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Canada

METAL ENTRAINMENT IN CONTINUOUS LIQUID PHASE DROSSES

Ъy

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November, 1994

A Thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the degree of Doctor of Philosophy

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to my father who inspired academic pursuit

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ABSTRACT

A comprehensive characterization of silver and bismuth refining crusts produced during the pyrometallurgical refining of lead was undertaken. Parameters such as intermetallic crystal size and composition, and degree of metal entrainment were determined. Silver crust was found to be composed mostly of the ϵ -phase (AgZn₃) with an average particle size of 50 µm. Liquid lead entrainment of 80 volume percent was measured. The intermetallic phase in bismuth crust was composed entirely of CaMg₂Bi₂ crystals with an average diameter of 50 µm. Lead entrainment in bismuth crust was approximately 90 volume percent. The high degree of metal entrainment of solid particles. The models used to predict swelling in colloidal particle systems (such as clay soils) were found to better approximate the high degree of liquid entrainment.

Experiments were performed in which particle beds of γ -phase (Ag₅Zn₈) intermetallic compound were infiltrated with liquid lead under controlled conditions and examined under the optical microscope. Image analysis revealed pronounced swelling of fine particle beds relative to coarse. The effect was most noticeable for average particle diameters less than 100 µm where the solids volume fraction decreased from 50 to 30 vol.%. Data showed samples to exhibit a constant increase in inter-particle spacing of approximately 50 µm. The increase in spacing explained the degree of swelling at low particle diameters and was also used to develop an expression to predict height of capillary rise.

Based on an osmotic pressure analogy in colloidal particle systems, a swelling pressure term was defined to explain the increase in inter-particle spacing. The swelling pressure was defined as equal and opposite to the capillary pressure tending to force particles to random packing. It was concluded that swelling was related to mass transfer at the solid-liquid interface of the intermetallic crystals giving a reduced static pressure due to a localized minimization of Gibbs energy. The static pressure change (swelling pressure) was attributed to overlap of mass transfer boundary layers where mid-point static liquid metal pressure is less than the pressure

in the bulk liquid. For the system studied, the mass transfer boundary layer was estimated to be approximately 100 µm in thickness.

Further experiments, using the sessile drop technique, were used to support the study findings by showing rapid spreading of liquid lead on Ag-Zn intermetallic substrates. The rapid spreading was attributed to mass transfer at the solid-liquid interface giving a reduced interfacial energy, $\gamma_{\rm sl}$, due to a localized reduction in Gibbs energy.

The analysis of experimental results led to the development of two new industrial processes in the lead industry aimed at reducing lead loss to silver and bismuth crusts. Tests employing continuous agitation during bismuth removal from lead promoted the growth of large $CaMg_2Bi_2$ crystals. The larger crystals minimized the effect of mass transfer boundary layer overlap and reduced lead entrainment from 90 to 80 volume percent. The addition of a low melting point KCl-ZnCl₂ salt during silver crust formation was found to remove up to 90% of entrained lead by the salt preferentially wetting Ag-Zn intermetallic particles. This was found to eliminate surface forces which retained liquid in the system of solid particles.

RÉSUMÉ

Une caractérisation détaillée des croûtes d'affinage d'argent et de bismuth produites durant l'affinage pyrométallurgiqe du plomb a été entreprise. Les paramètres tels que la grosseur et la composition des cristaux intermétalliques et le degré d'entraînement de métal ont été déterminés. La croûte d'argent était principalement de composée de la phase \Rightarrow (AgZn₃) avec une grosseur de particules moyenne de 50 µm. On a mesuré une part de volume de 80 % de plomb liquide entraîné dans la croûte. La phase intermétallique de la croûte de bismuth était entièrement composée de cristaux de CaMg₂Bi₂ ayant un diamètre moyen de 50 µm. L'entraînement du plomb dans la croûte de bismuth était de 90 % environ du volume. Le niveau d'entraînement de métal élevé observé dans les croûtes d'argent et de bismuth n'a pas pu être suffisamment expliqué à l'aide d'un modèle capillaire d'entraînement de métal liquide dans un lit statique de particules solides. Les modèles utilisés pour prédire le gonflement dans les systèmes de particules colloïdales (comme les sols argileux) ont donné une meilleure approximation du niveau élevé d'entraînement de liquide.

Des essais ont été réalisés avec des lits de particules de composé intermétallique de phase γ (Ag₅Zn₈) qui ont été infiltrés avec du plomb liquide en conditions contrôlées et examinés sous un microscope optique. Une analyse d'image a révélé un gonflement plus prononcé des lits de particules fines que des lits de grosses particules. Cet effet était particulièrement évident dans les particules moyennes de moins de 100 µm où la fraction volumique des solides a diminué de 50 à 30 %. Les données ont révélé une augmentation constante de 50 µm environ dans l'espacement interstitiel. Cette augmentation de l'espacement, qui explique le degré de gonflement du lit de particules de petit diamètre, a également été utilisée pour élaborer une équation visant à prédire la hauteur de l'ascension capillaire.

D'après une analogie de la pression osmotique dans les systèmes de particules colloïdales, un terme de pression de gonflement a été défini pour expliquer l'augmentation dans l'espacement interstitiel. La pression de gonflement a été définie comme étant égale et opposée à la pression

capillaire tendant à forcer les particules dans une disposition de tassement désordonnée. On a conclu que le gonflement était lié au transfert de masse à l'interface solide-liquide des cristaux intermétalliques, entraînant une pression statique réduite due à une diminution locale de l'énergie de Gibbs. La variation de pression statique (pression de gonflement) a été attribuée à un chevauchement des couches limites de transfert de masse où la pression statique entre deux particules dans le métal liquide est inférieure à la pression du liquide dans le bain. Dans le système étudié, l'épaisseur de la couche limite de transfert de masse a été estimée à 100 μ m environ.

D'autres essais, utilisant la méthode de la goutte sessile, ont été réalisés pour corroborer les résultats en montrant la diffusion rapide du plomb liquide sur les substrats intermétalliques Ag-Zn. Cette diffusion rapide a été attribuée au transfert de masse à l'interface solide-liquide, réduisant l'énergie interfaciale γ_{st} en raison d'une réduction locale de l'énergie de Gibbs.

L'analyse des résultats des essais a mené au développement, dans l'industrie du plomb, de deux nouveaux procédés industriels visant à réduire la perte de plomb dans les croûtes d'argent et de bismuth. L'agitation continue lors de l'extraction du bismuth dans le plomb a favorisé la croissance de gros cristaux de CaMg₂Bi₂. Ces cristaux plus gros ont minimisé l'effet de chevauchement des couches limites de transfert de masse et réduit l'entraînement de plomb de 90 à 80 du pourcentage volumique. L'ajout d'un sel de KCl-ZnCl₂ à bas point de fusion pendant la formation de la croûte d'argent a permis de retirer jusqu'à 90 % du plomb, par le mouillage préférentiel des particules intermétalliques d'ag-Zn par le sel, ce qui a éliminé les forces à la surface qui retenaient le liquide dans le système de particules solides.

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NOMENCLATURE

Т	=	temperature (°C)				
K _{sp}	=	solubility product				
ΔH	=	change in enthalpy (J-mol ⁻¹)				
ΔG	=	Gibbs energy change (J-mol ⁻¹)				
X	=	mole fraction				
R	=	universal gas constant (8.314 J-mol ⁻¹ -degK ⁻¹)				
Ya	=	solid-liquid interfacial energy (ergs-cm ⁻² or J-cm ⁻²)				
Υw	=	liquid vapour interfacial energy (ergs-cm ⁻² or J-cm ⁻²)				
Ύsv	=	solid-vapour interfacial energy (ergs-cm ⁻² or J-cm ⁻²)				
r	=	radius (cm)				
V _M	=	molar volume (cm ³ -mol ⁻¹)				
φ	=	molar heat of solution (J-mol ⁻¹)				
σ	=	supersaturation				
I	=	rate of nuclei formation (nuclei-cm ⁻³ -sec ⁻¹)				
z	=	frequency of attachment of single molecules to a unit area of nuclei				
n	=	number of nuclei per unit volume				
ρ	=	density (g-cm ⁻³)				
η	=	viscosity (g-cm ⁻¹ -sec ⁻¹)				
v	=	fluid velocity (cm-sec ⁻¹)				
u	=	linear growth rate (cm-sec ⁻¹)				
l,L	=	crystal length (cm)				
D	=	diffusivity (cm ² -sec ⁻¹)				
Re	=	Reynolds number				
ð	=	momentum transfer boundary layer thickness (cm)				
δ _c	=	mass transfer boundary layer thickness (cm)				
x	=	distance (cm)				
j,	=	molar flux in x direction (mol-cm ⁻² -sec ⁻¹)				



С	=	molar concentration (mol-cm ⁻³ or mol-l ⁻¹)
k _B	=	Boltzmann's constant (1.38 x 10 ⁻²³ J-deg ⁻¹)
k _M	=	mass transfer coefficient (cm-sec ⁻¹)
Sc	=	Schmidt number
Α	=	area (cm ²)
Ρ	=	pressure (J-cm ⁻³)
g	=	acceleration of gravity (9.81 m-sec ⁻²)
θ	=	solid-liquid contact angle (degrees)
μ	=	chemical potential
М	=	molecular weight (g-mol ⁻¹)
Ν	=	Avogadro's number (6.023 x 10 ²³ atoms-mol ⁻¹)
a	=	chemical activity
W	=	work (J-sec ⁻¹)
h	2	height (cm)
φ	=	volume fraction of solids

1. INTRODUCTION

The metallurgical industry has dealt with metal dross for thousands of years. Dross is defined as solid particles which may float or sink in a molten-metal system. The examples of the types and occurrence of dross are many and varied. However, in each case this material represents a burden to industry by requiring special handling, impacting on metal quality, or simply by entraining the valuable metal product. It is this latter effect, the loss of metal entangled in the dross phase, which is the principal subject matter of this investigation.

Despite the prevalence of drosses in the metallurgical industry, there is a surprising lack of fundamental literature which describes the mechanisms by which liquid metal can be held in a system of solid particles. Most of the work conducted in the area of metal loss to dross has focused on practical methods of reducing entrainment for specific systems. For example, a great deal of work has recently been conducted in the aluminum industry devising new processes to recover metal lost in oxide-dross skimmings⁽¹⁾. Although this type of work has been largely successful, our fundamental understanding of the underlying physical phenomena involved is less than complete.

Some of the most intriguing dross systems involve the separation of insoluble intermetallic compounds from liquid metal baths. These systems are unique in their ability to entrain tremendous quantities of the molten metal, sometimes carrying as much as 90-95 volume percent liquid metal. Often intermetallic compound drosses are unfortunate byproducts of industrial practices. Hot-dip galvanizing of steel sheet is such an example, where dissolved impurities in the zinc bath eventually build-up to the point where insoluble intermetallic compounds of iron, zinc, and aluminum precipitate from solution and form a troublesome dross layer. This layer interferes with the coating process as well as capturing a large quantity of the valuable zinc metal. Another example involves the re-melting of impure aluminum scrap. Impurities such as iron, zinc, and magnesium, can readily form unwanted intermetallic crystals. In scrap with a high impurity loading, this can lead to a tremendous loss of valuable metal.

Introduction

The pyrometallurgical refining of lead produces many dross phases. Unlike the above examples however, most of these drosses are formed deliberately to allow impurity removal. In terms of the quantity of metal lost to entrainment, drosses produced during silver and bismuth recovery from lead are the most problematic. In each, intermetallic compounds containing the impurity element are formed and skimmed from the molter lead bath. The degree of metal loss during these skimming operations presents a high cost burden because of the loss of valuable metal and the added difficulty of recovering the silver and bismuth values. Industrial practices have been developed which can lessen the degree of lead entrainment in silver and bismuth skimmings, but the loss is still a significant cost and burden. At a single smelter such as Noranda's Brunswick Mining and Smelting lead operation in Belledune, New Brunswick, the cost of lead loss during silver and bismuth refining is over \$2 million per year.

In order to develop new processes capable of reducing metal loss in dross phases, it is important to understand the basic mechanism involved. In this work the example of bismuth and silver refining dross has been used to investigate these fundamentals. It is hoped that a better understanding of these systems will shed light on the general area of metal entrainment in dross, particularly systems involving intermetallic compounds.

The thesis investigations have taken the following form;

- 1) <u>Characterization</u> of silver and bismuth refining crusts produced in industrial operations.
- 2) <u>Laboratory Investigations</u> of the surface interactions between silver-zinc intermetallic compounds and liquid lead followed by simulation of silver crust under controlled conditions to determine the variables affecting the degree of metal entrainment.
- Practical Application of laboratory results to design new processes capable of reducing lead entrainment in silver and bismuth crusts. This work involved full-scale plant tests and laboratory process development.

2. LEAD REFINING AND CRYSTAL GROWTH

2.1 Lead Refining

2.1.1 General Refining

Commercial lead is produced in a variety of ways. Most of the world's primary lead is produced through the classic sinter plant - blast furnace process while an increasing amount is being smelted in direct, high intensity operations such as the Kivcet, QSL, and Isasmelt processes^(2,3,4,5). Secondary, or recycled lead, is mainly re-melted in rotary kilns or simple shaft furnaces. Increasingly, the western world demand for lead is being met by secondary producers⁽⁶⁾. Total Western World production is estimated at 4.4 million tonnes per year where the majority of this material is used in lead-acid batteries.

Typical applications for lead, such as in the battery industry, demand very high purity metal. It is common that impurity levels must total less than 1000 parts per million (99.9% pure Pb) and often less than 100 ppm (99.99% Pb). Unfortunately, molten lead is an efficient solvent for many impurity elements typical to nonferrous extractive metallurgy. Less noble metals such as arsenic, antimony, cadmium, tin, and sulphur are common. Similarly, elements more noble than lead such as copper, tellurium, bismuth, thallium, silver, and gold are also found in impure lead bullion. Lead also has a limited solubility for oxygen. From the Pb-O binary phase diagram one can predict approximately 10 parts per million dissolved oxygen at 450°C⁽⁷⁾.

Metallic lead can be refined through a number of processes. In earliest times most lead was refined through crude fractional crystallization techniques known as the Pattinson process⁽⁸⁾. The application of fractional crystallization to lead refining has been recently revived by the research work of Esdaile et al.^(8,9), although the technique is not commercially practiced. Cominco Ltd. in Trail, British Columbia, partially refines crude lead bullion from its blast furnace pyrometallurgically, then casts anodes and completes the refining electrolytically in the Betts

Process⁽¹⁰⁾. However, the majority of crude lead produced both from primary and secondary sources, is refined using classical pyrometallurgical techniques.

An excellent overview of the physical chemistry of pyrometallurgical lead refining is provided by Davey^(11,12). In essence impurity elements are removed through the application of three basic principles of thermochemistry;

- i) selective oxidation,
- ii) strong reduction of liquid phase solubility with temperature, and
- iii) formation of insoluble intermetallic compounds via additions of reactive metals.

Figure 2.1 gives a schematic diagram of a typical lead refining process. In most industrial operations the refining steps are carried out in a series of open kettles fabricated from mild steel. The kettles have an average capacity of 100-300 tonnes of liquid metal. Heating is provided by external burners placed underneath the kettle. Figure 2.2 is a photograph of Brunswick Mining and Smelting Corp. Ltd.'s lead refinery operation, capable of processing 70,000-100,000 tonnes per year refined lead.



Figure 2.1 Schematic Diagram of a Pyrometallurgical Lead Refining Circuit⁽¹¹⁾.

The first refining operation involves the removal of copper from the crude lead. Copper is completely soluble in lead bullion at typical smelting temperatures of $1200^{\circ}C^{(13)}$. However, as the temperature of the bath approaches the freezing point of lead (327°C), the solubility of copper is dramatically reduced to approximately 0.06 wt.%⁽¹³⁾. This is the result of solution chemistry with a large positive deviation from ideality. At lower temperatures, the decreased solubility of copper raises its activity allowing ready reaction with other dissolved impurities such as sulphur and arsenic according to the following reactions;

$$\underline{3}Cu + \underline{As} \neq Cu_{3}As_{pot} \tag{2.1}$$

The solid products of reaction form as small particles which float to the surface of the liquid

$$2Cu + S \neq Cu_{2}S_{pol}$$
(2.2)

metal to form a so-called copper dross. The copper dross entrains more than 50% metallic lead and is termed a "dry dross" due to its relatively low lead content and dust-like appearance. Copper dross is easily skimmed and treated to recover the copper. These skimmings are the first of many to produce drosses arising from pyrometallurgical lead refining.



Figure 2.2 Photograph of the Lead Refinery at Brunswick Mining and Smelting Corp. Ltd.

The second step of lead refining involves the preferential oxidation of impurities which are less noble than lead; most notably arsenic, antimony, and tin. It is commonly referred to as softening since after these impurities are removed, solidified lead exhibits its typical softness and ductility that is not apparent in lead prior to this purification. Oxidation of impurities is accomplished with either oxygen enriched air, or chemical oxidants such as sodium hydroxide and sodium nitrate. In the case of gaseous oxygen softening, oxides of arsenic, antimony, and lead combine to form a low melting point (600°C) slag phase which is tapped from the refining kettle. In chemical softening, the oxide products of reaction, along with sodium oxides, form a solid dross which, once again entrains metallic lead. Like copper dross, these skimming are considered to be "dry" since they appear dusty with only 55-65% lead content. Both softening slag and dross are typically smelted to recover lead and antimony, usually as an alloy of the two elements.

The next stage of lead refining does not benefit from natural lack of solubility or simple oxidation of impurities. For precious metals such as silver, gold, platinum, palladium, rhodium, and noble impurities such as tellurium, removal from solution relies on more intriguing techniques. The Parkes process for the recovery of silver and other precious metals from lead, makes use of the temperature dependence of the strong thermodynamic attraction between metallic zinc added to the bullion and silver dissolved in the bullion. The reactions are helped by high zinc activities in solution due to a strong liquid immiscibility (ie. positive deviation) in the lead-zinc binary system^(14,15,16). In the Parkes process the temperature of the liquid lead solution is reduced and the dissolved zinc and silver react to form insoluble intermetallic compounds. These crystals eventually float to the surface of the lead bath where they can be skimmed in the form of an "intermetallic dross". Unlike drosses produced by sulphide or oxide compounds, silver skimmings entrain a great deal of metallic lead such that the dross mass appears to be a viscous fluid. These drosses are described as "wet" crusts. The so called "silver crusts" are treated to recover silver and other precious metals while returning lead and zinc to the process.

