Activity of lead in copper matte at very low lead concentration

Ty Tran, Steven Wright and Shouyi Sun*
CSIRO Minerals Down Under Flagship
CSIRO Process Science and Engineering, Bayview Ave, Clayton, Vic 3169, Australia

Abstract: The thermodynamic behavior of lead in Cu-Fe matte was investigated using a transportation technique where argon gas was bubbled into a bath of copper matte containing approximately 100 ppm lead at temperatures between 1300 and 1400°C.

The effect of flow rate, temperature and matte grade were investigated on the lead transport from a bath containing 100 grams of synthetic copper matte to the gas phase. The concentration of lead in the bath was followed with time. At argon flow rates between 3 l h^{-1} and 18 l h^{-1}, it was observed that the concentration change of lead in the matte was found to follow a first order relationship where the calculated concentration at time *t* ,is of the form:

$[Pb]= a.e^{-b.t}$

where a is equal to the initial lead content in ppm, $[Pb]_i$, and b is an exponential term and t is time in minutes. The partial pressure of lead species in the gas phase was calculated from the concentration changes in the matte and from the bubbling gas rate. At gas flow rates between 3 and 9 l h^{-1}, the lead removal appeared to be under equilibrium conditions. At higher gas flow rates, the apparent rate decreased, mainly due to splashing of matte into the cold zone of the furnace.

In these experiments with Ar as the carrier gas, the sulphur and oxygen partial pressures of the melt were not controlled. Chemical analysis of the major components in the matte showed only random variation with bubbling time, and so a thermodynamic solution model for copper matte was used to calculate the equilibrium sulphur pressure expected. From this approach the proportion of Pb, PbS and Pb_2 species in the gas could be calculated knowing the relevant reaction constants, e.g.:

$PbS(g) = Pb(g) + ½ S_2(g)$

From the proportions of the lead species in the gas, the value of the lead activity coefficient with respect to the gas state could be determined. For a 50% copper matte, it was found that the activity coefficient increased with temperature, from a value of 0.8 at 1300°C to 1.4 at 1400°C. At the white metal composition, this value was 0.28 at 1300°C. These results are compared with other relevant studies in the literature.

Key words: copper, matte, transportation, thermodynamics, lead, activity

1. Introduction

There are many toxic impurity elements associated with copper concentrates that must be eliminated in the processing to copper metal. It is important that these elements are not inadvertently released back into the environment as they can impact severely on human health. Lead is one such element that if it dispersed from the smelter site during processing can have serious health impacts on the surrounding population and the community support for the continuing operation of the smelter [1-5].

The CSIRO Minerals Down Under Flagship has a sustainability goal to develop cleaner processes that reduce the dispersion of toxic elements into the biosphere. There is real desire to reduce the spread of toxic elements to the environment during smelting processes. Thermodynamic modeling combined with flow sheeting of smelting operations can be a very useful tool to develop practices to minimize the deportment of the elements to the environment. However the modeling relies on good thermodynamic data of both major and minor species and phases. This paper documents the findings from an experimental study on the thermodynamic behavior of lead at low concentrations (< 0.01 wt%) in copper matte using a transportation technique. The transportation technique has been used successfully for volatile elements such as Pb and As at concentrations of between 0.3 to 0.5 weight percent in mattes [6-8]. These experiments determined the concentration change, and hence mass of the element transported to the gas phase. If the transport rate of was independent of gas flow, then the transport was under equilibrium control, the partial pressure of the volatile species in the gas was calculated and the activity coefficient of the elements in copper mattes determined. The results of these studies was reviewed with respect to the standard state of lead in the melt and found to be consistent with respect to the lead activity coefficients[9]. A mixed control model for removal of volatile elements from copper matte has also been developed in the literature [10] and it was reported that " the calculated results agreed well with the observed volatilization of minor elements. The predominant volatilizing species were determined to be Pb for lead. The contribution of liquid film mass transfer to the volatilization of minor elements was relatively small".

The aim of this study was to confirm the approach and results of previous studies of the behaviour of Pb in copper matte and extend the work to lower lead concentration and to higher temperatures as well as investigating the effect of copper concentration in the Cu-Fe-S matte (matte grade).

2. Experimental

2.1 Materials

The synthetic Cu-Fe-S mattes were prepared from a mixture of analytical grade FeS_2 and Cu_2S supplied as fine powders. These reagents were analysed for Pb by ICP-MS, and both contained <1ppm Pb. Metallic lead balls (99.99%) were used to dope the mattes to the desired Pb concentration.

High purity argon was used for the experiments. The Ar was passed through silica desiccant to remove trace levels of water and trace levels of oxygen was removed by using an oxygen scavenging furnace in the gas train where Ar was passed over copper turnings at 500°C.

2.2 Equipment

The crucible used to contain the matte was a closed one end Pythagorus working tube of 20 mm internal diameter (ID) and 500 mm long. The top of the "crucible" was sealed from the atmosphere by a brass end cap, an o-ring and a brass flange. The o-ring was compressed around the outside of the crucible between the end cap and the flange. The top of the end cap had sealable apertures. The crucible was immersed in a molybdenum disilicide element heated vertical tube furnace, to a depth that melt was in the centre of the hot zone (± 2°C region). The temperature of the matte was monitored by an alumina sheathed thermocouple running outside the crucible to within 30 mm if the crucible base. Inside the crucible, a central gas lance extended down to within 10 mm of the crucible base. The injected gas exited via a tube in the brass end-cap, connecting with nylon pressure tubing to a bubbler to maintain the furnace atmosphere. Also in the top of the end-cap was a re-sealable aperture for sampling the matte.

The crucible assembly was suspended from a water-cooled brass end-cap of a 50 mm ID by 1000 mm long working tube of a conventional vertical tube furnace. A thermocouple from the base was positioned approximately 5 mm below the crucible. Figure 1shows the crucible assembly in place in the furnace.

