \quad \text{Eqn 40}$$

and

$$J_i = -4\pi D_1^r (C_c - C_o) r_o r_c / (r_o - r_c) \quad \text{Eqn 41}$$

We have already described  $J_i$  in terms of the volumetric leaching rate ( $dV_c/dt$ ), as given in equation [49]. This yields the equation:

$$\nu (dV_c / dt) = -4\pi * D_1^r (C_c - C_o) r_o r_c / (r_o - r_c) \quad \text{Eqn 42}$$

Again, separating variables, and rearranging:

$$\int_{V_o}^{V_c} (r_c - r_o) / r_c * dV_c = \int_0^t 4\pi D_1^r (C_c - C_o) r_o / \nu * dt \quad \text{Eqn 43}$$

and, since  $r_0 r_c = (V_0/V_c)^{1/3}$ , we can write

$$\int_{V_0}^{V_c} (1 - (V_0/V_c)^{1/3}) dV_c = 4\pi D_i^r (C_c - C_0) r_0 t / \nu \quad \text{Eqn 44}$$

The left hand side of this equation [51] integrates to the value  $V_c + 1/2 V_0 - 3/2 V_0^{1/3} V_c^{2/3}$ . If the equation is divided by  $V_0 = f_v r_0^3$  and the parameter  $(1 - \alpha)$  for  $V_c/V_0$ , where  $\alpha$  is the volume fraction of solids reacted is substituted:

$$(1 - \alpha) + \frac{1}{2} - \frac{3}{2} (1 - \alpha)^{2/3} = 4\pi D_i^r (C_c - C_0) t / \nu f_v r_0^2 \quad \text{Eqn 45}$$

or

$$1 - \frac{2}{3} \alpha - (1 - \alpha)^{2/3} = 8\pi D_i^r (C_c - C_0) t / 3\nu f_v r_0^2 \quad \text{Eqn 46}$$

Equation [53] is that it permits the product layer diffusion model to be tested on uniformly sized particles, by plotting the function  $(1 - 2/3\alpha - (1-\alpha)^{2/3})$  for linearity and for inverse square dependence on  $r_0$ .