After silver recovery, the second last stage of lead refining involves the removal of bismuth from solution. Similar to silver and the precious metals, bismuth is more noble than lead and hence difficult to remove from solution. Fortunately, the development of the Betterton-Kroll process in the 1920s allows the removal of bismuth to very low levels (less than 10 ppm) by the addition of alkali metals such as calcium and magnesium^(11,17). These reagents react with dissolved bismuth to form an intermetallic compound with the form CaMg₂Bi₂. The solubility of the intermetallic compound is temperature dependent such that cooling of lead to just above its freezing point will permit efficient bismuth removal with practical additions of reagent metals⁽¹¹⁾. As with silver crusts, the intermetallic particles containing bismuth float to the top of lead refining kettles where they are skimmed for eventual recovery of bismuth metal. Once again, the degree of liquid lead entrainment is considerable, often as high as 98 wt.%.

The final stage of lead refining, termed "clean-up", involves the final oxidation of any remaining reactive impurities with sodium nitrate and sodium hydroxide. As with chemical softening, the oxide products of reaction form a relatively dry dross which is easily skimmed.

2.1.2 The Parkes Process

2.1.2.1 Physical Chemistry

The Parkes process for the recovery of silver and other precious metals from lead was a breakthrough in its time. Up to that point the recovery of silver involved labour intensive, and inefficient fractional crystallization techniques^(8,11). The ability to cheaply, and easily remove silver provided the world with high purity lead while giving producers a second source of income in the from of silver.

Since its discovery, the Parkes process has been the subject of a great deal of research^(11,12,14,16). Most of the work has focused on the thermochemistry of the system. Davey et al. have helped define the equilibria in the system Pb-Zn-Ag which has permitted lead refining operations to optimize their recovery processes to minimize zinc consumption while ensuring near complete removal of silver⁽¹⁶⁾. Recent thermodynamic modelling by Wang et al. has been directed towards the development of lower cost silver crust treatment processes^(18,19).

The main principle of the Parkes process can be illustrated by the simple ternary Pb-Zn-Ag diagram in Figure 2.3(a)⁽⁷⁾. Here a strong thermodynamic attraction of reagent zinc for silver is offset by the immiscibility of zinc in lead. The result is the formation of intermetallic compounds of zinc and silver which exhibit limited solubility in molten lead bullion. In Figure 2.3 there is a clear miscibility gap between molten lead and solid intermetallic particles at normal refining temperatures; 370-470°C. Equation (2.3) gives the simplified reaction of zinc with silver to form insoluble intermetallic phases;

$$Ag + rZn = AgZn, \qquad (2.3)$$

From the ternary phase diagram presented in Figure 2.3(b) it is clear that different bullion temperatures will result in varying orientations for the tie lines through the miscibility gap. Figure 2.3(b) shows the intermetallic phases of zinc and silver which can be formed at various solution concentrations and temperatures. The binary zinc-silver phase diagram shown in Figure 2.3(a), illustrates the point more clearly where various intermetallic phases are easily identified. Unlike many intermetallic compounds, those of silver and zinc, show variable stoichiometry for a given phase. Variable composition is often the case for intermetallic compounds where relatively weak metallic bonding predominates, compared to the strong ionic bonding found for many intermetallic compounds of fixed stoichiometry such as alkali bismuthides⁽²⁰⁾.



Figure 2.3 Binary and Ternary Phase Diagrams for the Pb-Zn-Ag System⁽⁷⁾.

The Gibbs energies of formation for phases in the Ag-Zn system are shown in Figure 2.4⁽²⁰⁾. For all three intermediate phases (β , γ , and ϵ phase) the minimum Gibbs energy does not exist at the stoichiometric ratio. This is reported to be typical behaviour for intermetallic compounds where metallic bonding predominates. Furthermore, the low value of the Gibbs energy of formation

for Ag-Zn compounds compared to other intermetallic compounds (approximately 2 kcal-mol⁻¹ vs. 15-30 kcal-mol⁻¹ for ionically bonded intermetallic compounds) reflects the weaker metallic bonding⁽¹³⁾.



Figure 2.4 Gibbs Energy Changes on Formation of the α -terminal solid solution and the β , γ , and ϵ -electron compounds in the Ag-Zn system⁽²⁰⁾.

In industrial practice two intermetallic phases are formed. At higher temperatures, 420-470°C, and with high silver concentrations the ϵ phase is formed having the basic stoichiometry AgZn₃. As the bath cools, and silver concentrations are reduced, η phase (Zn) particles are formed. The ratio of zinc to silver in each phase is variable, tending to increase in zinc concentration as the bath cools, or at lower silver concentrations. The phase of the zinc-silver intermetallic compound, while variable in composition, is defined by the crystal structure. The crystallographic information relative to the current study is included in Table 2.1^(21,22,23).

PHASE	β	ζ	γ	ε	η
COMPOSITION (%Zn)	26-46.2	30.9-38.6	48.7-52.6	58-83	92-100
APPROX. FORM	AgZn	AgZn	Ag,Zn,	AgZn,	Zn
STRUCTURE	cubic	hexagonal	cubic	hexagonal	bexagonal
TYPE_	CsCl (sc)	(hcp)	y brass	Mg (bcp)	Mg (bcp)
a (Å)	3.156	7.635	9.341	2.823	2.665
c (Å)	-	2.820	-	4.427	4.947
DENSITY (g/cm ³)	9.169	9.095	8.660	8.263	7. <u>14</u>

 Table 2.1
 Crystallographic Data for the Ag-Zn System.

Since the 1950s, Davey, has conducted a great deal of research to determine the equilibria involved during the cooling of lead bullion during desilverising. The result is a series of ternary phase diagrams for the lead-zinc-silver system showing the tie lines at the temperatures of interest. Figures 2.5 (a) through (c) give a summary of Davey's work. Of practical interest, he has included typical cooling curves to show the dynamics of silver crust formation, which he claims are always in equilibrium due to the slow rate of cooling which occur in most industrial practice.


Figure 2.5 Equilibrium Phase Diagrams for the System Pb-Zn-Ag⁽¹¹⁾.

2.1.2.2 Plant Practice

The relations determined by Davey have been used to develop two-stage, countercurrent desilverising procedures. The aim has been to produce the highest grade of silver crust possible, while minimizing the consumption of zinc. Essentially, two kettles are used, where high silver bullion enters the first (termed the primary kettle) at high temperature (450-470°C) and tends to form low zinc to silver ratio ϵ phase intermetallic compounds. These high grade crusts are skimmed, and treated to recover the silver, zinc, and lead. The lead bullion, still containing silver, is moved to the secondary kettle which is maintained at lower temperatures. Zinc additions are made to this kettle at approximately 420°C, and high zinc to silver ratio η phase

crystals are formed as the bath cools. These low grade crusts are continuously skimmed and returned to the primary kettle, where the η phase crystals dissolve in the hot lead, and re-precipitate as ϵ phase. The low grade crusts serve as the sole source of reagent zinc to the primary kettle. The secondary kettle is cooled to the lowest practical temperature and assayed for silver content. If the silver level does not match specification (usually 10 ppm Ag), then further zinc additions are made.

As discussed above, the aim of modern desilverising practice is to produce a crust high in silver, while consuming as little zinc as possible. For many South American operations this is particularly easy since crude lead bullion may contain as much as 1 wt.% silver. Most refineries are pleased to produce a silver crust with 5-6 wt.% Ag, and a ratio of Zn:Ag of $3^{(16)}$. However, despite efforts to manipulate the thermochemistry of lead desilverising to increase the silver crust of crusts, the majority of the crust weight remains entrained liquid lead.

2.1.2.3 Metal Entrainment in Parkes Process Crust

Liquid lead entrainment in silver crusts has long been recognized as a limitation in the cost effectiveness of desilverising by the Parkes process. However, little practical or technical progress has been reported in reducing the amount of lead reporting to the skimmings. Most of the efforts have been directed in two ways; (i) mechanical treatment, and (ii) high temperature liquation.

Mechanical treatment, or squeezing, of silver crusts was practiced in industry for many years. A device, known as the Howard Press, was used to apply pressure to the still hot crusts (over the lead melting point of 327°C) over a steel mesh screen. A small fraction of the lead could be separated from the intermetallic particles in this manner. However, the poor recovery of lead. and the difficulty in maintaining high temperatures, forced most operations to abandon this procedure in the 1950s.

The Broken Hill Pty. Ltd.'s Port Pirie Refinery in Australia employed a high temperature centrifuge to treat silver skimmings⁽²⁴⁾. The principal was much the same as the Howard Press, where a pressure was applied to the mixture of lead and intermetallic particles to force a separation. Relatively poor separation efficiency, and difficulty of operation resulted in the abandonment of this process as well.

A much more successful process has been the high temperature liquation of silver crust under a molten salt blanket. Figure 2.6 illustrates the process which is carried out in large cast iron kettles. Developed by Lefferer in the 1950's, the process uses high temperature to melt the intermetallic particles of silver and zinc⁽²⁵⁾. The temperature is maintained in order to preserve a sizable miscibility gap between a lead bullion phase (containing some silver and zinc) and a silver-zinc alloy, known as Triple Alloy. The lead-silver-zinc ternary diagram (Figure 2.3) illustrates the large liquid phase miscibility possible. As the intermetallic particles melt into droplets of Triple Alloy, they coalesce to from a separate metallic phase which floats on the lead surface. A typical composition of the triple alloy layer would be 30% silver, 60% zinc, and 10% lead⁽¹⁶⁾. Usually a CaCl₂-NaCl eutectic salt is employed while some operations now employ molten sodium borate (BORAX) layers to avoid the handling of chlorides. Virtually no theoretical work has been conducted to determine the role of the molten salt or slag, however it is presumed that they provide a barrier to rapid oxygen transfer and oxidation of the molten zinc alloy. The Triple alloy is further processed to recover silver and zinc, while the lead bullion is returned to the desilverising kettle.



Figure 2.6 Liquation of Silver Crust in Cast Iron Kettles⁽¹⁶⁾.

In liquation, the ability of solid intermetallic particles to entrain liquid metal is circumvented by removing the solid phase. However, the cost of liquation offsets many of the benefits derived from the liberation of lead.

The Brunswick Mining and Smelting Corp. Ltd. (BMS) Lead Smelter in Belledune New Brunswick has developed a simple and relatively effective method of treating silver skimmings to remove some of the entrained lead. Crusts are skimmed to a lead kettle containing bullion at relatively high silver levels at 450°C. Three charges of crust, 20-25 tonnes, are allowed to accummulate in this kettle. Some re-crystallization of silver-zinc intermetallic is said to occur due to the higher levels of silver. After sufficient crust is collected, the kettle is agitated at high speed for 5-10 minutes. This agitation changes the appearance of the crust from a metallic, "wet" dross, to a black, less metallic "dry" dross. The silver assay typically increases from 5 to 10-12 wt.% Ag. It is interesting to note that too much agitation causes excessive zinc oxidation,

and loss of silver to the bullion phase. For this reason, operator skill is critical component of this process. At this point, there has been no technical evaluation of the process to determine the mechanism of crust upgrading.

It is interesting to note that the literature does not contain any references which describe the mechanism by which liquid metals are entrained to such a degree by the intermetallic particles of silver and zinc. An understanding of the mechanism could help design new processes to free lead from the crusts at lower cost.

2.1.3 The Kroll-Betterton Process

2.1.3.1 Physical Chemistry

The removal of bismuth from lead bullion presents many of the same obstacles as for silver removal in the sense that it cannot be preferentially oxidized by oxygen or chlorine. The obstacle was overcome in the 1930s by ASARCO Ltd. in the United States^(11,26). Kroll, working for ASARCO at the time, found that alkali metals such as calcium or magnesium could react with bismuth in lead to form intermetallic compounds such as Mg₃Bi₂ and Ca₃Bi₂. The equilibria near the freezing point can be represented by the following equations where the soluble species are

considered to be infinitely dilute with the solid intermetallic compound at unit activity^(11,27). The equilibrium solubility product (K_{pp}) can be defined as;

$$\log_{10}(\mathbb{K}_{p}^{M_{g},H_{1}}) = \log_{10}([M_{g}]^{3}[Bi]^{2}) = 5.36 - \frac{4.280}{T}$$
 (2.4)

$$log_{10}(\mathbf{K}_{sp}^{Ca,\mathbf{N}_{1}}) = log_{10}([Ca]^{2}[Bi]^{2}) = 12.46 - \frac{11160}{T}$$
 (2.5)

where; [X] represents weight %X in lead and, T is in kelvin

However, early practice found that it was difficult to achieve complete debismuthisation with either reagent metal. Betterton and Lebedeff found more complete removal of bismuth could be achieved with both reagents. This process is generally referred to as the Kroll-Betterton process and is practised by most lead refineries in the world. The reaction can be written as;

$$Ca + 2Mg + 2Bi \neq CaMg_2Bi_2 \qquad (2.6)$$

where the relation between calcium, magnesium, and lead in solution near the freezing point can be given by⁽¹¹⁾;

$$log_{10}(K_{sp}^{Calder,N_1}) = log_{10}([Ca][Mg]^2[Bi]^2) = -7.37$$
 (2.7)

The crystal form of CaMg₂Bi₂ has been reported in the literature as hexagonal close packed with the lanthanum oxide structure (La₂O₃ structure D5₂) and a melting point of 1150°C⁽²⁰⁾. Atomic spacings of $a_0 = 4.730$ Å, and $c_0 = 7.680$ Å, give a theoretical density of 5.653 g/cm³ based on 5 atoms per unit cell.



Figure 2.7 Temperature Dependance of the Solubility of CaMg₂Bi₂ in Lead⁽²⁸⁾.

Unlike the Ag-Zn system, alkali metal bismuthides exhibit mainly ionic bonding resulting in high enthalpies of formation and fixed stoichiometric ratios. This is attributed to large differences in electronegativity between the constituent elements. Indeed, where ionic bonding predominates, Pauling's (or others) scale of electronegativity can be used to calculate the heat of formation for an intermetallic compound according to the equation⁽²⁰⁾;

$$\Delta H (kcal/mol) = -23.07Z(X_A - X_B)^3$$
(2.8)

where; Z is the number of valence links,

 X_A and X_B are the electronegativities of the component elements, and 23.07 is an experimentally determined constant.

In Table 2.2, calculated enthalpies energies of formation for calcium and magnesium bismuthides are compared to experimentally derived values. The technique is used to estimate the enthalpy

of formation of $CaMg_2Bi_2$ since no experimental value exists in the literature. The agreement between calculated values and experimental is very good, confirming the nature of the bonding. The high heat of formation for $CaMg_2Bi_2$ follows observations on the plant scale, where rapid cooling of saturated lead bullion is very difficult due to continued formation of intermetallic compounds and the subsequent release of heat.

COMPOUND	$\Delta H_t \exp(kcal/mol)$	ΔH_f cal. (kcal/mol)
Ca ₃ Bi ₂	$-21.4 \pm 1.0^{(13)}$	-22.6
Mg ₃ Bi ₂	$-7.4 \pm 0.2^{(13)}$	-1.8
CaMg ₂ Bi ₂	-	-8.7

 Table 2.2
 Heats of Formation for Alkali-Metal Bismuthides.

The relationship in Equation (2.7) was used by Davey to construct the lead corner of the Pb-Ca-Mg-Bi quaternary diagram as shown in Figure 2.8. It is clear from the phase diagram that to achieve near complete removal of bismuth from lead, a great deal of reagent metal must remain in solution. Equations (2.4) and (2.5) illustrate the temperature dependence of the solubility of intermetallic compounds in lead.



Figure 2.8 Lead Corner of the Pb-Ca-Mg-Bi Quaternary Phase Diagram⁽¹¹⁾.

Recent experimental work by Hancock and Harris has described the dilute solution equilibria in terms of temperature⁽²⁸⁾. The experimental data are shown in Figure 2.8 along with an expression for K_{pp} obtained by linear regression;

$$\log_{10}(K_{\varphi}^{CaM_{g},M_{1}}) = \log_{10}([Ca][Mg]^{2}[Bi]^{2}) = 12.007 - \frac{11437}{T}$$
(2.9)

This type of equation is useful in predicting the equilibrium saturation of lead bullion during the debismuthising process. However, operating plant data from BMS suggests that bismuth crusts do not form under equilibrium conditions. This is illustrated in Figure 2.9 where bullion assays during debismuthising were used to plot the actual solubility product as a function of

temperature. An average supercooling of 20°C was measured, indicating that the bullion is actually supersaturated. Nevertheless, the type of expression outlined in Equation (2.9) is needed if further understanding of these processes is to be gained.



Figure 2.9 Operating Plant Data Showing Supersaturation of Lead During Debismuthising.

Debismuthisation of lead using the Kroll-Betterton process differs from the Parkes process in that the intermetallic compound is of fixed stoichiometry. It is therefore impossible to minimize reagent consumption through crust recycle or countercurrent processes. However some crust recycle is reported in industrial practice since crusts formed near the freezing point of lead tend to contain more entangled lead that those formed at higher temperatures.

2.1.3.2 Metal Entrainment in Bismuth Crusts

In commercial debismuthising reagent metals are stirred into lead at 450-500°C. After complete dissolution of the appropriate amount of reagent, the lead is allowed to cool to just above the freezing point of the Pb-Ca-Mg-Bi eutectic. The bismuth crusts which are formed are skimmed from the lead surface during the cooling period and treated to recover bismuth metal. Bismuth crusts are particulary susceptible to liquid metal entrainment. It is normal to produce crusts with only 4-5 wt.% Bi and 95 wt.% Pb. This is partly the result of a low intermetallic density (5.65 g/cm³) compared to liquid lead (10.5 g/cm³), but mostly due to entrainment.

Few operations attempt to increase the grade of the crust by removing entrained lead. ASARCO practised for some time in the 1980's a hot vacuum filtration process where bismuth crusts were skimmed and placed on a fine steel mesh screen⁽²⁶⁾. Burners maintained the crust temperature above the freezing point of lead. A partial vacuum of 90 mm Hg could be maintained under the screen. In this way crusts averaging only 5 wt. % Bi, could be upgraded to 12 wt.% Bi through the removal of entrained metallic lead. Nevertheless, even after upgrading approximately 75% of the volume remained liquid lead.

A similar performance was reported by the Broken Hill Pty. Ltd's Port Pirie Refinery⁽²⁴⁾. Here crust produced in their continuous debismuthising kettle was treated in a hot centrifuge. Some lead was removed from the crust, yet a great deal of liquid lead remained with the intermetallic particles. The low grade of most bismuth crusts which were treated for bismuth recovery resulted in high costs since it was necessary to separate so much lead from the metal of interest. It was also costly from the point of view that partly refined lead was removed along with the crust, thereby reducing overall refined lead recovery.

Very little work has been published on the treatment of Kroll-Betterton process skimmings. Perhaps more importantly, little theory has been advanced to explain the degree of metal entrainment experienced. Through a better understanding of the mechanism of liquid metal entrainment, it may be possible to develop improved processes to treat the crust, or procedures to minimize metal loss.

2.2 CRYSTAL GROWTH FROM SOLUTION

For silver and bismuth removal from lead, intermetallic crystals are nucleated and grown from a saturated liquid solution of the metals. The processes are somewhat unique in that the crystal growth involves only the solute elements, while excluding the solvent; lead. It is critical to understand the mechanisms of crystal growth in order to properly understand the processes, and hopefully manipulate conditions to improve metal recovery and overall metal separations.