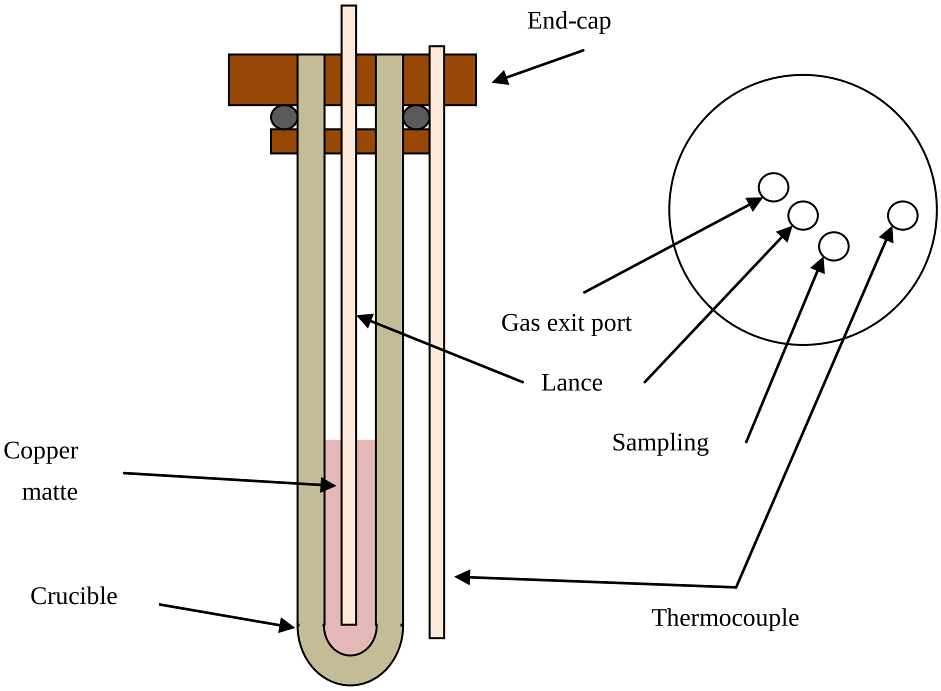

Figure 1**.** Schematic of the crucible assembly.

High purity Ar was used as the gas to transport the lead from the matte. The flow rate of gas used to transport the lead was controlled by an electronic mass flow controller and the flow calibrated by timing the volume traversed of a rising soap film in a volumetric burette.

2.3 Procedure

Approximately 100g batches of a matte containing 50% Cu was prepared by weighing FeS_2 and Cu_2S in the desired proportions. The powders were thoroughly mixed before being poured into a cold crucible. The crucible was then sealed by the brass end cap, o-ring and flange. The gas lance was then lowered into the crucible and positioned approximately 20mm above the solid powders. The gas exit tube was also located in place and the sampling hole was sealed.

The crucible assembly was suspended from the top of the furnace, with the crucible lowered into the cold furnace working tube. The exit gas line was then connected to the bubbler. The gas line from the mass flow controller was connected to the lance, and a low flow rate of argon at 5 $cm^3.min^{-1}$ was used to check the integrity of the furnace seals.

The furnace was slowly heated to the desired temperature, with a holding time at temperature of 4 hours to ensure the furnace and crucible attained thermal equilibrium. Argon at a flow rate of 20 $cm^3.min^{-1}$ was passed down the lance to protect the matte from oxidation during heating.

When the crucible had attained temperature, the lance was lowered into the matte, and the crucible allowed to thermally homogenize for 10 minutes with argon bubbling in the matte. After homogenization, approximately 0.1 g of Pb metal was added to the matte bath through the sampling port. The mixture was homogenized for a further 10 minutes. A matte sample was then collected by opening the sampling port, sliding a silica tube into the matte bath, aspirating a matte sample into the tube and withdrawing it quickly and resealing the crucible. The silica tube was then water quenched. The time clock was then started and the argon bubbling from the lance was set to a desired flow rate.

After 60 minutes of bubbling time, the lance was lifted above the matte, the clock stopped, and the same sampling procedure was carried out. After sampling, the lance was lowered, and the clock restarted. This procedure was repeated for a total gas bubbling time of 5 hours.

2.2 Chemical analysis

The matte samples were removed from the sampling silica tubes. Each sample was pulverised in a Tema ring mill with extra care taken to avoid cross contamination between samples. Approximately a 0.5g of representative sample was obtained from each of the pulverised samples and submitted for analysis by ICP-OES and ICP-MS.

Approximately 100mg portions from each sample was treated with bromine and nitric acid solution to quantitatively oxidise the sulphides present prior to decomposition with mixed HF, HNO_3 and $HClO_4$ solution. Samples were taken to near dryness before redissolving in nitric acid solution and being made to 100ml. These solutions were diluted by a factor of 20 to bring elements into a concentration range suitable for the ICP-OES and ICP-MS. Low level sulphur results were analysed using matrix matching.

3. Results

The conditions of experimental program is given in Table 1. The main variables studied were:

- Argon gas flow rate at a constant temperature of 1300°C and matte grade of 50% copper.
- Matte chemistry at a constant temperature of 1300°C and flow rate of Ar at 100 $cm^3.min^{-1}$,
- Temperature at 1400°C at a matte grade of 50% copper and Ar flow rate of 100 $cm^3.min^{-1}$. Higher temperatures were attempted, but the crucible failed soon after commencement of gas bubbling on each occasion causing loss of matte bath.

Chemical analysis of the samples from each series are given in Tables 2 to 4. Experiment designation 17, is common to all 3 series of transport experiments. It was generally observed that the concentration change of lead in the matte was found to follow a first order relationship where the calculated concentration at time *t*, is of the form:

$$[\text{ Pb }] = a.e^{-b.t} \qquad \ldots[1]$$

where *a* is equal to the initial lead content in ppm, $[\text{ Pb }]_i$, and b is an exponential term and t is time in minutes. The relative rates of removal of Pb from the matte with respect to the variables of flow rate, temperature and gas composition are analysed in the following sections, normalised with respect to the initial lead concentration in the matte. For these experiments, the targeted initial lead content was approximately 100 ppm, with the average initial concentration ~ 103 ppm.