Crystal growth from solution is dealt with in the literature from two perspectives, (i) precipitation of salts from aqueous solution, and (ii) the growth of high purity single crystals for electrical application^(29,30,31,32,33,34,18,35). For the latter, some metals, notably tin, lead, and bismuth have been used as convenient low melting point solvents⁽²⁹⁾. As the importance of semi-conductor materials increase, the science of crystal growth has been developed to the point where nucleation and growth mechanisms are well understood. Nevertheless, each system requires extensive experimentation, and empiricism, to evaluate the specific variables and rate controlling steps⁽³⁰⁾.

2.2.1 Nucleation Theory

The first stage of any crystallization is the formation of nuclei of the crystal phase. It is generally accepted that supercooling (T_n) of a liquid below some equilibrium liquidus value T_m , will result in an increase in the rate of nucleation. The exact degree of supercooling, defined as $T_m - T_n$, will

depend on factors such as the purity of the melt and the presence of particles which could serve as preferred sites of nucleation. Greater supercooling will increase the rate of nucleation until a maximum is reached. Further supercooling eventually reduces the nucleation rate due to reduced solute mobility at lower temperature; (Figure 2.10). This theory can be applied to primary solidification of the liquid as well as temperature dependent precipitation of dissolved impurities in the form of intermetallic compounds.



Figure 2.10 Temperature Dependence of Nucleation Rate⁽³³⁾.

For crystal growth from solution, nucleation is normally presumed to occur heterogeneously; on impurity particles or container surfaces. However, most theory has been developed to describe homogeneous nucleation throughout the solution⁽³¹⁾. In simple form, atomic movement in the supersaturated solution cause clusters of molecules known as "embryos" to form. The stability of the embryo depends on the overall change in Gibbs energy for the system given that the embryo has a radius, "r". This can be expressed by Equation (2.10);

$$\Delta G_{and} = 4\pi r^2 \gamma_{al} - \frac{4}{3}\pi r^3 \Delta G_V + \Delta G_E + \Delta G_C \qquad (2.10)$$

where; γ_{\perp} is the interfacial surface energy of the precipitate (J-cm⁻²), ΔG_{v} the difference in the Gibbs energy per unit volume between the solid and liquid phases (J-cm⁻³), and ΔG_{E} and ΔG_{C} representing free energy of strain and entropy respectively.

The latter two terms ΔG_E and ΔG_C are usually neglected since in most cases their contribution is negligible. As radius "r" increases from zero, the Gibbs energy change increases until a critical value r[•] is reached, after which it will decrease such that r[•] represents the critical radius for a stable nucleus. The value r[•] can be determined by setting the differential of Equation (2.10) (with respect to r) equal to zero;

$$r^* = \frac{2\gamma_d}{\Delta G_v} \tag{2.11}$$

The critical radius can be related to the degree of supercooling for a given solubility limit by the expression;

$$\Delta G_{V} = \frac{RT\sigma}{V_{M}}$$
(2.12)

and;

$$\sigma = \frac{\phi \Delta T}{RT^2}$$
(2.13)

where; V_M is the molar volume of solute (cm³-mol⁻¹), **R** the gas constant (8.314 J-mol⁻¹-°K⁻¹) ϕ the molar heat of solution (J-mol⁻¹), and σ the relative supersaturation, defined by Equation (2.13).

The relative supersaturation, σ , given in Equation (2.13) is valid for small values of ΔT . The dimensionless number is often referred to by Elwell and Scheel as a percentage value such that

 σ =0.1 would be considered 10% supercooling⁽³⁵⁾. This is a convenient way of expressing the driving force for nucleation.

Substitution of Equation (2.12) into Equations (2.10) and (2.11) gives the expression;

$$r' = \frac{2\gamma_{k} V_{M}}{RT\sigma}$$
(2.14)

It is clear from Equation (2.14) that an increase in supersaturation, σ , will result in a decrease in the critical radius. It is also clear that a dilute solution with a low molar volume of solute, V_M , will have the same effect on the critical nucleous radius.

Substitution of Equation (2.14) into Equation (2.10), and rewriting in terms of rate of nuclei formation, allowed the following expression to be derived by Volmer and Weber in $1926^{(30)}$;

$$I = \frac{16\pi z^{2} \gamma_{d}^{2} n V_{M}^{2}}{R^{2} T^{2} \sigma^{2}} exp\{-\frac{16\gamma_{d}^{2} V_{M}^{2}}{3kR^{2} T^{3} \sigma^{2}}\}$$
(2.15)

where; I is the number of critical nuclei generated per unit volume per second, z° the frequency of attachment of single molecules to a unit area of nuclei, and n the number of molecules per unit volume.

The nucleation rate I, will increase rapidly with supersaturation driven mainly by the exponential term. Figure 2.11 illustrates this effect for potassium sulphate nucleation and growth from aqueous solution. Below relative supersaturations of 10% (σ =0.1), nucleation is relatively slow compared to growth, yet above 10% there is a dramatic increase in nucleation rate. Equation

(2.15) has correlated well with experimental data up to supersaturations of 10% but beyond this, I is observed to vary according the rough power law; σ^9 .



Figure 2.11 Nucleation and Growth Rates for Potassium Sulphate⁽³⁵⁾.

2.2.2 Crystal Growth Theory

There is no one dominant rate limiting step during crystal growth from solution⁽³⁰⁾. In the most simplistic terms, once a crystal has nucleated in a solution, the growth process involves the transport of solute elements from the bulk of the solution to some point on the crystal surface where they may become part of that surface. Inherent within this simple description are two rate controlling steps; (i) mass transport in the bulk of solution, and (ii) surface reaction at the crystal interface. The rate of crystal growth from solution has been well reviewed by Elwell and Scheel

and the present review only attempts to give some of the basic concepts relevant to intermetallic growth in process metallurgy⁽³⁵⁾.

The first crystal growth from solution is usually in the range of high supersaturation since this is needed to provide the driving force for initial nucleation. This saturation is usually much higher than that at which the bulk of the subsequent growth occurs. As a result, the first crystals formed tend to be highly dendritic in nature, i.e., fast growth occurring along preferred growth directions. The initial fast growth reduces supersaturation and subsequent growth occurs more slowly However dendrite arms still exist in regions of high saturation and tend to capture solvent between these arms as they close. This early growth is considered unstable, yet generally gives way to flat crystal faces as super saturation recedes.

If a crystal is considered to have a stepped interface (Figure 2.12) in contact with a supersaturated solution, growth may proceed by the following stages⁽³⁰⁾;

- (i) transport of solute to crystal surface boundary layer.
- (ii) diffusion of solute through a solute concentration boundary layer.
- (iii) adsorption on the crystal surface.
- (iv) diffusion over the surface.
- (v) attachment to a step.
- (vi) diffusion along the step.
- (vii) integration into the bulk crystal.

The above mechanism is illustrated in Figure 2.13. The growth of a crystal may not follow all seven steps; for example, solute particles may diffuse directly to a step, or kink, site by surface migration and hence bypass steps (v) and (vi). From a practical point of view, it is necessary to determine which step will be rate controlling.

The first step of crystal growth, transport of solute to the boundary layer, can be modified by the energy input to the solvent given as agitation. For $c_{1y}s_{1x}$ growth from solution, it is generally considered that growth rates in unstirred melts are limited by mass transport in the liquid phase⁽³⁵⁾. When there is sufficient stirring to eliminate transport in the bulk liquid as a rate controlling step, one is left with the limitation of surface reaction.



Figure 2.12 Idealized Model of a Flat Crystal Interface⁽³⁵⁾.



Figure 2.13 Stages in Crystal Growth From Solution⁽³⁵⁾.

In the absence of heat transfer there are two boundary layers present at the crystal-liquid interface; a solute diffusion boundary layer and a momentum transfer boundary layer (hydrodynamic). If the rate of solute reaction (ie. crystal formation) at the crystal is assumed to be very fast the diffusion boundary layer thickness, δ_{ct} , has been given as;

$$\delta_{c} = \{0.463(\frac{\eta}{\rho_{sel}D})^{\frac{1}{3}}(\frac{\nu\rho_{sel}}{\eta l})^{\frac{1}{2}}\}^{l}$$
(2.16)

where; ρ_{sol} is the solution density (g-cm⁻³), η the solution viscosity (g-cm⁻¹-sec⁻¹), v the fluid velocity (cm-sec⁻¹), l the crystal length (cm), D the solute diffusivity (cm²-sec⁻¹), and 0.463 is a constant of integration.

It is readily evident from Equation (2.16) that an increase in fluid velocity will decrease δ_c and hence, increase crystal growth rate. This effect is illustrated in Figure 2.14 where growth rate remains constant with increasing liquid velocities until controlled by interface kinetics.



Figure 2.14 Variations in Linear Growth Rate With Solution Velocity⁽³⁵⁾.

There is also a temperature gradient through a boundary layer. If the crystal and solution temperatures can be maintained, then increased stirring will result in a decrease in the thermal

boundary layer thickness, δ_{T} , along with δ_{c} . A steeper temperature gradient enhances the stability of the growing crystal face. The effect is illustrated in Figure 2.15. The solid line T_{L} represents constitutional supercooling as solute depletion lowers the effective liquidus temperature at the interface. The dashed line (i) shows an applied temperature gradient which lies below the curve and results in rapid protuberance growth into the liquid (dendrite formation). Steepening the applied temperature gradient in line (ii) will result in a scable growth interface. Equation (2.17) gives an expression for instability for multicomponent crystal solidification;

$$v > \frac{D_{\bullet} \frac{dT}{dz}}{\sum_{i=1}^{j} \left\{ \frac{m_{i}(k_{i}^{*}-1)n_{i}}{\frac{D_{i}}{D_{\bullet}}} \right\}}$$
(2.17)

where; v is the linear growth rate (cm-sec⁻¹),
D_o is the diffusion coefficient of the solvent (cm²-sec⁻¹),
m_i is the slope of the liquidus curve,
n_i the impurity concentration (mol-cm⁻³), and
D_i the diffusivity, all for each constituent "I" (cm²-sec⁻¹).

The value \mathbf{k}_i is defined as the partition coefficient where;

$$k_i^* = \left(\frac{n_c^i}{n_{ml}^i}\right)_{z,\theta} \tag{2.18}$$



Figure 2.15 Interface Instability Caused by Temperature Gradient Change⁽³⁵⁾.

The values of \mathbf{n}_{c}^{1} and \mathbf{n}_{sol}^{1} are the concentration of "i" in the crystal and solution. It can be argued, however, that higher fluid velocities may not result in steeper temperature gradients where maintenance of a constant interface temperature is not possible. Improved convection could serve to increase the interface temperature closer to the bulk value. In this case higher fluid velocities will increase crystal growth instability.

2.3 Boundary Layer Considerations in Crystal Growth

As discussed in Section 2.2.2, the growth of intermetallic crystals from metal solutions involves boundary layers. These boundary layers can be momentum, heat transfer, and mass transfer. For metal refining processes, the molten metal bath is usually slow cooled, and rarely involves steep or extensive thermal gradients between growing crystals and the bulk solvent (metal). Therefore, one can focus on the effects of momentum and mass transfer through a boundary layer adjacent to a growing crystal.

2.3.1 Momentum Transfer Boundary Layer

In the simplest consideration of momentum transfer in liquid metal, one can consider the fluid as exhibiting Newtonian behaviour. That is the shear stress in the liquid is proportional to the velocity gradient according to the simple relationship^(36,37);

$$\tau_{xy} = -\eta \frac{dv_x}{dy}$$
(2.19)

where; τ_{xy} is the shear stress in the fluid, v_x the liquid velocity in the x direction, and η the liquid viscosity, a constant of proportionality.

Figure 2.16⁽³⁶⁾ illustrates the relationship between shear stress and liquid velocity for a Newtonian fluid.



Figure 2.16 Laminar Flow of Fluid Between Parallel Plates⁽³⁶⁾.

When considering intermetallic compound formation during the pyrometallurgical refining of lead, the liquid metal velocity is usually low or verging on negligible. One can then consider flow

over the growing crystal interface to be laminar. For flow over a flat plate (approximation of a growing interface), this is generally expressed in terms of the Reynolds Number, a dimensionless parameter defined by⁽³⁷⁾;

$$Re - \frac{V_{\perp}L_{\rm P}}{\eta} \tag{2.20}$$

where; Re is the Reynolds number,
V_ the fluid velocity in the bulk liquid,
L the crystal length, and
ρ the liquid density.

Usually a Reynolds number for pipe flow below 2000 describes laminar flow. However, this limit can change greatly depending on geometry and solid surface roughness. In the case of crystal growth from lead, if one assumes the typical viscosity of molten lead to be 2.0×10^{-2} poise $(g/cm/sec)^{(36)}$, a maximum velocity of 1.0 cm/sec, a liquid density of 10.5 g/cm³, and a crystal length of 100 µm, the above expression gives a Reynolds number of 5; well below the critical threshold for laminar flow.



Figure 2.17 Velocity Profile and Momentum Boundary Layer for Laminar Flow Over a Flat Plate⁽³⁶⁾.

The equations of continuity for the conservation of mass in many fluid flow configurations have been rigorously developed elsewhere^(36,37). For application to crystal growth from a melt and if one considers the case of laminar flow over a flat plate, then a boundary layer can be defined between the bulk liquid at $V_{...}$ and the crystal interface. This boundary layer (as shown in Figure 2.17) is defined as⁽³⁶⁾;

$$\delta = 5.0 \sqrt{\frac{\eta x}{\rho V_{\star}}}$$
(2.21)

where; δ is the momentum transfer boundary layer thickness, and x the distance along the flat plate (crystal interface).

It is clear from Equation (2.21) that as the bulk fluid velocity decreases, the boundary layer thickness increases. For molten metal refining where intermetallic particles tend to form stable crusts, the liquid metal velocity decreases, and the momentum boundary layer is relatively large.

2.3.2 Mass Transfer Boundary Layer

It is evident from the nature of crystal growth from solution, that a boundary layer must exist between the bulk of the supersaturated liquid metal and the growing interface. Higher concentrations of solute in the bulk will provide the driving force such that solute elements will diffuse through the boundary layer to a lower concentration at the interface. The driving force for diffusion can be expressed by⁽³⁶⁾;

$$\dot{J}_{Ax} = -D_{A} \left(\frac{\partial C_{A}}{\partial x} \right)$$
(2.22)

where; \mathbf{j}_{Ax} is the molar flux of solute A in the x direction (mol-cm⁻²-sec⁻¹),

 C_A the molar concentration of A (mol-cm⁻³), and

 $\mathbf{D}_{\mathbf{A}}$ the diffusivity of A in solution (cm²-sec⁻¹).

Equation (2.22) is often referred to as Fick's law of diffusion. Greater concentration differences through a boundary layer, or higher diffusivities (greater atomic mobility) will result in a higher flux.

For pure crystal growth from the melt, solid diffusion is not a relevant parameter. However liquid diffusivities are critical. In general, one can consider self-diffusion for a solvent, and interdiffusion for the solute species. Unlike solids, the mechanism for diffusion in liquid metals is not well understood, perhaps because of our lack of basis understanding of the structure of liquids in general⁽³⁶⁾. The simplest theory of liquid diffusion was proposed by Einstein where he considers diffusing atoms as non-reacting spheres moving through a medium with a given viscosity at a given velocity. This hydrodynamic approach is known as the Stokes-Einstein equation and has been modified by Sutherland to have the form;

$$D = \frac{k_B T}{4\pi r_0} \tag{2.23}$$

where; k_B Boltzmann's constant (1.38 x 10⁻²³ J-deg⁻¹), and r the radius of a sphere (ionic radius), Å.

Although the use of Stokes' law does not seem appropriate since it neglects inter-atomic forces, the above model shows surprising agreement with experimental values for liquid metals⁽³⁶⁾. Most metallic elements have similar ionic radii. From Equation (2.23) it is not surprising that diffusivities for most metals fall within the same order of magnitude; $10^{-4} - 10^{-5}$ cm²-sec⁻¹. There are other more detailed theories of liquid diffusivity. One such explanation known as the Fluctuation theory proposed by Cohen and Turnbull, postulates the extra volume of a liquid

(relative to the solid) allows some fluctuations to occur in atomic spacing. These fluctuations periodically allow an atom to move from one "loose" lattice site to another⁽³⁶⁾. Reynik quantifies the theory according to;

$$D = 1.72 \times 10^{24} Z X_{\bullet}^{\bullet} K + 2.08 \times 10^{9} Z X_{\bullet} T$$
 (2.24)

where;
$$\mathbf{Z}$$
 is the number of nearest neighbours (Å),

 X_o maximum diffusive displacement due to vibrations(Å), and K a force constant.

$$X_{s} = \overline{d} - 2r \tag{2.25}$$

where; d is the average interatomic distance in the liquid, and r is the ionic radius, both in Å.

Calculation of ionic radii based on Equations (2.23) and (2.24), give values very close to Pauling's neutral atom radii which suggests that liquid metal atoms carry their valence electrons with the diffusing ion core. Interestingly, the two models for liquid metal diffusion show a linear dependence of diffusivity with temperature. This is at odds with the reporting of most data, where D follows an Arrehius relationship suggesting a thermally activated mechanism. Geiger and Poirier suggest that Pauling's, and other model data, often follow experimental values because the value of the activation energy is small. Figure 2.18 gives some relevant experimental data for solute diffusivities in liquid metal.



Figure 2.18 Interdiffusion Coefficient Data in Liquid Nonferrous Alloys⁽³⁶⁾.

Simple diffusion models are adequate in the absence of fluid motion. However, one must consider both momentum and mass transfer together for mass transfer in a liquid metal system (crystal growth for example). Then it is convenient to define a mass transfer coefficient \mathbf{k}_{M} . Derivations of mass transfer coefficients are available in the literature^(36,37). For mass and momentum transfer along a flat plate (as discussed in Section 2.3.3.1) the mass transfer coefficient is given by;

$$k_{\rm M} = 0.646 \frac{D_A}{x} Sc^{-1/3} Re_x^{-1/2}$$
 (2.26)

where the dimensionless parameter describing mass transfer in a liquid phase are given by the Schmidt number (Sc). Note that Equation (2.26) has the same form as Equation (2.16). Generally the Reynolds number is thought of as the ratio of momentum forces to viscous forces. The Schmidt number on the other hand can be described as the ratio of boundary layer thickness between mass and momentum transfer.

$$Sc = \frac{\eta}{\rho D}$$
(2.27)

One may consider the mass transfer coefficient as a product of the Schmidt and Reynolds numbers.