Table 1. Conditions for the transport experiments using argon gas

	Temp (°C)	Cu (wt%)	Initial Pb (ppm)	Gas rate ($cm^3.min^{-1}$)	Total Time (min)
16	1300	50	103	100	300
17	1300	50	104	100	300
18	1300	50	101	200#	180
19	1300	50	108	300##	150
20	1300	50	103	50	300
21	1300	50	108	150	60
23	1300	50	103	150	300
24	1300	60	101	100	300
25	1300	70	101	100	300
26	1300	80	98	100	300
27	1400	50	103	100	300

[#] Frozen crust form after 180mins, prevented further sampling.

[##]Sampling rate at 30min interval. Frozen crust formed after 60mins. Increased temperature by 100°C for 10mins. Partially melted crust

Table 2. Chemistry of the matte samples collected from the flow rate series of experiments at 1300°C

Ar $cm^3.min^{-1}$	Sample ID	Time (min)	Pb ppm	Cu %	Fe %	S %	Ar $cm^3.min^{-1}$	Sample ID		Pb ppm	Cu %	Fe %	S %
50	20-0	0	106	49.5	26.1	24.0	100	17-0a	0	107	50.6	25.9	23.7
	20-1	60	100	49.7	25.8	24.0		17-0b	0	107	51.4	26.3	24.0
	20-2	120	92	50.1	25.8	24.0		17-1	60	95	49.3	24.9	23.3
	20-3	150	83	48.8	25.0	23.6		17-2	120	82	50.8	25.4	24.0
	20-4	180	76	49.7	25.3	24.1		17-3	180	69	51.5	25.5	24.3
	20-5	240	70	50.4	25.5	24.3		17-4	240	57	50.3	25.0	23.7
								17-5	300	45	50.5	24.6	23.7
150	23-0a	0	106	49.5	25.5	23.5	200	18-0	0	105	50.6	25.9	23.7
	23-0b	0	106	50.0	25.8	23.7		18-1	60	98	51.4	26.3	24.0
	23-1	60	90	50.0	25.4	23.7		18-2	120	90	49.3	24.9	23.3
	23-2	120	79	50.5	25.3	23.9		18-3	180	89	50.8	25.4	24.0
	23-3	180	68	50.1	24.8	23.7							
	23-4	240	62	50.1	24.6	23.9							
	23-5	300	58	51.2	25.0	24.5							
300	19-0a	0	111	50.6	25.9	23.7							
	19-0b	0	111	51.4	26.3	24.0							
	19-1	30	110	49.3	24.9	23.3							
	19-2	60	99	50.8	25.4	24.0							
	19-3	90	96	51.5	25.5	24.3							
	19-4	120	77	50.3	25.0	23.7							
	19-5	150	70	50.5	24.6	23.7							

Table 3. Chemistry of the matte from the matte grade experiments at 1300°C and flow rate of 100 $cm^3.min^{-1}$ Ar

Sample ID	Time min	Pb ppm	Cu %	Fe %	S %
24 -0a	0	104.2	62.4	15.2	23.0
24-0b	0	104.3	63.1	15.3	22.9
24-1	60	98	60.7	14.2	22.9
24-2	120	89	61.9	14.7	23.2
24- 3	180	77	62.3	14.6	23.1
24-4	240	69	61.9	14.6	23.3
24-5	300	59	63.2	14.5	23.3
26-0	0	99.5	78.5	0.3	19.4
26-1	60	67	78.6	0.3	19.8
26-2	120	65	78.7	0.4	19.8
26-3	180	61			
26-4	240	50	78.6	0.5	19.6
26-5	300	43	78.4	0.5	19.7

Sample ID	Time min	Pb ppm	Cu %	Fe %	S %
25-0	0	104.3	73.3	4.8	21.3
25-1	60	98	72.0	4.6	20.9
25-2	120	87	72.6	5.1	21.2
25-3	180	76	74.0	4.7	21.6
25-4a	240	65	71.3	4.6	20.8
25-4b	240	67	72.1	4.6	21.0
25-5	300	57	72.5	4.7	21.3

Table 4. Chemistry of the matte samples collected from the experiment at 1400°C and 100 $cm^3.min^{-1}$ Ar

Sample ID	Time min	Pb ppm	Cu %	Fe %	S %
27-0a	0	106	49.9	25.6	24.1
27-0b	0	107	50.2	25.9	24.3
27-1	60	88	50.6	25.6	24.5
27-2	120	64	50.5	25.3	24.5
27-3	180	48	50.4	25.3	24.4
27-4	240	35	50.6	25.2	24.5
27-5	300	24	50.7	25.1	24.6

3.1 Effect of flow rate

The change of lead content in the 50% copper matte at 1300°C containing 100 ppm of lead with argon bubbling rates of between 50 and 300 $cm^3.min^{-1}$ are given in Table 2 and shown graphically in Figure 2. The lines of best fit based on an exponential fit to the change in Pb concentration are shown in the figure and the values for the parameters are given in Table 5. As commented earlier, the experiment at the gas flow of 200 $cm^3.min^{-1}$of Ar, was affected by freezing matte splash in the cold zone of the furnace.

Table 5. Values of the a and b parameters (Equation 1) for the exponential lines of best fit to the flow rate series of transport experiments.

Ar $cm^3.min^{-1}$	a	b
50	106	-0.0014
100	107	-0.0021
150	106	-0.0024
200	105	-0.0012
300	100	-0.0032

The mass of the bath was corrected for both the amount of sample collected and for loss due to splash in the cold zone of the furnace. No correction for splash was required for the experiments with gas flows of 150 $cm^3.min^{-1}$ or less.