Since the mass transfer coefficient is a ratio of the two quantities, then a mass transfer boundary layer can also be defined in much the same terms with a ratio of the two boundary layers (mass, δ_c , and momentum, δ) defined by the expression⁽³⁶⁾;

$$\frac{\delta_c}{\delta} = \frac{1}{1.026Sc^{1/3}}$$
(2.28)

where; δ_c is the mass transfer (concentration) boundary layer thickness.

Applying the above equations for liquid metals, one can use typical order of magnitude values for viscosity, diffusivity, and density to show that $\delta_c \ll \delta$. For liquid lead and intermetallic crystals grown from solution, one can estimate typical momentum and mass transfer boundary layer thicknesses for varying liquid metal velocities. For a temperature of 400°C typical constants for lead metal are;

viscosity (400°C) ⁽³⁶⁾ ;	$\eta_{\rm Pb} = 0.022 \text{ g-cm}^{-1} \text{-sec}^{-1}$
diffusivity Bi in Pb (400°C) ⁽³⁶⁾ ;	$D_{Bi} = 4.0 \times 10^{-5} \text{ cm}^2 \text{-sec}^{-1}$
Density Pb (400°C)	$\rho_{Pb} = 10.5 \text{ g-cm}^{-3}$

Liquid Velociy (cm-sec ⁻¹)	δ (μm)	ð _c (μm)		
Crystal Size; length/2 = 25 µm				
$V_{-} = 0.01 \text{ cm-sec}^{-1}$	1144	298		
$V_{-} = 0.1 \text{ cm-sec}^{-1}$	362	94.6		
$V_{*} = 1.0 \text{ cm-sec}^{-1}$	114	29.6		
Crystal Size; length/2 = 500 µm				
$V_{-} = 0.01 \text{ cm-sec}^{-1}$	5120	1334		
$V_{-} = 0.1 \text{ cm-sec}^{-1}$	1620	422		
$V_{*} = 1.0 \text{ cm-sec}^{-1}$	512	_134		

Table 2.3 Momentum and Mass Transfer Boundary Layers for Liquid Lead at 400°C.

From Table 2.3 it is clear that when liquid metal velocities are low, both the momentum, and mass transfer boundary layer thickness increases significantly. For lead refining where static beds of intermetallic particles of about 50 μ m are formed and assuming liquid velocities in the range 0.1 cm-sec⁻¹, one would expect a large mass transfer boundary layer thickness in the order of 100 μ m.

3. SURFACE CHEMISTRY

The nature of metal refining with growth of crystals from solution, or indeed any solid particles in liquid metal, brings into question the role of surface chemistry. Indeed the concept of surface energy has already been applied in the discussion of nucleation theory presented in Section 2.2.1. From common industrial practice, where some drosses are termed "dry", while others "wet", one can envision the importance of surface chemistry for a three phase, solid, liquid, vapour system.

3.1 Capillary Forces

Interfaces such as gas-solid, gas-liquid, and liquid-solid have a Gibbs energy associated with their existence⁽³⁸⁾. It is reasonable that the Gibbs energy should have a positive value since a negative value would suggest the continual expansion of the surface. This is of course the case with gases or miscible liquids where the system tends to solution rather than identifiable surfaces. The energy associated with a surface is given the symbol γ and generally termed the surface tension or surface free energy. Surface Gibbs energy is a more realistic term when describing the phenomenon since tension denotes an actual "skin" or covering. As an energy term, one can define surface energy as⁽³⁸⁾;

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{\mu T} \tag{3.1}$$

where; G is the Gibbs energy, and A the surface area at constant temperature and pressure.

Laplace and Young defined the basic expression for capillarity in 1805 by considering a small section of arbitrarily curved surface. The two radii of curvature \mathbf{R}_1 and \mathbf{R}_2 are considered as

shown in Figure 3.1. The surface is displaced a distance outwards such that the change in area will be;

$$\Delta A = (x + dx)(y + dy) - xy = xdy + ydx \qquad (3.2)$$

The amount of work done in forming the new surface is given as;

$$Work = \gamma (xdy + ydx) \tag{3.3}$$

A pressure difference, ΔP , across the surface with area xy and through a distance dz can be given as;

$$Work = \Delta Pxydz \tag{3.4}$$

On equating the two work terms and, and substituting proper geometrical terms for dx and dy, one obtains the final expression;

$$\Delta P - \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{3.5}$$

This is the basic equation of capillarity. If the two radii are equal, as in a sphere, then the equation reduces to $\Delta P=2\gamma/r$. Similarly for a plane surface, the two radii are infinite and the change in pressure must be equal to zero.

The Young-Laplace equation can be used to describe capillary rise. If liquid wets the wall of a capillary it must lie parallel to the two narrow planes. This forces the surface to take a concave shape to remain continuous and the pressure difference across the surface must be given by Equation (3.5). For a circular capillary of narrow diameter, the curvature can said to be

hemispherical. In this case the two radii of curvature are equal and Equation (3.5) becomes the limiting expression;

$$\Delta P = \frac{2\gamma}{r} \tag{3.6}$$

where; **r** is the radius of the capillary.

If a height, **h**, gives the distance of a meniscus above a flat liquid surface for which the ΔP is zero, then the ΔP in the above equation must be equal to a hydrostatic pressure of liquid in the capillary. Equation (3.6) then becomes;

$$\Delta \rho g h = \frac{2\gamma}{r} \tag{3.7}$$

where; h is the height of liquid in the capillary $\Delta \rho$ the difference in density between gas and liquid g the gravitational acceleration.

Figure 3.2 gives a schematic representation of capillary rise in a simple circular tube.







Figure 3.2 Schematic Diagram of Capillary Rise in a Narrow Tube; much magnified in relation to dish⁽³⁸⁾.

In the case where the liquid does not completely wet the capillary surface such that the angle of contact, θ , is zero, then the radius of curvature \mathbf{R}_1 (Equation 3.5) becomes $r/\cos\theta$. Since \mathbf{R}_1 and \mathbf{R}_2 are equal, one can write the general form of the equation;

$$\Delta \rho g h = \frac{2 \gamma cos \theta}{r} \tag{3.8}$$

For most practical examples of capillary rise where the surface energy of the liquid is high, and the capillary radius low, then Equation (3.8) becomes an excellent approximation of reality. The technique of capillary rise is often used to determine the surface energy of liquids particularly when the liquid perfectly wets the capillary walls; θ equal to zero.

3.2 Wetting of Solids by Liquids

The wetting of solids by liquids generally involves a three phase system, solid, liquid, vapour at thermodynamic equilibrium. The earliest expression of this relation was attempted qualitatively by Young in his classic treatise of 1805⁽³⁹⁾. Young's mechanistic approach was described algebraically by Dupré in 1869 and is generally termed Young's equation as shown below⁽⁴⁰⁾;

$$\gamma_{\mu} - \gamma_{\mu} = \gamma_{\mu} \cos\theta \qquad (3.9)$$

where γ is the interfacial tension between the solid-vapour (sv), solid-liquid (sl), and liquidvapour phase. The angle θ is considered the contact angle between liquid and solid phase as defined in Figure 3.3. It should be noted that the Young-Dupré relationship refers to interfacial, or surface, tension rather than energy. This derives from early speculation that surface actually formed "skins" which could be represented as forces.



Figure 3.3 Schematic Diagram of a Sessile Drop on a Solid Substrate Showing Surface Energies as Vector Quantities⁽³⁸⁾.

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The first exact treatment of solid wetting was performed by Gibbs who derived Young's equation considering surface energy (while neglecting gravity). Many, such as Bickerman, strenuously object to the interchangeable use of the terms surface tension and surface energy because of the rigorous derivation of the energy balance compared with the qualitative approach taken by Young when deriving the expression for so-called surface tension⁽⁴¹⁾. However, in the modern literature the two terms are considered to have the same meaning, and are often used interchangeably.

Gibb's work was followed by Johnson in 1959 who again derived Young's equation this time considering gravity⁽⁴¹⁾. He concluded that Young's equation was valid under most physical conditions including complete wetting where the contact angle is zero. Johnson's work illustrated the importance of gravity in determining the nature of wetting including the shape of a sessile drop.

The essential feature of Young's work through to the derivations of Johnson, is the assumption of thermodynamic equilibrium between all three phases. This rarely occurs when considering high temperature metallurgical applications, or indeed crystal growth from saturated solutions. When chemical equilibrium has not been established, one must consider the role of mass transport through the phase boundaries, and its effect upon the overall energy balance.

3.2.1 Wetting Under Chemical Equilibrium

When describing the system shown in Figure 3.3, and neglecting gravitational effects, the total change in Gibbs energy for the system at constant temperature and pressure can be written as⁽⁴²⁾;

$$dG = \sum_{i} \mu_{i}^{\alpha} dn_{i}^{\alpha} + \sum_{i} \mu_{i}^{l} dn_{i}^{l} + \sum_{i} \mu_{i}^{\nu} dn_{i}^{\nu} + \gamma_{sl} dA_{sl} + \gamma_{sv} dA_{sv}$$

+ $\gamma_{sv} dA_{sv} + \sum_{\alpha\beta} \left\{ \sum_{i} \left(\frac{\partial G^{\alpha\beta}}{\partial n_{i}^{\alpha}} \right) dn_{i}^{\alpha} + \sum_{i} \left(\frac{\partial G^{\alpha\beta}}{\partial n_{i}^{\beta}} \right) dn_{i}^{\beta} + \sum_{i} \left(\frac{\partial G^{\alpha\beta}}{\partial n_{i}^{\alpha\beta}} \right) dn_{i}^{\alpha\beta} \right\}$ (3.10)

where; α , β , l, v, s are distinct phases,

 α , β are the interfacial phases,

 μ_i is the chemical potential of component i in the designated phase,

 \mathbf{n}_i is the total number of moles of component i (by concentration or adsorption), and

G is the total Gibbs energy of the designated phase.

The inclusion of the chemical potential, or activity, of components of the solution in the above expression has a great impact on wetting considerations in later examples. It is crucial for true wetting that the chemical potentials of components have achieved real thermodynamic equilibrium.

If we consider total thermodynamic equilibrium, then dG=0, and the variations of mass are independent of the variations of area, Equation (3.10) can be split such that⁽⁴²⁾;

$$\gamma_{al} dA_{al} + \gamma_{av} dA_{av} + \gamma_{bv} dA_{bv} = 0 \qquad (3.11)$$

and;

$$0 = \sum_{i} \mu_{i}^{\alpha} dn_{i}^{\alpha} + \sum_{i} \mu_{i}^{\beta} dn_{i}^{\alpha} + \sum_{i} \mu_{i}^{\gamma} dn_{i}^{\nu}$$
$$+ \sum_{\alpha,\beta} \left\{ \sum_{i} \left(\frac{\partial G^{\alpha\beta}}{\partial n_{i}^{\alpha}} \right) dn_{i}^{\alpha} + \sum_{i} \left(\frac{\partial G^{\alpha\beta}}{\partial n_{i}^{\beta}} \right) dn_{i}^{\beta} + \sum_{i} \left(\frac{\partial G^{\alpha\beta}}{\partial n_{i}^{\alpha}\beta} \right) dn_{i}^{\alpha\beta} \right\}$$
(3.12)
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In the above expression, Equation (3.11) describes the conditions for mechanical equilibrium while Equation (3.12) gives the conditions for chemical equilibrium.

If the liquid droplet is assumed to be small enough such that its equilibrium configuration is spherical, then such a droplet placed on a flat, rigid, solid surface will form a solid-liquid interface if⁽⁴²⁾;

$$\delta G = \delta \int_{al} \gamma_{al} \, dA_{al} + \delta \int_{sv} \gamma_{sv} \, dA_{sv} + \delta \int_{bv} \gamma_{bv} \, dA_{bv} < 0 \tag{3.13}$$

This Gibbs energy decrease shown above results in the deformation of the liquid drop. The solid-liquid interfacial area increases, and the deformation will continue until a minimum Gibbs energy state, as described by Equation (3.11), is reached. Therefore, in a system where the bulk volumes are non-reactive (no mass transport), the Gibbs energy changes for the system are only the result of changes in the interfacial areas⁽⁴²⁾.

Figure 3.4 shows a progression of contact angles for a liquid on a rigid solid surface. The area of the liquid-vapour interface decreases as the contact angle decreases from 180-90°. As the contact angle further decreases from 90-0° the surface area of the liquid-vapour interface again increases. This is in contrast to the solid-liquid interfacial area which increases steadily with a decreasing contact angle. Since we can say that $dA_{a} = -dA_{av}$ Equation (3.13) becomes;

$$\delta G = \delta \int_{kl} (\gamma_{kl} - \gamma_{kv}) dA_{kl} + \delta \int_{kv} \gamma_{kv} dA_{kv} \qquad (3.14)$$

Equation (3.14) can be used analytically to predict the contact angle based on the relative values of the surface energies. Table 3.1 gives a summary of the possible configurations⁽⁴²⁾.



Figure 3.4 Equilibrium of Forces on the Periphery of a Sessile Drop; (a) acute contact angle, and (b) obtuse contact angle⁽⁴²⁾.

y relationship	$(\gamma_{d} - \gamma_{sy})$ term	γ _v term		
$\theta = 180 - 90^{\circ}$				
$\gamma_w < \gamma_d > \gamma_w$	(+)	(-)		
$\gamma_{w} < \gamma_{s} < \gamma_{v}$	(+)	(-)		
$\gamma_{w} > \gamma_{d} > \gamma_{v}$	(-)	(-)		
$\gamma_{w} > \gamma_{s} < \gamma_{w}$	(-)	(-)		
	<u>θ = 90 - 0°</u>			
$\gamma_w < \gamma_s > \gamma_w$	(+)	(+)		
$\gamma_{w} < \gamma_{d} < \gamma_{w}$	(+)	(+)		
$\gamma_w > \gamma_d > \gamma_v$	(-)	(+)		
$\gamma_{w} > \gamma_{d} < \gamma_{w}$	(-)	(+)		

Table 3.1 Possible Contact Angle Configurations.

From Table 3.1, the important parameter of a system at equilibrium which determines wetting is the value $\gamma_{\rm st} - \gamma_{\rm sv}$. A negative value would result in wetting.

According to Aksay et al., the formation of an interface can be considered to be analogous to the formation of a solution and correspond to an adjustment of surface structures to form some intermediate interfacial structure whose interfacial tension, γ_{d} , is between γ_{sv} and γ_{bv} (see Table 3.1)⁽⁴²⁾. The actual magnitude of γ_{d} is dependent on the degree of chemical bonding at the interface between liquid and solid. Bonding such as Van der Waals forces or the attraction of polar molecules are examples of chemical bonding under chemical equilibrium conditions. When the liquid surface energy is less than the solid, a reduction of the interfacial energy approaching the value of γ_{bv} would result in complete wetting, or a zero degree contact angle.

When liquid-solid interfacial energy is less than either solid or liquid surface energies, then a transient condition is said to exist. This will result in the altering of interfacial structures by chemical reaction (mass transport) until γ_{st} is once again intermediate to γ_{sv} and γ_{bv} .

3.2.2 Wetting Under Non-Equilibrium Conditions

The conditions of chemical equilibrium at constant temperature and pressure are given by Equation (3.12). When these conditions are not satisfied the system (solid, liquid, vapour) will react until the interfaces achieve a state of chemical equilibrium. The attainment of equilibrium is a dynamic process and as such the interfacial energies, and hence contact angle, will change continuously until the equilibrium configuration is reached. It is at this point that terminology becomes important. Essentially, wetting should be considered an equilibrium phenomenon, while the dynamic changes in the interface during the attainment of equilibrium are best termed "spreading".

Mass transfer across interfaces can be regarded as absorption from one phase to the other. This is substantially different from adsorption where no mass transfer occurs (as when there is only interaction at the interface such as in the formation of Van der Waals bonds), and is much more significant since volume and composition changes are often very large.

Mass transfer across the interface results in a net decrease in the Gibbs energy of the system; otherwise there would be no driving force for reaction. At the first instant of reaction however, only the immediate boundary region between the two phases is involved in the reaction. With concentration gradients now present, it can be argued that the entire Gibbs energy decrease due to reaction is concentrated in the boundary region. The magnitude of the decrease in interfacial Gibbs energy is equal to $(\Delta G^{\alpha\beta}/A)$. The interfacial energy is therefore reduced by the amount⁽⁴²⁾;

$$Y_{\alpha\beta} = g^{\alpha\beta} - \sum_{i} \mu_{i}^{\alpha\beta} \Gamma_{i}$$
(3.15)

where; Γ_i is the Gibbs absorption isotherm, and $g^{\alpha\beta}$ is the Gibbs energy change per unit area.

This is illustrated schematically in Figure 3.5. In the diagram, $\gamma^{o}_{\alpha\beta}$ is the initial interfacial energy and the final value is given by $\gamma_{\alpha\beta}$. The literature reports, in cases of strong reaction such as a large negative Gibbs energy change (with boundary layer thickness of only 20 Å), a decrease in interfacial energy as much as 1000 erg/cm². This results in spontaneous spreading or emulsification phenomena⁽⁴²⁾.



Figure 3.5 Variation of Dynamic Interfacial Energy With Time During a Chemical Reaction Between Two Phases⁽⁴²⁾.

From Figure 3.5 it can be seen that the interfacial energy increases towards its equilibrium value after attaining a minimum value. This is due to continued reaction in the bulk phases as diffusion proceeds (reflected in the terms $\sum_i (\partial G^{\alpha\beta} / \partial n_i^{\alpha}) dn_i^{\alpha}$ and $\sum_i (\partial G^{\alpha\beta} / \partial n_i^{\beta}) dn_i^{\beta}$). In other words, as concentration gradients in the phases lessen, the impact of a localized drop in free energy is minimized.

There are many different types of chemical reaction which can be considered for a solid-liquidvapour system. The combinations are lessened if one assumes that the solid-vapour and liquidvapour phases are at equilibrium. With this simplification, possible cases are;

- i) solid is not saturated with components of the liquid phase.
- ii) the liquid is not saturated with components of the solid phase.
- iii) both phases are unsaturated with respect to each other.

iv) a reaction product forms at the interface.

The first type of reaction is illustrated schematically in Figure 3.6. Initially at time t_o a quasiequilibrium state involving no interfacial reaction exists and Young's equation can be expressed for the initial, dynamic surface energies γ_i° . As the liquid begins to saturate the liquid-solid boundary layer, a Gibbs energy change will occur by an amount Δg^{4} due to the free energy of solution.



Figure 3.6 Schematic Representation of the Various Dynamic Stages of a Sessile Drop; when the solid is not initially saturated with components of the liquid⁽⁴²⁾.

If the rate of mass transfer in the solid does not exceed the speed at which the liquid interface can move, then the reaction will follow the path (a-b-c-d) in Figure 3.6. The original γ_{w} will remain constant since the solid exposed at the three phase boundary is unchanged. Spreading will occur due to a decrease in the solid-liquid interfacial energy and the contact angle will decrease to a new pseudo-equilibrium value at t₁. However at this point reaction in the solid proceeds until a new γ_{sv} value is obtained which has decreased by an amount Δg^{d} . The driving force for wetting is now decreased and the contact angle increases to a new equilibrium value. During this "pull-back" stage the drop may break into many smaller drops if the original drop thickness was very small during the spreading process⁽⁴²⁾.

On the other hand, where rates of diffusion of liquid components in the solid are fast relative to the speed at which the liquid can spread the drop would follow path (a-b'-c'-d) in Figure 3.6. Now γ^{o}_{st} and γ^{o}_{sv} are decreased simultaneously by an amount Δg^{st} . The liquid periphery would remain in contact with the reacted solid; the driving force for wetting is not drastically altered and the contact angle would remain relatively constant as the system moves towards its new equilibrium configuration. Either scenario modifies the basic Young-Dupré equation such that^(43,44);

$$W_{AD} = \gamma_{av} - \gamma_{al} + \gamma_{bv} = (\gamma^{e_a} + \Delta g^{al}) - (\gamma^{e_a} + \Delta g^{al}) + \gamma_{bv} \qquad (3.16)$$



Reaction type (ii) involving saturation of the liquid with some solid components can be represented schematically in Figure 3.6. The pseudo-equilibrium can initially be represented by Young's equation. After initial dissolution of solid in the liquid phase, the liquid at the three phase contact will assume its equilibrium energy. This means that γ°_{μ} and γ°_{ν} will be altered by reaction such that each is decreased by the amount Δg^{a} . Therefore, during this initial reaction, a sudden drop in the contact angle would be expected, or in other words immediate spreading.

This would be followed by contraction of the droplet as the bulk of the liquid attains equilibrium. When there is rapid mass transport and a viscous liquid, one would not expect a great deal of spreading due to the rapid attainment of global chemical equilibrium. For solid dissolution in a liquid phase, the Dupré equation becomes;

$$W_{AD} = \gamma_{av} - \gamma_{al} + \gamma_{bv} = \gamma_{av} - (\gamma^{\bullet_a} + \Delta g^{al}) + (\gamma^{\bullet_b} + \Delta g^{bv})$$
(3.17)

The effect of a type (iii) reaction (both solid and liquid phases unsaturated with respect to each other) on sessile drop behaviour could be the same as that outlined for either reaction (i) or (ii). Since there is simultaneous mass transport in both liquid and solid the nature of dynamic wetting will be dictated by the fastest reaction. Generally mass transport is faster in liquid phases and one would expect type (ii) behaviour to predominate in such cases.

Type (iv) reactions, where a distinct reaction product forms, are more difficult to treat in a simple energy balance, although sessile drop behaviour will probably follow that for reaction $(i)^{(42)}$. The analysis is made difficult by the prospect of a reaction product layer which could isolate the liquid from the original solid surface. A general form of the Young-Dupré would be;

$$W_{AD} = \gamma_{b}(1 + \cos\theta_{g}) + \gamma_{c} - A\Delta g^{c} \qquad (3.18)$$

where; γ_c is the interfacial energy

 $\theta_{\mathbf{E}}$ the equilibrium contact angle. A the interfacial area of the reaction layer, and $\Delta \mathbf{g}^{\mathbf{c}}$ the Gibbs energy of formation of the reaction product.

It should be noted at this point that the type of interfacial reaction which one would expect in the precipitation of intermetallic compounds (in the presence of a vapour phase) during metal refining is best described by reaction type (ii). The practical example is somewhat different from that presented, in that the solution at the crystal interface is depleted in solute, rather than concentrated relative to the bulk solution. Therefore, Equation (2.16) or Equation (2.28), describes the boundary layer thickness for solute diffusion. One could also consider this boundary layer as a chemical potential gradient since solution at the outer edge has a greater driving force for crystal growth than solution at the reaction (crystal growth) interface. It is presumed that maintenance of such a mass transport boundary layer will constitute a continual driving force for wetting of the solid crystal interface. One can readily imagine where strong reaction gives a dramatic decrease $\sin \gamma_4$ (see Figure 3.3) that a situation might arise where $\gamma_m - \gamma_4 > \gamma_b$. Based on Aksay's model, dynamic spreading will occur such that solid surfaces may be isolated from the vapour phase with zero degree contact angles.

3.3 Practical Surface Energies

A great deal has been said about surface energies of solids and liquids relative to a vapour phase. Generally these values are expressed as erg/cm^2 or dyn/cm (g/sec^2). Most of the values have been determined experimentally using such techniques as the sessile drop or capillary rise experiment. Surface energies for solids are much less tangible and impossible to measure in the same way as liquid surface energies. Indeed Bikerman makes a strong argument that solid surface energies cannot be the same as liquid surface energies due to the discontinuous nature of a solid crystalline interface⁽⁴⁰⁾.

3.3.1 Liquid Surface Energies

The surface energy of a liquid usually means the energy of the interface between a liquid and its vapour in equilibrium. In practice, the attainment of true equilibrium often takes a great deal of time, and dynamic surface energies (although close to equilibrium) are actually measured experimentally⁽⁴⁰⁾. For liquid metals or glasses, the surface energies are usually determined in a

gas which is believed to be inert with respect to the liquid. In the case of metals, this gas is often hydrogen, which serves the dual purpose of supplying an inert atmosphere while also displacing oxygen which destroys a truly metallic surface by producing an oxide reaction product layer with many metals. Vacuums are also used in practice yet it is difficult to completely remove oxygen in this manner.

Table 3.2 gives some typical surface energies for liquids which are of importance to this study. It is interesting to note the difference between the surface energy of metals compared to water or molten salts⁽⁴⁰⁾. In general, an order of magnitude difference is measured between the two types of liquids; one ionic in nature, the other experiencing weak metallic bonding.

LIQUID	TEMPERATURE (°C)	SURFACE ENERGY (dyn/cm)
Water	20	72.58-72.91
Ethanol	20	22.32
Copper	1120	1269
Silver	1100	909
Zinc	550	778
Lead	400	446
Sodium	98	202
LiCl	1000	110
KCI	1000	83

Table 3.2Surface Energies of Selected Liquids⁽⁴⁰⁾.

The γ values listed in Table 3.2 are always quoted with a reference temperature. It is interesting to suppose that heating a liquid in equilibrium with its own vapour will eventually reach its critical point (assuming it does not decompose). At a critical point there is no difference between liquid and vapour, and hence no surface tension can exist⁽⁴⁰⁾. This determines the general trend

in heating a liquid, where surface tension decreases with increasing temperature. Therefore, the further a liquid temperature is from its critical point the higher the surface tension. This relationship, does not hold true for liquids whose basic molecular composition changes during heating. Lead silicates are an example of this exception. In general though, the relationship of surface tension and temperature follows;

$$\gamma_{el} = \alpha (T_c - T - T_s) \tag{3.19}$$

where; T_c is the critical temperature,

T the temperature of interest,

 $T_x = 6^{\circ}C$ to cope with barely measured surface tensions near the critical point, and **a**, the characteristic parameter for each liquid.

The basic form of the relationship is illustrated for water in Figure $3.7^{(40)}$.



Figure 3.7 Effect of Temperature on the Surface Energy of Water⁽⁴⁰⁾.

Due to the linear nature of Equation (3.19), expressions which relate surface tension to temperature can take many forms. One such equation for liquid lead (under $H_2(g)$) has the form⁽⁴⁵⁾;

$$\gamma_{Pb} = 444.5 - 0.100(T - T_{mp}) \qquad (T \le 550^{\circ}C) \qquad (3.20)$$

where T_{mp} , is the melting point of lead (327°C). This gives a liquid surface tension for lead which ranges from approximately 445 dyn/cm at the freezing point, to 422.7 dyn/cm at 550°C. It is clear that over large temperature differences such as 200+°C, there is little change in surface tension. The literature contains other expressions to calculate surface energy based on extensive properties of the substance. One of the more intriguing was proposed by Stefan who draws a link between the latent heat of vaporization and the total surface energy⁽⁴⁰⁾;

$$2\left(\frac{M}{N}\right)^{2/3}\left(\gamma_{k} - T\frac{\partial\gamma_{k}}{\partial T}\right) \cdot \frac{M\lambda}{N}$$
(3.21)

where; λ is the latent heat of vaporization on a gram basis, M the molecular weight, and N, Avodagro's number.

The model is interesting since it relates the tendancy for atoms to leave a defined surface to the overall energy associated with that surface. In this way the model attempts to deal with the fundamental nature of a liquid surface. The factor 2, in Equation (3.21) varies for many liquids, proving that there is not a precise relation between energies of vaporization and energy required to transfer a molecule to the surface layer.

3.3.2 Surface Energies of Metal Solutions

The present discussion of liquid surface energy has so far considered only pure liquids. For liquid solutions, the determination of liquid surface tension is more difficult. Simple models for

binary solutions such as that proposed by Defay and Priogine have assumed weak chemical interactions of species and hence a regular solution model⁽⁴⁶⁾. However, most solutions show some interaction of the elements which can be described by thermodynamic parameters such as activity coefficients. For example, the lead-zinc binary system shows strong positive deviation from ideality (large miscibility gap) in terms of solution and not surprisingly, the binary surface tensions vary in much the same way as the thermodynamic properties. Figure 3.8 illustrates the powerful effect of lead additions to zinc on the overall surface energy of the binary alloy⁽⁴⁷⁾. This compares to a similar plot of lead activity versus surface energy; Figure 3.9⁽⁴⁷⁾.



Figure 3.8 Effect of Lead Additions on the Surface Energy of Zinc-Lead Alloys⁽⁴⁷⁾.

Butler has proposed a model of binary liquid surface energies which takes into account differing activities of solute at the free liquid surface versus the bulk liquid. This is expressed by the equation⁽⁴⁵⁾;

$$\chi = \gamma_A + \frac{RT}{S_A} \ln \frac{a'_A}{a_A} = \gamma_B + \frac{RT}{S_B} \ln \frac{a'_B}{a_B}$$
(3.22)

- where; γ , γ_A , γ_B are the liquid surface energies of the binary solution, component A, and component B, respectively,
 - $\mathbf{a}_{\mathbf{A}}$ and $\mathbf{a}_{\mathbf{B}}$ are the bulk liquid chemical activities of components A and B,
 - $\mathbf{a'}_{A}$, and $\mathbf{a'}_{B}$ are the chemical activities on the liquid surface, and
 - S_A and S_B are the surface monolayer areas of the components.

The surface energies and bulk solution activities can be measured directly for a given system, while the surface chemical activities and surface monolayer areas are calculated.



Figure 3.9 Effect of Lead Activity on the Surface Energy of Zinc-Lead Alloys⁽⁴⁷⁾.

Yeum et al. have used this equation to describe experimental results for a number of binary metal systems exhibiting both strong positive and negative deviation from ideality⁽⁴⁶⁾. For their calculations, the surface activities are determined by assuming similar solution thermodynamics at the surface (compared with the bulk solution) but with activity coefficients altering according to the coordination number of the atoms at the surface. In other words, the activity coefficients at the surface will change based on a ratio of coordination numbers between bulk and surface atoms. With constant composition, the surface activities will be affected by the same ratio.

A simpler, model was proposed by Thresh et al. where they assumed that differences between the bulk and surface equilibria to be negligible in many cases. The variance in surface energy for a binary solution is thus a function of the bulk solution thermodynamics only and is expressed by the equation⁽⁴⁷⁾;

$$\gamma = \frac{a_1 \gamma_1 + a_2 \gamma_2}{a_1 + a_2}$$
(3.23)

However, the calculated values of surface energy are often higher than those derived experimentally, although the relationship has the correct form since it matches well the shape of experimental curves.

Equation (3.23) suggests that the effect of small concentrations of a solute will be proportional to the difference between its surface energy and that of the solvent, and that its effects will also be conditioned by the magnitude of its activity in the solution. Therefore, solutes with smaller surface tensions than the solvent, and large positive deviation from ideality (large activities), may significantly depress surface energies when dissolved in small quantities. Similarly, solutes with higher surface energies than the solvent, and negative deviation from ideality, will have little effect upon the overall liquid surface energy in small amounts. The lead-zinc system (Figure 3.8) is an example where small amounts of lead (low surface energy and high activity) can

significantly reduce the liquid surface energy from that of pure zinc. Small additions of zinc to lead on the other hand, give little change in the overall liquid surface energy of the system.

3.3.3 Solid Surface Energies

Surface energies of solids are much more difficult to measure than those of liquids, and hence are less common in the literature. Indeed, from a theoretical perspective, solid surfaces are much more complex than liquids since one cannot postulate the perfectly flat, homogeneous, interface idealized in liquids. Solid surfaces, crystalline in nature, will have surface discontinuities, defects, and contours which, due to the atomic nature of crystalline substances, have differing energies. Nevertheless, one can define a solid surface energy as the reversible work in creating a unit area of new surface at constant temperature, volume, and number of moles such that^(48,49);

$$\gamma = \lim_{dA\to g} \frac{dw}{dA}$$
(3.24)

where; dw is the amount of work associated with the increment dA.

Calculations of solid surface energies are difficult since one is generally considering the bonding energy of a crystalline solid, and the energy necessary to break certain bonds in exposing a planar surface. It is also worthy to note that solid surfaces are mobile in the sense that in equilibrium with a vapour phase, bulk and surface diffusion can allow regeneration of solid surfaces within a reasonably short time. This implies continuous movement of surface atoms between the bulk solid, surface layer, and vapour phase.

One of the more practical methods of solid surface energy determination is the cleavage technique which makes use of Equation $(3.24)^{(48)}$, whereby the amount of work is directly measured upon the creation of a new surface by crystal cleavage. However, results can be

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influenced by gas adsorption, and a subsequent recovery of the surface after initial cleavage. Another method, particularly applicable to cubic metals, is the zero creep test where the material is fashioned into a thin wire⁽⁴⁸⁾. The measurements are usually carried out at high temperature where the atoms are quite mobile. The experiment consists of finding the applied stress that will prevent either shrinkage or elongation of the wire when grain boundaries form a type of "bamboo-like" structure along the wire surface. This technique has been used in Figure 3.10 to determine solid surface energies for copper as a function of temperature. The data is also compared to liquid surface energies for the same element. The 25% increase in surface energy at the freezing point agrees well with other data where the solid value is 1.1-1.3 times the liquid value at T_m . Indeed, metallic solid surface energies are often extrapolated from liquid data on this basis. It is interesting to note that the crystallographic orientation of the surface will effect the value of the solid surface energy. The close packed plane will have a value 10% lower than other crystal planes and in some instances of crystal growth, the morphology of the crystal (polyhedral for example) will be due to a minimization of high surface energy plane areas.





4. PARTICLE-LIQUID SYSTEMS

When considering the nature of drosses or crusts formed in metallurgical operations, it seems natural to consider the interaction of solid and liquid surfaces and hence the role of capillary forces. It is known that drosses, which can entangle various amounts of liquid metal, are formed of many tiny particles, the spaces between which one can consider as "bundles" of capillary tubes. It is not common practice in the metallurgical literature to consider dross in this light, yet there are many similar physical phenomena which have been successfully modelled in this way. Soils are probably the best known example. Other examples, perhaps more pertinent when considering metallurgical applications, are the modelling of filtration and thickening during mineral beneficiation, and the infiltration of sintered metallic or ceramic pre-forms (skeletons) with liquid metal in the fabrication of composite materials.

Other commonly modelled particle-liquid systems are suspensions where the solids concentration effects the fluid properties of the mixture. Particle-liquid suspensions often exhibit non-newtonian behaviour, for example a change in viscosity with applied shear stress. Such mixtures are referred to as pseudoplastic, or "shear thinning"^(50,51).

4.1 Mechanisms of Water Retention in Soils

Section 3.1 gave the equations for capillary rise in a single tube with fixed geometry. The most important parameter in Equation (3.8) was the value of the liquid-solid contact angle, θ . It is clear that a contact angle greater than 90° will give no capillary rise. The other parameter of importance is **r**, the effective capillary radius. As the radius decreases, capillary forces increase. Yong has successfully applied these fundamental relationships to water retention in soils, where the bed of particles is assumed to create a network of capillary tubes due to the spaces between adjacent particles, and water is assumed to wet the particles (contact angle less than 90°)⁽⁵²⁾.

4.1.1 Water Retention in Non-Clay Soils

Simple capillary-rise models of water retention in soils often do not agree precisely with measured values since spaces between particles are not really bundles of capillaries, but more like cellular pores interconnected through openings of various sizes⁽⁵²⁾. Nevertheless, the basic form of the relationship holds true for many types of soils including sands, defined as non-reactive particles usually greater than 1µm in diameter.

The basic equation of capillary pressure was used by Buckingham⁽³²⁾ to develop the "potential energy" concept of soil water retention. In Buckingham's model, the capillary potential is defined as the work required per unit weight of water to pull water away from the mass of soil. The potential decreases as the water content increases. This concept is illustrated in Figure 4.1 which schematically describes one of Buckingham's experiments where a column of dry soil is placed into a pan of water and allowed to reach an equilibrium saturation with the water. Water moves upwards into the dry soil in response to a gradient of capillary potential while constantly being drawn downwards by gravitational forces. It is interesting to note that the soil is never completely saturated (pores filled) with water since the network is of varying size throughout.



Figure 4.1 Buckinghan's Experimental Apparatus Used to Determine a Soil's Water Potential⁽⁵²⁾.

It is interesting to note that Buckingham's experiments are not reversible in the sense that upon draining from complete saturation with water, a column will have a different water retention profile than in the case of wetting a dry soil. More water will be retained during draining because complete drainage cannot be attained until the pressure drop exceeds the capillary pressure due to the smallest pore. This hysteresis of wetting is illustrated in Figure 4.2, where water rise is curtailed due to varying pore diameter and similarly water draining is prevented due to unavoidable restrictions in pore diameter during the random packing of particles.



Figure 4.2 Schematic Diagram Illustrating the Hysteresis of Wetting; liquid infiltrating will encounter a large pore diameter while drainage will see a constriction⁽⁵²⁾.

While pore diameters may change due to varying particle size and the random packing of particles in nature, it is clear that capillary forces in packed beds will tend towards maximum particle packing. Bikerman returns to the basic definition of capillary rise in a solid-liquid-vapour system where the surface wetting forces of a liquid (responsible for the meniscus) will tend to draw the walls of a capillary tube together in the presence of a meniscus. This is illustrated in Figure 4.3 where capillary forces drive particle B from its initial position (the discontinuous line) towards particle A. The effect of capillary attraction on the volume of moist

powders is again illustrated in Figure 4.4. The contractile force of meniscus M, may collapse the vault above C and thus reduce the volume of the system AB.



Figure 4.3 Effect of Capillary Attraction on the Volume of Moist Powders; particle B is driven from its initial position (the discontinuous line)⁽⁴⁰⁾.



Figure 4.4 Effect of Capillary Forces on the Volume of Moist Powder⁽⁴⁰⁾.