The lead removal expressed as $mol.min^{-1}$ can be calculated from the analyzed concentration change over the bubbling period or from calculated concentration changes from the line of best fit. The as stated previously, the concentration dependence is of the form:

$$[\ Pb\ ]= a.e^{-b.t}$$

This form was still suitable after correction for sampling and splash, where the moles of lead transported per minute were calculated by the following relationship:

$$r_{Pb} = M_0.([Pb]_0-[Pb]_t)/10^6/207.2/t \qquad \ldots[2]$$

where r_{Pb} is the rate of lead transported, M_0 is the mass of bath prior to bubbling, $[Pb]_0$ and $[Pb]_t$ is the concentration of Pb in part per million at the start and at time, t; t is the bubbling time. The lead transport rate calculated using the corrected bath mass is compared in Figure 3a. The lead removal rate is directly proportional to the flow rate for flows up to 150 cm^3.min^{-1} and then decreases at the higher flow rates. The calculated partial pressure of the total lead species in the gas as a function of flow rate is shown in Figure 3b. Within the scatter of the results, the total lead partial pressure was constant over the 50 to 150 flow range, and then decreased at the higher flow rates.

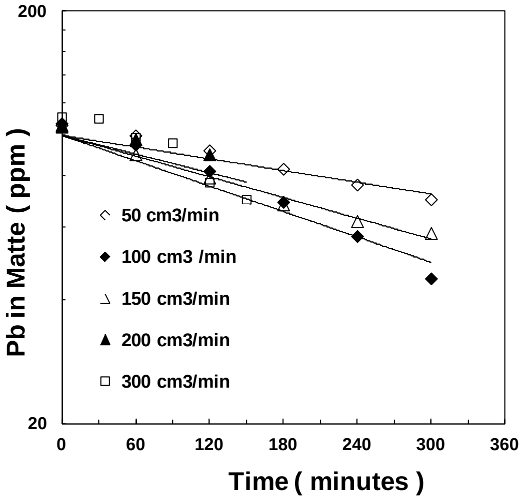

Figure 2. Analyzed Pb content of a 50% Cu matte at 1300°C bubbled with Ar flow rates of 50 to 300 cm^3.min^{-1}. Note shorter bubbling duration for the 200 cm^3.min^{-1} and 300 cm^3.min^{-1} experiments.

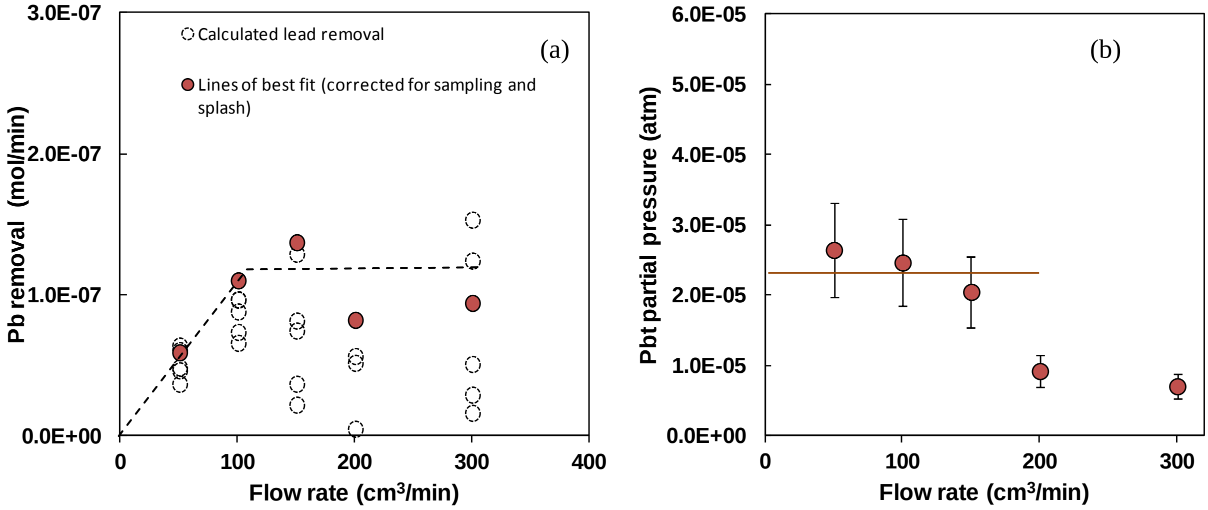

Figure 3. Comparing the Pb removal rate of a 50wt% Cu matte containing 100 Pb at 1300°C bubbled with Ar at flow rates between 50 and 300 cm^{3}min^{-1}. (a) lead removal rate expressed as mol.min^{-1} from 100 g of copper matte from individual sampling intervals and from the lines of best fit; (b) The total lead partial pressure in the gas as a function of the gas flow rate, excluding the 200 cm^3.min^{-1} experiment.

When the total lead partial pressures are calculated and plotted against the Ar bubbling rate, and the measurement uncertainties are considered, then at flows between 50 and 150 cm^3.min^{-1}, the lead partial pressure in the gas can be considered independent of the gas bubbling rate, ie the gas was saturated with lead. Further supporting evidence for this conclusion comes from the literature. Roine and Jalkanen [6] also performed a transport study of lead from copper mattes containing 0.2 wt% Pb at 1200°C and found that the gas phase was saturated with lead when 10 gram baths of matte that were stirred with up to 50 cm^3.min^{-1} of argon. Zhong and Lynch [8] studied the transportation of lead from copper mattes containing 0.5 or 0.3 wt% Pb. Baths of 173 to 200 grams of matte was bubbled with up to 50 cm^3.min^{-1} of argon, and the surface of the bath was swept with 850 cm^3.min^{-1} of Ar carrier gas. Only a small amount of gas stirring was required to maintain the supply of Pb to the bath surface. The volatilized lead was collected on a cold finger, weighed and analyzed for Pb to determine the mass of lead removed. They deemed that under the conditions of their experiment, the transport of lead was under saturation conditions. This was confirmed for the injected gas at rates up to 50 cm^3.min^{-1} and also for the carrier gas at flow rates up to 1200 cm^3.min^{-1}. From their results, much higher flow rates than used in this study will be required to move the rate controlling step from equilibrium control. ,

Similar behavior was observed for lead in a study of removal volatile elements from a 100 gram copper bath by Sohn and co-workers who studied the removal rate of lead using Ar and Ar+O_2 gas mixtures [10]. They developed a mixed control model for the removal of the volatile elements and found for lead and injection of Ar, the removal was under equilibrium control, and the gas was saturated with lead. Given that the matte bath mass and gas flow rates used are in between that of the previous studies, the bubbling conditions were able to maintain the supply to lead from the bulk matte to the bubble surface, and that the lead species in the gas bubbles exiting the matte were at equilibrium with the liquid matte.