4.1.2 Water Retention in Clay Soils

Models of water retention in clay soils differ from the simple models described by Yong for comparatively large grained, sandy $soils^{(52)}$. Clays are generally described as consisting of particles with diameters of 1 μ m or less. Table 4.1 gives approximate particle size and surface areas for typical clays.

Mineral	Thickness (Å)	Surface Area (m ² /g)
Montmorillonite	20	800
Illite	200	80
Kaolinite	1000	15

 Table 4.1 Typical Size and Surface Area for Clays.

Clays differ from sandy soils in their ability to swell in the presence of moisture. For fine clay particles, the clay bed may swell in volume well beyond the theoretical random packing of the particles. The process in reversible in the sense that drying of particles gives a corresponding reduction in volume until a minimum is reached, at which point particles are assumed to be arranged in their most dense packing. The volume changes of clay soils during wetting and drying present civil engineers with unique problems, since the swelling pressure of fine clays can often exceed several tonnes per square foot⁽⁵²⁾.

The mechanism of clay swelling is based on a force of repulsion between adjacent particles. This has been attributed in the literature to two basic forces; (i) the hydration of the particle surface and any exchangeable cations on that surface, and (ii) the osmotic pressure developed through the diffuse ion layer existing between the particle surface and the free pore water⁽⁵²⁾. The hydration force gives extreme swelling pressures in the order of tonnes/ft² over very small volume gains (short range repulsion), while osmotic swelling of clays occurs over larger

interparticle spacing and decreases as the distance between particles increases (as swelling proceeds).

4.1.2.1 Hydration of Clays and Exchangeable Cations

Clay particles in soils are always hydrated, surrounded by layers of adsorbed water molecules. The forces bonding water molecules to the particle surface are responsible for many of the porewater properties of clays, particularly at low moisture levels. Yong discusses the hydration of clay as the result of the interaction of polar water molecules and the charged surface of a typical clay particle⁽⁵²⁾.

A typical clay particle may have substitution of one cation for another in the crystal lattice or imperfections, particularly along edges (known as broken-bond charges) and may give a net negative charge for the clay surface. Water will be attracted to the charged surface since it is a polar molecule, and the first molecular layer of water can be held at the interface by hydrogen bonding with oxygen atoms in the clay crystal lattice. Successive layers of water molecules are held less strongly by hydrogen bonding, and with each layer the bonding quickly approaches that of free water. However, the initial adsorbed layers of water can have boundary layer densities as high as 1.4 g-cm⁻³ and ion diffusivities 100 times greater than free water⁽⁵²⁾. The thickness of the hydration layer is disputed, but an average value of 15Å has been reported in the literature.

The negatively charged surface of clay also has the effect of attracting cations in solution. They are termed exchangeable since one cation can be readily replaced by another of equal valence, or two of one-half the original valence. For example a clay with predominantly sodium as the exchangeable cations can be washed with a calcium chloride solution where each calcium ion will replace two sodium ions. The process, known as cation exchange can be written as;

$$2Na_{day}^{\prime} + CaCi_2 = Ca_{day}^{\prime \prime} + 2NaCi \qquad (4.1)$$

In terms of ease of replacement, a higher ion valence (or greater ion radius) will give greater replacing power. For example calcium will easily replace sodium (2⁺ versus 1⁺), and calcium will also replace magnesium due to its greater ionic radius (atomic number of 20, versus 12 for magnesium).

The exchangeable cations are not held tightly in a layer against the solid surface, but rather some distance away depending on the balance of coulombic (attractive) and diffusive forces. Diffusion forces are those described by Fick's law (Equation (2.22)) where ions will diffuse to areas of lower ionic concentration. The balance of coulombic attraction and diffusion results in a diffuse layer of cations with its concentration highest near the particle surface and decreasing towards the bulk solution. This layer is known as the diffuse ion layer, and its interaction with an adjacent layer on another particle, is chiefly responsible for extended swelling pressures in clays. Figure 4.5 illustrates the concept of the adsorbed water (often referred to as the Stern layer⁽³⁸⁾) and the diffuse ion layer.





The theoretical distribution of cations at a negatively charged surface was derived by Gouy and later by Chapman⁽³⁸⁾.

$$n = n_{o}(\cosh 0.16z\sqrt{c_{o}x})^{2}$$
 (4.2)

where; **n**, is the number of cations per unit volume at any distance x from the surface, **n**_o the number of cations per unit volume in the pore water away from the surface, z the valence of cations,

 c_o the concentration of cations (molarity) in the pore water, and x the distance from the surface (Å).

Using the Gouy-Chapman equation, one can calculate the concentration of cations at any distance from the particle surface. The thickness of the diffuse ion layer will increase with decreasing z (charge) and pore water ion concentration as illustrated in Figure 4.6.



Figure 4.6 Effect of Charge Valence and Ion Concentration on the Thickness of the Diffuse Ion Layer⁽⁵²⁾.

4.1.2.2 Interaction of Diffuse Ion Layers

Extended swelling of clay particles (beyond that of interacting hydration layers) can be attributed to the forces of repulsion caused by the interaction of overlapping diffuse ion layers. The repulsion can be visualized as being due to water attracted between the particles forcing them apart. The water movement is the result of osmotic activity in which the system attempts to reduce the concentration gradient existing between the bulk pore water and the solution contained in the overlapping diffuse ion layers⁽⁵²⁾.

The nature of the repulsive force between two overlapping diffuse ion layers can be illustrated in Figure 4.7. Here the electric potential of the solution ψ is plotted as a function of x for two parallel surfaces. Langmuir argued that the total force acting on the planes can be regarded as the sum of an osmotic pressure force since the ion concentration midway between the two particles differs from that of the adjacent bulk solution⁽³⁸⁾. Langmuir's derivation of the equation for interparticle concentrations has been simplified by Yong as⁽⁵²⁾;

$$C_c = \frac{\pi^2}{z^2 B(d + x_s)^2 10^{-16}}$$
(4.3)

where; C_c is the concentration of cations midway between two clay plates (mol/l),
d the half-way point between two plates (Å),
x_o a correction factor (1-4 Å) depending on charge valence and density, and
B equal to 10⁻¹⁵ cm/mol (a constant that depends upon temperature and the dielectric constant).

The derivation of osmotic pressure from concentration data considers the molar Gibbs energy of an ideal solvent with mole fraction $x_1^{(53)}$;

$$\overline{G} = \overline{G}^{\bullet} + RTinx_{i} \tag{4.4}$$

where; G° is the Gibbs energy of the pure solvent.



Figure 4.7 Effect of Two Neighbouring Particles on the Diffuse Ion Layers⁽³⁸⁾.

If an external pressure is applied to the solution, the Gibbs energy of the solvent may be increased to the point where it is equal to the pure solvent. The effect of pressure on Gibbs energy is given by;

$$dG - V dP \tag{4.5}$$

for a process at constant volume, V. The osmotic pressure π , is defined as the pressure on the solution in excess of the pure solvent and the increase in molar Gibbs energy can be written as;

$$\Delta \overline{G} = \overline{V} \int_{\Phi}^{\pi} dP = \pi V \qquad (4.6)$$

One can then combine the effect of solution concentration and external pressure on the total Gibbs energy of the solvent to get;

$$\overline{G} = \overline{G}^{\bullet} + RTinx_{I} + \pi V \tag{4.7}$$

When the solvent in solution is in equilibrium with the pure solution, Equation (4.6) becomes;

$$\pi V - -RTlax_1 \tag{4.8}$$

By substituting $x_1 = (1 - x_2)$, expanding the logarithm, and defining $x_2 \approx n_2/n_1$, and $V = V/n_1$, where V is the volume of the solution and n_1 and n_2 are the numbers of moles of solvent and solute respectively, one obtains;

$$\pi \frac{V}{n_1} = RT \frac{n_2}{n_1} \tag{4.9}$$

or,

$$\pi = \frac{RT}{V} n_2 = C_c RT = RT(C_c - C_c)$$
(4.10)

where; C_o is the ion concentration in the bulk solution (mol/l).

Therefore, Equation (4.3) can be used to estimate the mid-point solution concentration, C_e , and knowing the bulk solution concentration, C_o one can estimate the osmotic swelling pressure for a bed of clay particles⁽⁵²⁾.

Osmotic swelling is generally restricted to sub-micron (colloidal) size particles since the value of C_c rapidly approaches the bulk solution concentration at values of d greater than 100 Å⁽³⁸⁾. Because repulsion forces are short range in aqueous solutions (in the order of 10s of Å⁽⁵²⁾), the particle diameter must be small in order for an interparticle distance in the order of 100 Å to have any noticeable effect on bed volumes. Figure 4.8 illustrates the application of osmotic pressure calculations to the swelling of a montmorillonite clay with varying pore water salt

concentrations⁽⁵⁴⁾. The calculated curves match experimental values, particularly for lower salt concentrations.



Figure 4.8 Effect of Ion Concentration on the Swelling Pressure of a Sodium-Montmorillonite Clay⁽⁵⁴⁾.

4.2 Coal and Mineral Dewatering

The mineral beneficiation industry has as an objective at times to produce mineral or coal concentrates containing as little water as possible. In industry, mineral slurries of low solids content are thickened in large tanks where hindered settling conditions provide an underflow slurry with considerably less moisture. These, high solids content slurries are often vacuum filtered to remove the bulk of the water before a final drying operation (rotary driers etc.). It is important to remove as much water as possible in the comparatively inexpensive filtration step in order to minimize capital and energy costs for concentrate drying.

The use of surface active compounds (surfactants) have found an application in the filtration and dewatering industry in an effort to promote more efficient water removal^(55,56,57,58,59). Several authors have reported dramatic reductions in final cake moisture through the use of cationic, anionic, and non-ionic surfactants when dewatering relatively coarse (0.5 mm) coal suspensions^(58,57,59). The reduction in entrained water has been attributed to reductions in the solid liquid contact angle (promotion of hydrophobicity) and hence, a reduction in capillary pressure within the cake. Other authors, working with much finer suspensions of coal and hematite (-1μ m) have reported similar results for certain surfactants yet dispute the claim that reductions in hydrophobicity are responsible^(55,56).

4.2.1 Capillary Models of Dewatering

Versluys⁽⁶⁰⁾ in 1917 described three equilibrium states for the dewatering of a wide variety of porous beds under an applied pressure or suction. Figure 4.9 illustrates schematically the relationship between moisture and an applied pressure⁽⁵⁷⁾. Initially, when suction is low, or the bed is thin (low pressure drop), the interstitial voids between particles are saturated and the bed is said to be in the capillary state. As the vacuum is increased a stage is reached where the applied pressure exceeds the negative capillary pressure at the air-water interface, and water displacement commences. This displacement is described as the "funicular state" in which a continuous network of water exists in equilibrium with air throughout the porous assembly. As suction is increased, further flow of liquid occurs until there is insufficient water to form a continuous liquid film. At this stage a "pendular state" is formed in which discrete lenses of water form at the points of particle contact and any further removal of moisture from the bed occurs primarily as a result of evaporative diffusion. Several authors have proposed that it is the funicular state of dewatering which can be altered by a change in capillary forces; principally through an increase in the solid-liquid contact angle, $\theta^{(38,57,59)}$.



Figure 4.9 Relationship Between Retained Moisture and Applied Pressure for Filtration⁽⁵⁷⁾.

When considering capillary forces in the filtration of coarse mineral particles, several authors have expressed Equation (3.8) in terms of a capillary pressure;

$$P_c = \frac{2\gamma_b \cos\theta}{r} \tag{4.11}$$

where; \mathbf{P}_{e} is the capillary pressure, γ_{w} the surface energy of the bulk solution, θ the solid-liquid contact angle, and \mathbf{r} the apparent capillary radius in the packed bed.



Figure 4.10 Reduction in Moisture Content of a Coal Bed with Surfactant Additions; constant applied pressure⁽⁵⁷⁾.

Gala and Chiang point out that the addition of surfactant chemicals to particle slurries could have the effect of changing both liquid surface tension and the contact angle. A reduction in either value, or both, would lead to a reduced capillary pressure, P_c , and a reduction in moisture for a given applied suction to the filter cake. Figure 4.10 illustrates the general trend for coal filtration where surfactant addition reduces the capillary pressure. Other experimental data supports the hypothesis that changes in surface tension (due to surfactant addition) correlates well with a reduction in moisture content of a filter cake at a given applied pressure. However, this trend is only observed for low concentrations of surfactant. As more surfactant is added, moisture levels often rise despite a continued decrease in surface tension. This is illustrated in Figure 4.11 where Gala and Chiang have measured the dewatering behaviour of minus 32 mesh coal with a cationic surfactant; DPC (dodecyl pyridinium chloride)⁽⁵⁸⁾. For a cationic surfactant, the increase in moisture content at high surfactant additions has been explained by Gala and Chiang as being due to changes in the contact angle. At low concentrations of DPC, the anionic surface of the coal will attract a single layer of DPC with the cationic end of the molecule oriented towards the particle surface, and the hydropbobic tail towards the solution. This configuration will lead to increased hydrophobicity, or a lowering in the contact angle. However, further additions of surfactant will give a second layer of DPC molecules on the coal surface, this time the hydrophilic end of the molecule is oriented towards the solution causing an increase in the solid-liquid contact angle. This change in surface wettability accounts for increased moisture contents at high surfactant concentrations. Similar, types of relationships are reported for anionic surfactants where changes in both surface tension and contact angle combine to alter the capillary pressure as defined in Equation (4.10).



Figure 4.11 Dewatering Behaviour of -32 Mesh Coal With Increasing Concentrations of a Cationic Surfactant (DPC)⁽⁵⁸⁾.

4.2.2 Dewatering of Fine Mineral Slurries

The capillary model of residual moisture in filter cakes has been applied to fine coal and hematite particles (average diameters around 1μ m), and found wanting. Work by Mwaba using an anionic surfactant showed that small additions were effective in reducing entrained moisture in filter tests. However, continued additions resulted in a return to high levels of entrained water. The pattern was similar to tests performed by Gala and Chiang except that Mwaba showed continued reductions in both liquid surface tension and solid-liquid contact angle with increasing surfactant concentrations. Despite reduced capillary pressure, moisture levels increased as illustrated in Figure 4.11⁽⁵⁶⁾.

Mwaba's experimental results illustrate that capillary pressure arguments alone do not account for moisture retention in fine particle beds. Indeed, without offering a mechanism, the author suggests that the effect of surfactant molecules on the diffuse ion layer surrounding mineral particles may be responsible for the observed behaviour. It is possible that the size range of particles used in his study (sub-micron) allowed diffuse ion layers to play a part in the forces causing water retention. In much the same way as sub-micron size clay particles are influenced by the diffuse ion layer, fine mineral particles may interact to cause an osmotic pressure resulting in particle repulsion and therefore water retention.

4.3 Metal Infiltration of Sintered Particles

The technique of molten metal infiltration of sintered particle compacts has become increasingly important in the fabrication of specialty materials, particularly metal-matrix composite materials. Infiltration allows near-net-shape articles to be fabricated which exhibit improved mechanical properties due to the combined influence of the two phases. The application of powder metallurgy and production of composite metal systems was first applied in the 1940s for heavy

duty electrical conductors (copper infiltrated cast iron), and latter in the 1950s for the development of high performance jet engine turbine blades. Pre-sintering of metallic, or ceramic particles ensures the optimum blend of mechanical properties, while controlling the density (volume fraction) of the particle phase. The technique also allows the production of near-net shapes, thereby eliminating costly forming processes.

A great deal of research work has been conducted on the ability of the liquid metal to wet a solid substrate. Without wetting of the solid there can be no bonding of liquid to solid and hence inferior mechanical properties result. Furthermore, without wetting (defined as a contact angle, $\theta_{u} < 90^{\circ}$) there can be no capillary rise forces for liquid to infiltrate the systems of micro-pores developed during the powder sintering process. To determine the ability of sintered beds to draw, and hold liquid metal, the contact angle is usually measured under equilibrium conditions.

4.3.1 Capillary Rise Models of Metal Infiltration

Early work in the field of melt infiltration has considered the mechanism of infiltration to be a simple capillary model^(61,62,63). When contact angles are less than 90°, the liquid will flow through the capillary bundles in an effort to minimize the energy of the system. The decrease in surface energy will be balanced by a gravitational potential energy term. This has been expressed by White⁽⁶⁴⁾;

$$dG = dG_s + dG_s + dW = 0 \tag{4.12}$$

where; dG is the change in free energy of the system,

dG, the change in surface free energy,

dG, the change in gravitational energy, and

dW is the work done against the additional applied pressure.

In considering the sintered bed of particles as bundles of capillary tubes, White defines an effective particle radius which determines, along with the surface energy, the magnitude of the capillary pressure⁽⁶⁴⁾;

$$r_{eff} = \frac{2(1 - \Phi_p)}{\Phi_p \rho_p A_p}$$
(4.13)

where; Φ_p is the volume fraction of solid powder, ρ_p is the mass density of solid powder, and A_p the specific surface area of powder per gram.

If melt infiltration is simply governed by capillary forces, then the rate of liquid rise in a particle system can be modelled based on Poiseuille's law for flow through narrow tubes⁽⁶⁵⁾. Ligenza and Bernstein, with refinements by Semlak and Rhines, developed the following equation for the height of capillary rise as a function of time for flow in a packed particle bed^(66,62,67);

$$h = \frac{2}{\pi} \sqrt{\frac{\gamma_{b} \cos \theta r_{eff} t}{2\eta}}$$
(4.14)

where; h is the height of liquid rise, t the time of liquid rise, and η the liquid viscosity.

Equation (4.14) can be expressed in terms of a rate of infiltration where $^{(62)}$;

$$h = K\sqrt{t} \tag{4.15}$$

and;

$$K = \frac{2}{\pi} \sqrt{\frac{\gamma_{iv} \cos\theta r_{eff}}{2\eta}}$$
(4.16)

As an order of magnitude calculation, Equation (4.13) can be applied to the infiltration of liquid lead (at 400°C, $\gamma_{\rm N} = 447$ g-cm⁻², $\eta_{\rm Pb} = 0.022$ g-cm⁻¹-sec⁻¹) into a porous structure with an
effective capillary radius of 15 μ m. Here, the height of capillary rise after one minute would be approximately 20 cm, giving a rate, K, equal to 2.6 cm-sec^{-1/2}. With decreasing capillary radius, the rate of liquid infiltration would be expected to decrease due to the greater viscous drag in a narrow capillary tube. Nevertheless, the rates of liquid infiltration according to the Semlak-Rhines model are high and allow pre-from melt infiltration to be a viable fabrication technique from a commercial point of view.

Equation (4.16) has been modified by Muscat to more accurately reflect the reality of capillary rise in a complex system of pores⁽⁶⁹⁾. Effects such as the variation in pore radius and path can be expressed by a "tortuosity" factor ,T, while the hysteresis effect of an advancing liquid interface on the equilibrium solid-liquid contact angle can also be considered by applying a time dependent term for the contact angle;

$$\cos\theta_{t} = \cos\theta_{-} (l - ae^{-ct})$$
(4.17)

where, θ_t is the contact angle at time t, θ_{-} is the equilibrium contact angle, and a and c, are constant for a particular system.

The basic form of Equation (4.14) can be rearranged to give a similar expression where;

$$h^{2} = \left(\frac{1}{T}\right) \frac{r_{eff} \gamma_{lv} \cos\theta_{\omega}}{2\eta} \left(\left(t - \frac{a}{c}\right) + \frac{ae^{-ct}}{c} \right)$$
(4.18)

Where an equilibrium contact angle is achieved instantly, the form of the expression for height of infiltration must simply consider tortuosity and can be reduced to;

$$h = \sqrt{\left(\frac{l}{T}\right) \left(\frac{r_{eff} \gamma_{lv} \cos \theta t}{2\eta}\right)}$$
(4.19)

Essentially, Equation (4.19) presents the factor (r_{eff}/T) as a means of matching experimental data to calculated effective pore radii, based on particle size analysis. In the case of the "order of

magnitude" calculation presented above, a very large tortuosity factor would have to be used to significantly alter the calculated rate of infiltration.

The work by Semlak and Rhines on the kinetics of infiltration has confirmed the role of viscous metal drag. Part of their experimental work looked at the effect of temperature on the infiltration kinetics of 120-170 mesh copper powders by liquid lead. An Arrhenius plot of rate of infiltration (K) versus 1/T gives an activation energy of approximately 8.4 kJ/mol. This value matches that for the viscous flow and self-diffusion of liquid lead given by Geiger and Poirier³. It is interesting to note that great effort was made to saturate the lead with copper (at each temperature) prior to infiltration experiments. This was done to minimize the effect of copper solubility in pure lead which was found to increase the rate of capillary rise. The increased rate observed with unsaturated lead was attributed to an increase in the effective radius (r_{eff}) due to dissolution of copper in pure lead.

Semlak and Rhines and other researchers⁽⁶⁶⁾ conducted experiments exclusively on sintered skeletal structures. Although the porosity varied, particles were connected by solid state diffusion prior to emersion in liquid metal. Since infiltration times were low (2-10 seconds), and the melt maintained at saturation, one expects the skeleton to remain fixed in volume due to the solid particle connections.

4.3.2 Reactive Infiltration of Sintered Powders

A body of research is beginning to emerge dealing with the infiltration of sintered skeletons with liquid metal under non-equilibrium conditions^(61,63,68). That is, there is a chemical potential for solid and liquid to react to some degree during infiltration. The most common form of reaction is liquid phase solubility of some component of the solid particle. However, other mechanisms could be the formation of a separate phase at the solid-liquid interface⁽⁶¹⁾.

In 1964, Goetzel and Shaler refer to the phenomenon of detergency with respect to metal infiltration⁽⁶¹⁾. In a description of detergency, Goetzel et al. refer to the additions of certain components to the liquid phase, or coatings of the solid phase, which manipulate the equilibrium surface energies of the system to promote wetting, and hence infiltration by capillary forces. For such situations, changes of chemical composition, or other means, will alter the solid-liquid contact angle (render $\theta_{1} < 90^{\circ}$) such that wetting occurs.

An example of detergency is the use of oxygen in the infiltration of alumina by liquid silver. Under normal circumstances, pure silver will not wet alumina giving a contact angle greater than 90°. Without wetting, infiltration does not occur. However, small additions of copper and oxygen to the silver alloy will promote excellent wetting of the solid alumina, and rapid infiltration of a sintered compact. Goetzel and Shaler conclude that these subtle additions have the ability to change the equilibrium configuration in such a way as to promote wetting. It is now known, however, that the copper and oxygen react to form a copper oxide compound which readily reacts with the alumina interface to form a copper-aluminum-oxygen spinel. This is actually an example of non-equilibrium spreading as described in Section 3.2.2. Here, a localized minimization of Gibbs energy due to spontaneous chemical reaction at the solid-liquid interface gives a reduction in the interfacial energy $\gamma_{\rm s}$ according to equation (3.15).

More-recent work has acknowledged the effect of non-equilibrium, or "reactive wetting"^(68, 69). Work on the infiltration of sintered aluminum nitride by aluminum has highlighted the effect of chemical reaction on the rate of infiltration. Toy and Scott⁽⁶⁸⁾ found that sessile drop tests conducted to determine contact angles in the aluminum-aluminum nitride system showed no wetting ($\theta > 90^\circ$) below 1130°C. However, above this temperature liquid aluminum was found to spread completely over the sample specimens ($\theta \approx 0^\circ$) indicating the initiation of an interfacial reaction.

Infiltration experiments with pore radii in the range 0.6-0.8 μ m and solid volume fraction of 59-63% were conducted at several temperatures above 1130°C. Results suggested a linear rate of metal infiltration rather than the parabolic relation for capillary induced infiltration expressed in Equation (4.15) and measured by Semlak et al. Indeed, an application of Equation (4.14) would predict a rise of approximately 50 cm in 30 minutes while experimental data gave only 0.35 cm. An increase in pore size was found to increase the linear rate (as one would predict for viscous flow limited infiltration). However a subsequent arrhenius plot of rate data gave activation energies in the range 330-460 kJ/mol. This data has been reproduced in Figure 4.12. High activation energies of this order do not agree with 8.4 kJ/mol predicted for the viscous flow of aluminum. Toy and Scott concluded that the high activation energy indicates chemical reaction control of the rate of infiltration and that models based on capillary flow do not apply.



Figure 4.12 Arrhenius Plots of Infiltration Rate Data for Sintered Silicon Nitride by Aluminum Metal⁽⁶⁸⁾.

Experiments performed on the infiltration of titanium powder by liquid lead and indium⁽⁷⁰⁾ (activation energies of 92 and 67 kJ/mol respectively), and titanium carbide by aluminum⁽⁶⁹⁾,

show similar deviation from the theory of simple capillary rise. Changes in the magnitude of the activation energy for different systems shows the strong influence of interfacial reaction on the infiltration mechanism. This is illustrated by Muscat's work on the kinetics of aluminum infiltration of titanium carbide sintered particles. In his experiments, kinetic data shows a strong dependence of the activation energy on interparticle spacing. Activation energies were found to increase along with increasing pore size; 90 to 450 kJ-mol⁻¹⁽⁶⁹⁾. It was concluded from the high activation energies that interfacial reaction was driving the infiltration. In the case of low interparticle spacing, it was reasoned that diffusion paths were small and hence allowed quick attainment of chemical equilibrium. Larger spacing, on the other hand, gave longer diffusion paths and hence limited the ability of the system to attain chemical equilibrium. Longer diffusion paths were concluded to make rate more dependent on reaction than viscous drag.

4.4 Rheology of Solid-Liquid Suspensions

It has been mentioned in Section 1 that perhaps a more apt description of an intermetallic-liquid metal dross is that of a fluid of high viscosity with non-Newtonian behaviour. Furthermore, it has been suggested that, similar to other particle liquid suspensions, drosses could under some circumstances be considered pseudoplastic (or shear thinning) materials.

In general, particles in liquid are acted upon by three main forces⁽⁵⁰⁾. Firstly, there may be interparticle forces such as attraction and repulsion which usually are based on electrostatic charges or simple van der Waals forces. For aqueous systems these forces are only significant for sub-micron sized particles as discussed in Sections 4.1 and 4.2. Secondly a Brownian (thermal) randomising force can be considered significant, again for very small particles. Thirdly, and most important for large particles, one must consider the viscous forces acting on the particles as discussed in Section 2.3. In a simple manner, the viscous forces are proportional to

the local velocity difference between the particles. In this way the suspension viscosity is considered relative to the continuous phase and may increase beyond the simple liquid viscosity.

For particles of complex shape suspended in a liquid, the Krieger-Dougherty equation is given⁽⁵⁰⁾;

$$\eta = \eta_{s} \left(l - \frac{\Phi}{\Phi_{m}} \right)^{-(\eta/\Phi_{m})}$$
 (4.20)

where; η_s is the liquid viscosity, η the suspension viscosity (apparent viscosity), ϕ the volume fraction of particles, ϕ_m the theoretical maximum packing of particles, and $[\eta]$ the intrinsic viscosity which is based on particle shape

For a dilute suspension with spherical particles, the intrinsic viscosity is given as 2.5. From the form of the equation it is clear that as the volume fraction approaches a limiting theoretical value ϕ_m , the suspension viscosity will approach infinity. From the point of view of intermetallic drosses, it would appear that a stable volume fraction of entrained metal (1- ϕ) will be reached when a large viscosity is realized such that the settling rate of particles approaches an infinitely slow value. The literature offers little information on particle settling in non-Newtonian fluids⁽⁷¹⁾.

The above Krieger-Dougherty equation has been derived for a very low shear rate case. However it has been found to apply to a range of higher shear stresses for many pseudoplastic (shear thinning) fluids. The apparent reduction in viscosity as shear is increased, the definition of shear thinning, can be explained by a re-alignment of the suspended particles. This realignment will reduce the intrinsic viscosity $[\eta]$ as well as the limiting packing volume ϕ_m . Figure 4.13 illustrates this where the upper curve approaches the asymptotic limiting viscosity at low shear, while the lower curve, at higher shear, has a generally lower viscosity and does not approach its limiting conditions for the same volume fraction of solids.



Figure 4.13 Relative Viscosity of a Particle-Liquid Suspension vs. Particulate Volume Fraction^{(50).}

5. CHARACTERIZATION OF SILVER AND BISMUTH CRUST

The literature contains many references to the recovery methods and treatment of both silver and bismuth crusts produced during pyrometallurgical lead refining^(11,19,25). However, no coherent theory has been advanced which explains the degree to which liquid lead is entrained within the crust. Indeed, apart from average crust assays, the crystal morphology, crystal size, and interparticle spacings remain largely unknown. Therefore, the first objective of the current study was to characterize both silver and bismuth crusts in terms of microstructure and relate the findings to the various processing variables.

5.1 Analytical Techniques

The examination of crust samples from silver and bismuth recovery in lead refining involved a series of well established analytical techniques. Initially, overall sample chemical composition was determined by wet chemical analysis. This was often followed by X-Ray diffraction of selected samples to determine the form of intermetallic compounds within each crust. Samples were then prepared for metallographic analysis which included inspection under an optical microscope, quantitative metallography using image analysis techniques, and finally scanning electron microscopy of selected samples.

5.1.1 Chemical Analysis

Samples of silver and bismuth crusts were collected directly from the refining kettles at Brunswick Mining and Smelting Corp. Ltd. in Belledune, New Brunswick. Care was taken to choose representative samples from the crust layers (often weighing as much 10 tonnes per kettle batch). This was achieved by taking composite samples. At the sampling temperatures, the lead component of the crust was usually well above its freezing point, and as such, required fast cooling of the samples to preserve the nature of the two phase mixture. This was easily accomplished in practice by quenching the samples on cool steel plates.





An accurate assessment of crust composition for a particular set of operating parameters often required the formation of a composite sample for chemical analysis. Composite samples included crusts from various locations on the kettle surface and often samples taken from the kettle skimmer as crusts were removed from the kettles during normal refinery operation. Shavings from the various crust lumps were collected and mixed to form the composite sample. This helped diminish the effect of inhomogeneity within the crust for each batch. These shavings were digested in acid solution and metal assays made by atomic absorption (AA) spectroscopy. For the range of chemical compositions of interest, AA is a very accurate analytical technique with expected error of $\pm 1\%$. The greatest source of error when determining the composition of industrial refining crusts, is the sampling procedure. Even with composite samples, Brunswick Smelter plant engineers estimate the error to be $\pm 10\%$ for individual elemental assays for a given batch of crust (silver or bismuth). Figure 5.1 shows a photograph of silver crust in a refining kettle at the Brunswick lead refinery. The sampling difficulties due to inhomogeneity are obvious.

Often, lead bullion samples were collected at the same time as crust samples. The sampling of bullion is considerably easier than crust since the metal solution is homogeneous. Samples were collected with large spoons under the crust layer. Any entrained crust material was allowed to float to the sample surface in the spoon, and metal sample discs (5 cm diameter, 2 cm thickness) were cast from the clean metal underneath. Extra care was taken to remove the first 2-3 mm of metal from the upper and lower surfaces of the metal disc prior to assaying. This cleaning ensured that no crust was carried over during the sample casting. Samples were then drilled to obtain metal shavings to be digested in acid solution and then analyzed by AA spectroscopy. At other times, cleaned sample discs were analyzed directly without digestion by an X-Ray fluorescence (XRF) technique. The error incurred by elemental determination using XRF is considered greater than AA (\pm 3 wt.%) but still is considered accurate within the scope of the current study. XRF analysis was undertaken at the Brunswick Smelter analytical laboratory, while wet chemical assays were performed at the Noranda Technology Centre (NTC) in Pointe Claire, Quebec.

5.1.2 X-Ray Diffraction

In order to determine the intermetallic phase or phases present in a particular silver or bismuth crust sample, selected samples were analyzed using powder X-Ray Diffraction (XRD) techniques. Fine shavings of crusts were prepared from composite crust samples and powder diffraction patterns obtained for each sample. Diffraction peaks were compared against known standards using the JCPDS data base.

The powder technique was considered accurate for intermetallic phases comprising at least 1-2 wt% of the crust samples. Therefore, this technique was only useful in determining the presence of the principal intermetallic phases. Trace intermetallic compounds were unlikely to be detected. XRD was performed at the Noranda Technology Centre, and Lakefield Research (Lakefield, Ontario), a division of Fakconbridge Ltd. Typical output from the computerized crystallographic database used to determine silver-zinc intermetallic species is given in Appendix 1.

5.1.3 Metallography

Metallographic samples were prepared by first mounting crust samples using a cold mounting epoxy (Ancansco) and allowing 24 hours curing time. Mounted samples were then ground manually in four stages using successively finer grinding paper; 220, 800, 2400, 4000 grit papers. Silver crust grinding was done wet, while bismuth crusts required dry grinding due to the rapid oxidation of CaMg, Bi, crystals in water. Samples were polished in two successive stages using Buehler DP-MOL cloth with 6 um diamond paste followed by DP-NAP cloth and 1 um diamond paste. Leco brand oil based lubricant was used in favour of water to avoid oxidation of intermetallic phases. For bismuth crusts, examination under the optical microscope was performed soon after final polishing due to the tendency for the intermetallic phase to react with moisture in the atmosphere. Acetic acid based etchants, normally used in lead metallography, were avoided due to rapid degradation of intermetallic species. However, in the case of both silver and bismuth crusts, adequate contrast is provided between the lead metal matrix and intermetallic phases without the use of etching solutions. It should be noted that the soft lead metal phase makes sample preparation very difficult. While hard intermetallic phases polish cleanly, the lead matrix often exhibits unavoidable scratches, and embedded grinding media (diamond) due to its softness.

Optical metallography was performed using a Leco 500 inverted metallograph. Required magnifications ranged from 50-200 times, which were easily within the abilities of this device to produce sharp images. Micrographs were taken using Polaroid 55 negative film and polarized light filters which provide improved contrast between the lead matrix and intermetallic particles.

Certain crust samples were examined under Noranda Technology Centre's Scanning Electron Microscope (SEM). This type of analysis, using backscatter electron images, often gave improved resolution of the internactallic particle-metal boundary layer due to improved depth of focus. Polished samples were carbon coated using an Edwards 306-A carbon evaporator. The SEM, a Zeiss DSM 960, included an electron microprobe capable of analysis using both Electron Dispersive Spectroscopy (EDS) and Wavelength Dispersive Spectroscopy (WDS). For the elements of interest in silver and bismuth crusts, quantitative WDS analysis was used to help in phase determination. A computer algorithm employing a ZAF correction was used to process the signal and return a quantitative analysis. This tool was particularly useful in distinguishing intermetallic phases in the silver crust samples. For example the γ -phase Ag₃Zn₈ was found to give nearly equal silver and zinc assays while the ϵ -phase AgZn₃ gave around 35% silver and 65% zinc. An example of WDS microprobe output is given in Appendix 2 for silver-zinc intermetallic crystals comparing γ and ϵ phases.

5.1.4 Image Analysis

Image analysis (IA) was found to be a very useful tool in performing quantitative metallography (optical) on crust samples. In conjunction with the Leco 500 microscope, a video camera attachment can transmit an image to the Leco 2001 Image Analyzer (running on Leco Version 2.02 software). The image is converted to a digital map with 1024 by 1024 pixels. A filter algorithm (part of the IA software) is used to help sharpen the contrast between phases by eliminating different shades of grey at the particle matrix interface. At this point the particle images are "eroded" and then reinstated in terms of total area. By eroding the particles a line, the width of one pixel, can be inserted between touching particles. This allows the software to distinguish between individual particles when analyzing the image. After enhancing the image, colours can be assigned to each shade of grey. For crust samples, there were often only two phases, the matrix metal and an intermetallic phase. It was then relatively simple for the software to differentiate between the two phases.

Once an image had been acquired and processed, the image analyzer was capable of determining the average particle length, width, aspect ratio (ratio of length to width), interparticle spacing, and relative area percentage. For area percent, quantitative metallographic theory allows one to assume the same volume percent given a sufficient number of equiaxed particles within the image. Appendix 3 gives a typical output for a particular crust sample. Here, and for all other samples, five fields (or images) were used for each crust sample in order to increase the amount of information from the point of view of statistical accuracy, but also to address and inhomogeneity within each crust sample. The same combination of objective and ocular lenses were used (50 x magnification in a standard micrograph) to generate every field for image analysis. This was critical when comparing samples of differing particle size in order to ensure sufficient numbers of particles were visible within each field, especially in the case of samples with large intermetallic particles.

5.2 Characterization of Silver Crust

Davey suggests that industrial silver crust contains both ϵ and η phase intermetallic particles⁽¹¹⁾. As described in Chapter 2, the higher grade ϵ crystals are contained within crusts formed in the silver rich primary kettle, while low grade η phase crystals are formed in the cooler, silver deficient, secondary kettle. The phases present in each kettle tend to match the equilibrium relations of Figure 2.5 quite closely. However, the crystal size, morphology, and degree of lead entrainment are not well documented. Indeed, most references to silver crust grade (wt.% Ag) tackle the problem from the point of view of thermodynamics, where higher silver levels in lead bullion, and higher refining temperatures may lead to the formation of high silver ϵ crystals due to varying stoichiometry, or indeed the formation Ag₅Zn₈ γ -phase crystals⁽¹⁶⁾. As a result, the grade of crust is enhanced by reducing the zinc content of the intermetallic phase without really affecting the degree of lead entrainment, which is the principal cause of low grade crusts.