3.2 Effect of temperature

The effect of temperature on the transport of lead from a 50% copper matte containing 100 ppm of lead was examined at temperatures of 1300, 1400 and 1500°C. The 1500°C experiment failed due to containment issues. The analysis results at 1300 and 1400°C are given in Tables 2 and 4 and the change of lead content in the matte with time is shown in Figure 4. The lead removal rate nearly doubled from a slope of -0.0029 at 1300°C to -0.005 at 1400°C.

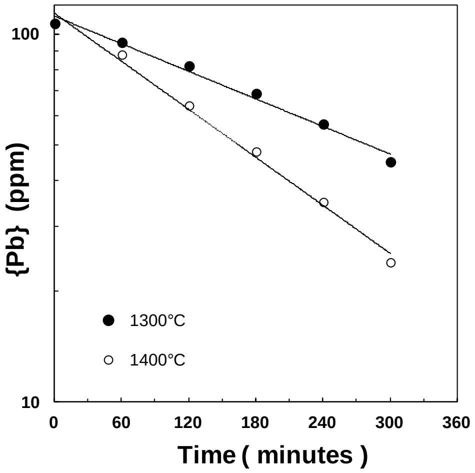

Figure 4. Comparison of the change in Pb content of a 50% copper matte bubbled with Ar at 100 cm^3.min^{-1} at 1300°C and 1400°C.

3.3 Effect of matte grade.

The effect of the matte grade or copper content on the transport behaviour of lead was studied at matte grades between 50% copper and 79% copper (white metal). The raw data are presented in Tables 2 and 3 and plotted as a function of time in Figure 5. At medium to high matte grade (50-73% Cu), matte grade does not appear to have a significant influence on the behaviour of lead in the matte at low lead concentrations. The data for removal of lead from a 79% copper matte (white metal) was fitted over the period of 60 to 300 minutes, whereas for all the other experiments where the matte grade was varied, the data were fitted over the whole 5 hour period. The a and b terms for the lines of best fit are given in Table 6.

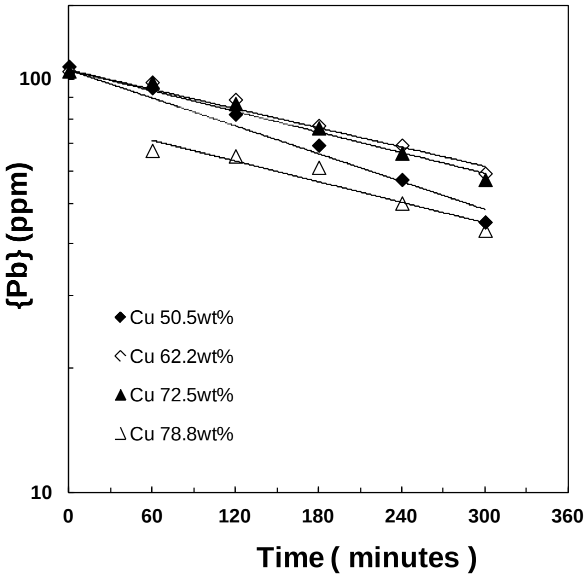

Figure 5. Change in Pb content of the matte with time for different Cu matte grade at 1300°C bubbled with Ar at 100 $cm^3.min^{-1}$.

Table 6. The a and b terms (Equation 1) for the lines of best fit to the transportation of lead form copper mattes of varying grade at 1300°C bubbled with argon at 100 $cm^3.min^{-1}$.

Matte grade (wt% Cu)	a	b
79	80	-0.0019
73	105	-0.0019
62	105	-0.0018
50	105	-0.0026

4. Discussion

The mass of lead lost per minute as a function of the lead concentration in the matte was calculated using the lines of best fit to the lead concentration data and from the mass of the matte bath. From this rate, the lead partial pressure was calculated using the gas rate, the ideal gas law, assuming that the lead was mainly reporting in the gas as a monomer species.

There are two relevant studies to which these results can be compared:

- Roine and Jalkanen examined the volatility of lead and other volatile metals for several matte grades at 1200°C using a 10g matte bath and flow rates between 10 and 50 $cm^3.min^{-1}$ [6].

- Zhong and Lynch studied the rate of lead loss from 170 to 200 g of matte as a function of matte grade at temperatures between 1200 to 1300°C [8]. In their experimental study, they bubbled 40 $cm^3.min^{-1}$ of Ar into the matte and used 850 $cm^3.min^{-1}$ carrier gas giving a total gas volume of 890 $cm^3.min^{-1}$.

When the lead partial pressures are calculated and plotted against the lead concentration in the matte, there is a straight line dependency between the lead partial pressure and concentration as shown in Figure 6. The partial pressure dependency with concentration exhibits the same slope as of previous work by Zhong and Lynch [8].

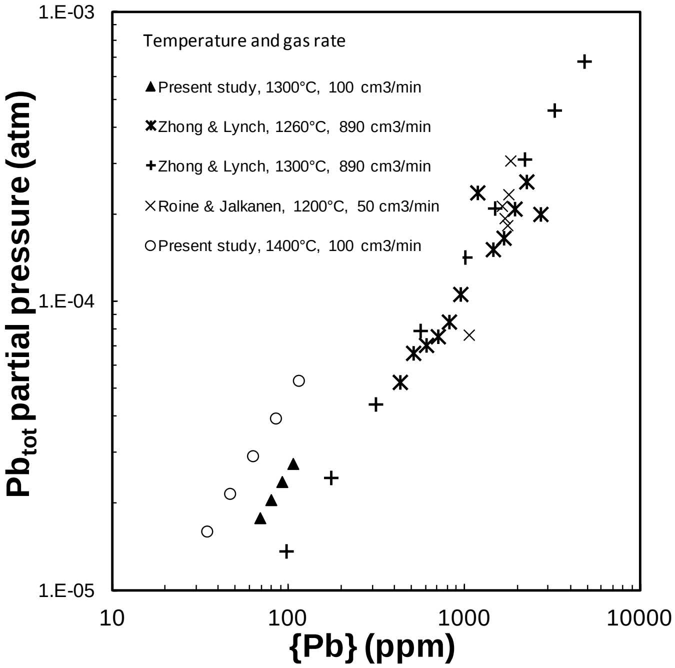

Figure 6. Calculated partial pressure of total Pb as a function of Pb content in the matte from this study at 1300°C and that from the literature [6,8].

The total partial pressure of lead in the vapour phase is

$$P_{Pb(tot)} = P_{PbS} + P_{Pb} + P_{Pb2} + P_{PbO} \quad \ldots[3]$$

The previous studies have determined that in systems where the sulphur partial pressure is high, lead is volatilised mainly as PbS with only a small contribution from Pb and Pb_2 and PbO, and thus $P_{Pb(tot)} \approx P_{PbS}$. The total partial pressure of lead can also be approximated from the rate of lead vaporised and the gas flow rate:

$$P_{Pb(tot)} \approx R_{Pb(vap)}/MW/(Q/V_{STP} + R_{Pb(vap)}/MW) \quad \ldots[4]$$

Where MW is the molecular weight of lead and Q is the flow rate of the gas in the transportation experiment, and V_{STP} is the molar volume of an ideal gas at STP. The calculated total partial pressure of lead is shown in Figure 6. The partial pressures calculated from the experiments at 1300°C and 1400°C, show the trend that the partial pressure of lead increased as the temperature and lead content in the matte increased.

In the transportation experiments with Ar gas of this study, the sulphur and oxygen partial pressures of the melt were not controlled, and this approach was similar to the previous studies. Using the matte model in the MultiPhase Equilibrium (MPE) software [11], the sulphur partial pressure can be estimated from the composition of the matte by chemical analysis and the volume of Ar gas used. According to the analytical results shown in Tables 2-4, the composition of the major components of the mattes did not vary over the 6 hours of an experiment. For a melt containing 50.6% Cu, 25.9% Fe and 23.7% S, the calculated pS_2 was 6.27×10^{-6} atm. In the previous studies, Roine and Jalkanen estimated the pS_2 from the melt composition using the matte model of Bale and Toguri [12] and Zhong and Lynch cite unpublished research (reference 7) in their paper. Nagamori and Sohn have observed this difference and unified the data to investigate the activity coefficient of lead species in white metal [9]. The sulphur pressures from the previous studies are compared with the MPE calculated partial pressures based on the matte compositions of the previous studies in Table 7.

Table 7. Comparison of sulphur partial pressures of this study and previous studies [6,8].calculated from the matte composition by the MPE[11].

Study	Cu	Fe	S	Temp	p_{S2} atm	
	wt%	wt%	wt%	°C	Paper	MPE
Present	50.6	25.9	23.7	1300	-	6.3×10^{-6}
Roine & Jalkanen	56.4	19.7	23.9	1200	1.9×10^{-6}	4.3×10^{-6}
Zhong & Lynch	56.1	19.7	24.2	1260	2.2×10^{-6}	2.1×10^{-5}
Zhong & Lynch	56.1	19.7	24.2	1300	5.0×10^{-6}	5.3×10^{-5}

Increasing the gas volume by 1000 times shifted the sulphur partial slightly to a pressure of 6.76×10^{-6} atm. Both of the previously published studies [6,8] reported that the partial pressure of Pb in the gas phase decreases (and γ_{Pb}) decreases as the sulphur partial pressure increases. In Table 7, the data from the previous studies conducted at sulphur partial pressures similar to that estimated for this study are compared with the current work. The lead partial pressure decreases as the lead content decreased and for a fixed lead content increases with temperature. From this data, the activity coefficient of lead in the melt can be evaluated.

The partial pressure of $PbS_{(g)}$ and $Pb_{(g)}$ can be calculated from equation 3, assuming the p_{Pb2} and p_{PbO} are much smaller than p_{PbS} and p_{Pb}. Then from the following equation, where the reaction constant is known (153 at 1300°C), and p_{S2} is evaluated from the MPE, the partial pressures of PbS and Pb can be evaluated.

$$Pb_{(g)} + \tfrac{1}{2} S_{2(g)} = PbS_{(g)} \quad \ldots[5]$$

At the calculated p_{S2} from the melt composition, the ratio of p_{PbS}/p_{Pb} was 0.38 and 0.5 at 1300 and 1400°C respectively. This ratio was independent of the lead content in the matte. The mole fraction of Pb was calculated assuming the matte is dissociated and comprises distinct ions of Cu^{+}, Fe^{2+}, S^{2-} and Pb^{2+}. The variation of the $Pb_{(g)}$ partial pressure with lead content in the matte was plotted in Figure 7a and the activity coefficient calculated and shown as a function of lead mole fraction in Figure 7b. The standard state for lead in these calculations is with respect to elemental lead gas, and so the activity coefficient (γ_{Pb}) is with respect to the $Pb_{(g)}$ state. These results confirm that Henry's law was obeyed at low lead concentrations in the matte.

From the analytical variation of the matte composition, it was observed that the variation of p_{S2} would be expected to be between 0.3 to 3.5 times the value calculated for the average matte composition for each experiment. This partial pressure range, leads to an additional uncertainty range of +0.1 to -0.05 for the lead activity coefficient (for the values between 0.2 and 1.4). The previous studies also showed no strong dependence of lead content on activity coefficient of lead. On that basis, it is reasonable to infer there was no concentration dependence on the lead activity coefficient in the matte. The activity coefficient of Pb increased with temperature, from a value of 0.8 at 1300°C to 1.4 at 1400°C.

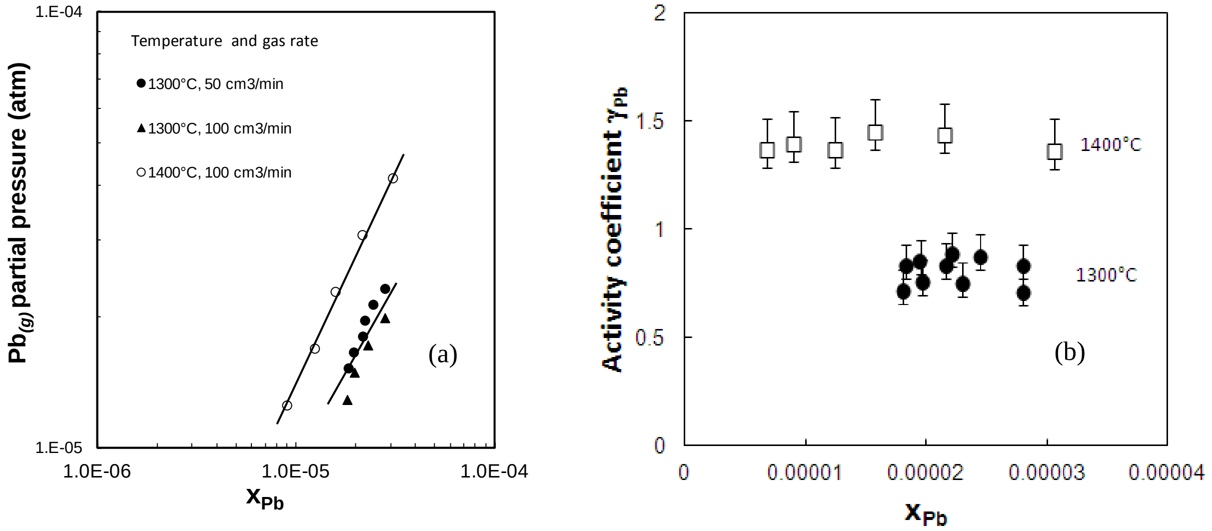

Figure 7. a) Calculated partial pressure of $Pb_{(g)}$ from this study at 1300 and 1400°C. b) Calculated activity coefficient of Pb with respect to $Pb_{(g)}$ from this study at 1300 and 1400°C as a function of lead content in the matte.

For the series of experiments examining the effect of matte grade on the lead transport, the average matte composition, the initial lead concentrations and the calculated sulphur partial pressure, and the values used to determine the lead activity coefficient are given in Table 8 and the plot of the activity coefficient versus matte grade is presented in Figure 8. As the matte grade increases from 50% to 72%, the activity coefficient decreases as the matte grade increased. At the white metal composition, there is a slight increase in the activity coefficient.

Table 8. Average matte composition, calculated lead mole fraction, sulphur partial pressure and activity coefficient of Pb with respect to Pb(g) for the experiments examining the effect of matte grade where Ar was bubbled into the matte at 100 $cm^3.min^{-1}$.

Cu wt%	S wt%	Pb ppm	x_{Pb}	$p_{Pbtot(g)}$ atm	p_{S2} atm	p_{PbS}/p_{Pb}	$p_{Pb(g)}$ atm	$\gamma_{Pb(g)}$
50.6	23.7	100	$2.8x10^{-5}$	$3.2x10^{-5}$	$6.3x10^{-6}$	0.38	$2.3x10^{-5}$	0.80
62.2	23.1	105	$2.6x10^{-5}$	$2.0x10^{-5}$	$4.4x10^{-5}$	1.0	$1.0x10^{-5}$	0.40
72.5	21.2	105	$2.7x10^{-5}$	$2.2x10^{-5}$	$1.3x10^{-3}$	5.5	$3.3x10^{-6}$	0.51
78.8	19.4	80	$2.1x10^{-5}$	$1.6x10^{-5}$	$1.1x10^{-5}$	0.88	$8.8x10^{-6}$	0.28

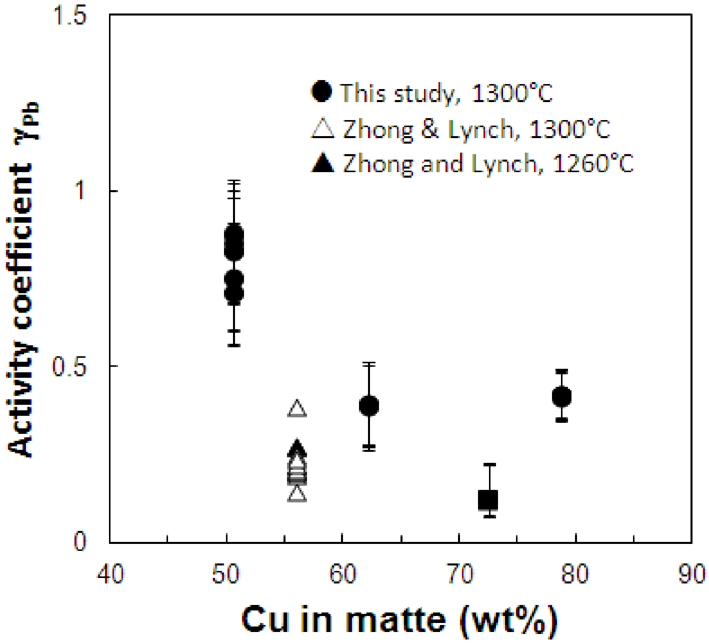

Figure 8. Calculated activity coefficient of Pb with respect to $Pb_{(g)}$ as a function of matte grade from this study at 1300°C, and compared with that from the results of Zhong and Lynch[8].

The activity coefficient for liquid lead can be determined from the standard reaction and thermodynamic data:

$$Pb_{(l)} = Pb_{(g)} \qquad \ldots[6]$$

Where $\Delta G = 182000 - 90.08 * T\ (K)$ [10]

Evaluating this relationship at 1300°C yields

$$\gamma_{Pb(l)} = 21.8 * \gamma_{Pb(g)} \qquad \ldots[7]$$

So the $\gamma_{Pb(l)}$ for a 56% copper matte from this study is 17.4. This value is higher, but consistent with the other studies. Roine and Jalkanen [6] determined that $\gamma_{Pb(l)}$ for 56% mattes at 1200°C had a value of 20±4 at the sulphur pressures of this study. At nearly constant sulphur pressure, the activity coefficient of lead decreased as the matte grade increased. Similarly, Zhong and lynch [8] reported a value of $\gamma_{Pb(l)}$ of 9.33, comparable to that determined in this study.

5. Conclusions

Transportation experiments on copper matte containing low levels of lead were conducted under conditions where the gas phase was saturated with lead vapour. The calculated total lead partial pressure above a 50% copper matte is of the same magnitude as previous studies. The MPE matte model was used to calculate the sulphur partial pressure of the mattes during the transportation experiments, which was not controlled, as pure Ar was used as the transporting gas. This allowed for the calculation of the Pb and PbS partial pressures in the gas phase, and calculation of the lead activity coefficient with respect to the gas state. The contribution of $Pb_2(g)$ to the lead species in the gas was estimated to be insignificant.

The following observations were made with respect to the lead transport, partial pressure, matte composition and activity coefficient.

- At gas flow rates between 50 and 150 $cm^3.min^{-1}$, the gas phase was saturated with lead and the lead removal appeared was under equilibrium control. At higher gas flow rates, the rate decreased, mainly due to splashing of matte into the cold zone of the furnace.
- At a constant matte grade, the activity coefficient of Pb was constant with respect to lead content for mattes containing between 100 and 70 ppm of lead. These results confirm the expectation that Henry's law should be obeyed at low concentration of lead in the matte.
- The lead activity coefficient increased with temperature, from a value of 0.8 at 1300°C to 1.4 at 1400°C.
- The MPE calculated that the equilibrium sulphur pressure changed as the matte grade and temperature changed, influencing the PbS/Pb ratio in the gas phase. This ratio was calculated to vary between 0.38 and 5.5 for the various compositions and temperatures studied.
- The activity coefficient of $Pb_{(g)}$ decreased as the matte grade increased from 50% Cu to the white metal composition. For a 50% Cu matte at 1300°C, the activity coefficient had a value of 0.8. At the white metal composition, this value was 0.28

This study has shown that a transportation method can be a very useful approach to determining thermodynamic behaviour of volatile species in mattes at low concentrations. Care must be taken with the sampling, but the approach used of aspirating sample into a silica tube was found to give reliable results.

Acknowledgement

The authors with to acknowledge the financial support of the CSIRO Minerals Down Under National Research Flagship. The authors also wish to thank Tom Austin who helped with the experimental work and the sample preparation and also wish to acknowledge the care and precision of the CSIRO Process Science and Engineering Analytical Services Team who performed the sample analysis.

References

[1] http://www.minesandcommunities.org/article.php?a=1669

[2] M. J. Steele, B.D. Beck, B.L. Murphy, H.S. Strauss. Assessing the contribution from lead in mining wastes to blood lead. *Regulatory Toxicology and Pharmacology*, 1990, 11(2), p. 158-190.

[3] B.L. Gulson, J.J. Davis, K.J. Mizon, M.J. Korsch, A.J. Law, D. Howarth. Lead bioavailability in the environment of children: blood lead levels in children can be elevated in a mining community. *Archives of Environmental Health*, 1994, 49(5), p. 326-331.

[4] E. K. Silbergeld. Preventing lead poisoning in children, *Annual Review of Public Health,* 1997, 18, p. 187-210.

[5] http://www.derm.qld.gov.au/environmental_management/mt_isa_lead_monitoring_information.html

[6] A.Roine, H. Jalkanen. Activities of As, Sb, Bi and Pb in copper mattes. *Metallurgical Transactions B*, 1985, 16,

p129-141.

[7] A. Roine. Activities of As, Sb, Bi and Pb in copper mattes – Effect of O, Ni and Co. *Metallurgical Transactions B*, 1987, 18, p203-212.

[8] T. Zhong, D.C. Lynch. Henrian activity coefficient of Pb in Cu-Fe mattes and white metal. *Metallurgical and Materials Transactions B*, 1998, 29, p429-436.

[9] M. Nagamori, H.Y. Sohn, Dissolution of lead and bismuth in white metal ($CuS_{0.5}$) at matte-smelting temperatures.*Metallurgical and Materials Transactions B*. 2000, 31(3), p543-546.

[10] H.S. Sohn, Y. Fukunaka, T. Oishi, Z. Asaki, H.Y. Sohn. Kinetics of As, Sb, Bi and Pb volatilization from industrial copper matte during Ar + O2 bubbling. *Metallurgical and materials transactions*. B, 2004, 35(4), p 651-

[11] L. Zhang, S.Jahanshahi, S. Sun, C. Chen, B. Bourke, S. Wright, M.A. Somerville. CSIRO's Multi-Phase Reaction Model and Its Applications in Industry. *Journal of Metals*, 2002, 54, p.51-56.

[12] C.N Bale, J.M. Toguri. *Canadian Metallurgical. Quarterly*, 1976, 15, pp. 305-318.