5.2.1 Crust Assays

Silver crusts demonstrated tremendous variability in chemical assay depending on both thermodynamic factors and process parameters. Table 5.1 summarizes the ranges of composition which have been identified through crust sampling and review of historical data from Brunswick Mining and Smelting. The most unique sample, high grade crust made from lead bullion containing 0.8% Ag, was made outside regular production practice by adding lead-silver alloy to the desilverising kettle in a deliberate attempt to make silver crust with γ -phase crystals (Ag₃Zn₈). Subsequent X-Ray analysis confirmed the formation of the γ -phase. The sample is unique to most lead refining operations since silver levels are rarely high enough in lead bullion to allow formation of the γ -phase.

It is difficult to draw conclusions based on chemical assay and XRD data alone. However, silver crust from high silver lead, and normal production crusts from primary and secondary desilverising tend to have lower silver and zinc content compared to upgraded crust. This poses an interesting problem since the form of the intermetallic remains the same during upgrading (ϵ -phase). Therefore, the increase in silver content must be due to the removal of liquid lead from the network of crystals by mechanical or chemical means. More complete analysis can only be made on the basis of metallographic inspection.

Crust Type	Predominant Phase	Average wt.% Zn	Average wt% Ag	Average Particle	Volume % Intermetallic Phase	
				Diameter (um)	Calculated	Measured
Primary crust (Kettle #9 BMS)	€-phase	11.8	3.8	50	19.0	21.5
Secondary crust (Kettle #10 BMS)	€-phase; trace η-phase	6.2	1.4	25	9.5	14.3
Upgraded crust (Kettle # 8 BMS)	e-phase	12-20	6-10	-	-	-
Crust made from high Ag bullion [•]	γ-phase	9.2	7.7	88.6	19.8	24.5

-

Silver Crust Sample	Normalized wt.%	Normalized wt.% Zn	Zn:Ag
Figure 5.6 (secondary)	21.3	78.7	3.69
Figure 5.7 (primary);	28.5	71.5	2.5
trace	(9.1)	(90.9)	(10)
Figure 5.8 (high grade)	48.3	51.7	1.07
Figure 5.9 (upgraded)	34.1	65.9	1.93

 Table 5.2
 Microprobe Quantitative Analysis of Silver-Zinc Intermetallic Phases.

5.2.2 Silver Crust Metallography

Typical micrographs of various silver crusts are presented in Figures 5.2 through 5.5. The four main types of crust, identified in Table 5.1, give significantly different microstructures. The most important difference is best exhibited by the upgraded crust sample shown in Figure 5.5. Here, the lead metal matrix is discontinuous, often revealing intermetallic particle surfaces exposed to the atmosphere. Subsequent SEM analysis of the same sample shows poor wetting of intermetallic particles; probably due to surface oxidation. Electron microprobe examination of particle surfaces show the formation of zinc and lead oxide.

The other three types of silver crust share the characteristic of a continuous lead metal phase. Indeed, for all three types (Figures 5.2-5.4), the volume fraction of particles appears to be well below the maximum packing density of randomly oriented particles (around 50 vol.%). Subsequent image analysis of these samples confirms that the intermetallic phases occupy less volume than random packing would indicate. Table 5.1 compares volume fractions measured by image analysis versus a calculation of intermetallic volume fraction based on chemical assay and the average intermetallic phase density given in Table 2.1. Good agreement between the two methods tends to confirm the accuracy of the image analysis techniques for the intermetallic dross.

It is interesting to note that progressively higher silver contents in the intermetallic phase (η through γ -phase) tended to give a more regular crystal habit than low silver crystals. Table 5.2 gives electron microprobe analysis of the intermetallic particles for samples shown in Figures 5.6 through 5.9. The data confirms the XRD phase identification presented in Table 5.1, where higher silver content of the intermetallic species tends to correspond with larger crystal size. Figure 5.2 reveals irregular spheres with relatively low particle diameter for the secondary desilverising crusts (mostly comprising η -phase crystals). Figure 5.4. on the other hand, gives more regular, larger crystals, when the higher temperature γ -phase is formed. Table 5.1 gives average particle diameters as determined by image analysis. The basis for the trend towards more regular crystal habit is unclear for the γ -phase crystals since the solid surface energies for the various crystal planes are unknown. However, one may comment that larger differences in solid surface energy must exist between crystal planes in the γ -phase as compared to the ϵ or η phase crystals. Differences in solid surface energy can lead to well defined crystal habits as the crystal attempts to minimize certain high energy surfaces. This is partially substantiated from heat of formation data given in Figure 2.4. Here, a slightly higher molar heat of formation for the γ -phase, as compared to the ϵ -phase, suggests more ionic bonding, and hence the likelihood of solid surface energy variance between crystal planes^(20,38). Principally metallic bonding exhibited by ϵ and η -phases, should not show the same degree of variance.

The average crystal size reported in Table 5.1 is quite variable for different samples of the same type of crust. This variance is probably caused by processing parameters such as the rates of bath cooling or reagent metal addition. Faster cooling would tend towards a higher rate of nucleation (as shown in Figure 2.11) and hence a greater population of smaller crystals. However, Table 5.1 indicates a trend towards larger intermetallic crystals for the phases formed at higher temperatures with greater silver and zinc concentration in solution (see Figure 2.5).

This is explained by the temperature dependence of liquid phase mass transport as defined by the mass transfer coefficient at the crystal interface. As discussed in Section 2.3.2, the mass transfer coefficient, k_M , is a function of hydrodynamic conditions and the diffusivity (Equation (2.26)). For equal liquid metal velocities, k_M will be controlled by the diffusivity of dissolved species, which increase as a function of temperature as illustrated in Figure 2.18. Simply stated, crystal growth rates will be higher at higher temperature, and as such, the melt should exhibit less supersaturation due to this higher rate of growth. At lower temperatures, crystal growth rate is retarded, and the melt will become supersaturated more easily, thereby favouring increased rates of crystal nucleation, and the formation of many smaller crystals.

5.2.3 Metal Entrainment in Silver Crust

Despite changes in intermetallic phase, particle size, and temperature, Figures 5.2 through 5.4 show a remarkable degree of similarity in the extent of liquid lead entrainment amongst the intermetallic crystals. As discussed above, data suggests greater metal entrainment than random packing of particles would allow. Figure 5.5 is unique because the continuous matrix of lead metal is broken. Since the basic form of the ϵ -phase intermetallic remains the same as Figure 5.3, and the size of crystals is the same, it seems obvious that oxidation of crystal surfaces (as shown in Figure 5.6) reduces the ability of the crystals to hold liquid metal.



Figure 5.2 Optical Micrograph of Typical Secondary Desilverising Crust at BMS-S; ε-phase crystals (light phase) with average particle diameter of approximately 20 μm. (100x)



Figure 5.3 Optical Micrograph of Typical Primary Desilverising Crust at BMS-S; ϵ -phase crystals (light phase) with average particle diameter around 50 μ m. (100x)



Figure 5.4 Optical Micrograph of a High Grade Silver Crust at BMS-S; Ag-Zn intermetallic compound identified as γ -phase with a larger average particle diameter of 100 µm. (100x)



Figure 5.5 Optical Micrograph of Upgraded Silver Crust at BMS-S; mounting epoxy (A), ϵ -phase Ag-Zn (B), oxide reaction product (C), and lead phase (D). (100x)



Figure 5.6 SEM Micrograph of Typical Secondary Silver Refining Crust; microprobe analysis gives a Zn:Ag ratio of 3.69.



Figure 5.7 SEM Micrograph of Typical Primary Silver Refining Crust; microprobe analysis gives a Zn:Ag ratio of 2.5.



Figure 5.8 SEM Micrograph of a High-Grade Silver Crust; microprobe analysis gives a Zn:Ag ratio of 1.07.



Figure 5.9 SEM Micrograph of Upgraded Silver Crust Showing Particles Separated From a Continuous Lead Phase. Some Oxidation of Exposed Particle Surfaces Detected. Based on the theory of particle-liquid systems outlined in Chapter 3, the ability of a static bed of particles to entrain liquids by capillary forces, depends on wetting of the solid surfaces. For the present situation, wetting is defined as having a solid-liquid contact angle, θ_a , less than 90°. It is well known in the literature, that liquid metals do not tend to wet metal oxide surfaces⁽⁶¹⁾. For this reason one can suppose that oxidation of silver-zinc intermetallic particles during silver crust upgrading (Figures 5.5 and 5.9) increases the contact angle and prevents capillary forces from retaining a continuous metal matrix; (presently it is only presumption that liquid lead wets un-oxidized, or microscopically clean, intermetallic crystals. Sessile drop experiments described in Chapter 6 were conducted to quantify these assumptions, and will be discussed in Chapter 7). However, following the current line of reasoning, the degree of lead metal remaining in upgraded crusts may be the result of incomplete oxidation of all crystal surfaces, and the inability of liquid to completely drain from the complex network of capillaries. It could be argued that the partially oxidized crusts correspond to the pendular state described by Nicol during mineral dewatering (Figure 4.9)⁽⁵⁷⁾. Figure 5.10 gives a schematic diagram of the proposed effect of partial intermetallic surface oxidation for upgraded crust.



Figure 5.10 Schematic Diagram of Intermetallic Crystal Surface Oxidation; liquid metal is still entrained where the surface in unaffected.

As mentioned in Section 5.2.2, for untreated silver crusts the volume fraction of entrained liquid lead is well above that expected for random packing of particles. It is also interesting to note that the degree of metal entrainment appears to decrease with increasing average particle size. Figure 5.11 gives a plot of volume fraction versus average particle size for untreated silver crust. However, the relationship indicated by the data may be influenced by other variables such as;

- 1) <u>Crust Thickness</u> which tends to vary between each batch, but is usually in the range 5-10 cm.
- Degree of Agitation since crusts are often agitated for short periods of time to ensure complete reaction of reagent metals.
- 3) <u>Temperature</u> since the form of the intermetallic is based partially on temperature, this variable may also effect the physical forces which entrain lead.



Figure 5.11 Measured Volume Fraction Intermetallic Compound vs. Average Particle Diameter for Typical Silver Crusts.

5.3 Characterization of Bismuth Crusts

Analysis of bismuth refining crusts is more straight forward than those in desilverising since the intermetallic compound formed $(CaMg_2Bi_2)$ is of fixed stoichiometry. As a result, bismuth removal is completed in a single vessel since there is no advantage to be gained in terms of reagent usage by devising a multi-stage, countercurrent, process. The only variable in normal bismuth crust processing is the treatment of crust after skimming. In a simple upgrading step, crust from many skimmings is collected in a second kettle and lead is allowed to drain from the mass. The mechanism by which these crusts are upgraded is presumed to be an increase in static liquid pressure (due to bed depth) which counters those forces which entrain the liquid metal.

5.3.1 Crust Assay and XRD

Bismuth crusts were sampled carefully in the same way as silver crust in an effort to avoid the effects of inhomogeneity within a single batch. Several different classifications of sample were taken depending on the temperature within each refining cycle. Normally, crust is skimmed four times during a single batch as the bath cools. An additional classification was reserved for crust upgrading where many skimmings are placed in a single heated kettle and some lead is allowed to "percolate" from the system, collecting in the bottom of the kettle. Table 5.3 gives average crust assays based on Atomic Absorption Spectrometry. The data in this table are based on recent sampling and unpublished "historical" data from Brunswick Mining and Smelting Ltd.

CRUST TYPE (with average temp.)	% Bi	% Ca	% Mg	$\Phi_p(\%)$ calculated
1st Skimming (420-400°C)	4.0	0.46	0.62	8.65
2nd Skimming (400-380°C)	6.6	0.68	0.92	13.90
3rd Skimming (380-350°C)	6.7	0.70	0.94	14.10
4th Skimming (350-321°C)	2.5	0.31	0.43	5.48
Upgrading (approx. 400°C)	8.2	0.86	1.09	17.01

 Table 5.3 Typical Bismuth Crust Assays.

To determine the form of the intermetallic compound, XRD was performed on selected crust samples. Strong peaks were always detected for lead and $CaMg_2Bi_2$. For the intermetallic phase, the diffraction angles were identified from JCPDS standard pattern 31-190. Output from a typical sample of bismuth crust is shown in Appendix 4 (the XRD work was performed at Lakefield Research). Minor diffraction peaks were detected for Mg_2Pb and $CaPb_3$. It is likely that these phases form on final solidification of the entrained lead during sample collection. It is well known from Davey's work that the saturation of lead with calcium, magnesium, and bismuth depresses the melting point of lead (327 to 320°C) and allows formation of a quaternary eutectic liquid. Final solidification of this phase results in the formation of a tiny amount of binary intermetallic compounds. It is certain therefore, that these phases have no effect on the nature of bismuth crusts above the melting point of the lead solution.

5.3.2 **Bismuth Crust Metallography**

Attempts were made to correlate skimming order with microstructure. For the many samples examined it was impossible to find a correlation with the order or temperature at which crusts were skimmed. From a general point of view, crusts which tended to be skimmed second or third in the debismuthising cycle showed greater intermetallic volume density. Upgraded crust

showed the highest volume fraction of particles to match the higher bismuth assay. Surprisingly, particle size remained relatively constant from one sample to the other. Figures 5.12 and 5.13 give typical optical micrographs of bismuth crusts. Image analysis puts the average particle size at approximately $45 \mu m$.

Figures 5.14 and 5.15 are typical SEM images of bismuth crusts showing the clear interface between particle and liquid lead, and the well defined polyhedral morphology of the $CaMg_2Bi_2$ intermetallic compound. Unlike the random Ag-Zn phases, the clear crystal interface and morphology are more typical of intermetallic compounds with mostly ionic bonding. This observation is supported by the fixed stoichiometry of the intermetallic compound. The tendency towards a regular structure is due to a minimization of surface energy where one crystal orientation may have a lower interfacial energy due to different atomic configuration. Here shape becomes important, as the crystal attempts to reduce overall surface energy by minimizing the area of certain crystal orientations. The general high energy of formation for $CaMg_2Bi_2$, -8.7 kcal-mol⁻¹ (calculated in Table 2.2), gives some idea of the significance of the bonding energy in this system.



Figure 5.12 Optical Micrograph of Typical Bismuth Crust from BMS-S (4.2% Bi); CaMg₂Bi₂ crystals exhibit an ordered structure and relatively constant particle size (45 μm diameter).(200x)



Figure 5.13 Optical Micrograph of Upgraded Bismuth Crust at BMS-S (10.1 % Bi); similar crystal structure and size compared to normal crust. (200x)



Figure 5.14 Optical Micrograph of Typical Bismuth Crust; showing well defined crystal interfaces. (800x)



Figure 5.15 High Magnification SEM Micrograph of a CaMg₂Bi₂ Intermetallic Particle in Bismuth Crust. (SEI)

It is curious that the order of skimming should have an effect upon the grade of bismuth crust without obvious changes to the microstructure. This is highlighted by the upgrading crust where crystal size remains relatively constant, but the volume fraction of lead decreases. After seemingly discounting crystal size and morphology as possible variables, it remains to consider skimming temperature and depth of crust in the kettle at the time of skimming.

5.3.3 Metal Entrainment in Bismuth Crust

Crust samples in debismuthising show even greater metal entrainment than desilverising crusts. Despite low intermetallic particle density for $CaMg_2Bi_2$ (4.5 g-cm⁻³) crystals, the typical assay for bismuth in refining crusts is around 4.8% Bi. This gives calculated particle volume fractions of 10-15%. As discussed above, the intermetallic particle size remains relatively constant as does the shape and chemical composition of the crystals.

Industrial practice in debismuthising does not include any form of bath agitation other than that used initially to help dissolve reagent metal (calcium and magnesium alloy) in the hot, impure, lead. With an absence of agitation, it is unlikely that changes in surface wetting have much bearing on the entrainment phenomenon. This is particulary true in the "so-called" upgrading steps, where bismuth crusts are simply allowed to collect in a separate kettle without mechanical treatment other than an increase in effective crust depth as material is accumulated.

5.4 Discussion of Entrainment Mechanisms

As discussed in Section 5.2.3, silver-zinc intermetallic crystals which have undergone some surface oxidation, appear to allow liquid lead to drain from a complex network of pores. If these pores are considered to be capillary bundles, then the forces which retain liquid could be considered capillary in nature and subject to surface wetting of the particles; specifically the solid-liquid contact angle, θ_{a} . It has been suggested above, that surface oxidation may increase the equilibrium contact angle to some value greater than 90°. Therefore, for untreated crust, solid-liquid contact angles less than 90° may be responsible for retained liquid due to capillary forces.

Unfortunately, the assumption of a simple capillary model for liquid metal entrainment in intermetallic particle beds may not explain the large volume fraction occupied by the continuous metal phase. Indeed, Bikerman and Yong both conclude that under equilibrium conditions, static beds of particles will tend to contract due to three phase contact (vapour-liquid-solid) as illustrated in Figure 4.3 and Figure $4.4^{(40,52)}$. The attractive forces exerted upon the solid particles should allow the system to approach volume fractions of solids which would normally be occupied with random packing. Since intermetallic particle diameter is relatively constant for each batch (due to processing parameters), the volume fraction should correspond to approximately 50 vol. % solids.

Unlike the beds of sand investigated by Buckingham⁽⁵²⁾ (Section 4.1.1), intermetallic particles are starting from near infinite saturation by liquid in the melt as they nucleate and grow in the metal bath. Once attaining a critical diameter, it is presumed that the particles float to the liquid metal surface, joining other crystals in a bed of particles referred to as the crust. The particles will continue to grow since the entrained liquid metal is still supersaturated with respect to the intermetallic phase under normal cooling conditions. From a capillary model point of view, the bed of particles will initially be completely saturated with liquid metal which will continue to drain due to capillary attraction and gravitational forces until an equilibrium configuration is achieved, defined by the capillary pressure (Equation (3.6)). The magnitude of the gravitational force will be controlled by the depth of the intermetallic crystal bed. Figure 5.16 illustrates a simple capillary model of intermetallic crusts in lead refining.



Figure 5.16 Schematic Diagram of Capillary Forces in an Intermetallic Compound Crust During Lead Refining.

In describing the forces at play in a bed of floating particles one must first consider the gravitational forces in the absence of surface forces (capillarity). As such, the height of liquid metal infiltration into the bed will be governed by the difference in liquid and solid density; or in other words the buoyancy of the particles. One can write a simple pressure balance:

$$h_{l}(\rho_{l} - \rho_{s})\Phi_{p}g = h_{2}\rho_{s}\Phi_{p}g \qquad (5.1)$$

where, h_1 is the infiltrated height,

 h_2 the "unwet" particle height,

 ρ_1 and ρ_2 the liquid and solid densities,

 $\Phi_{\mathbf{p}}$ the solid volume fraction in the bed, and

g the acceleration of gravity.

From the above equation, it is clear that the immersed portion of the floating particle bed will be at its closest packing due to the buoyancy force. If one now considers surface forces as raising the liquid-solid-vapour interface further through the bed, one can insert an expression for capillary rise. Equation (5.1) becomes;

$$h_{I}(\rho_{I} - \rho_{p})\Phi_{p}g = h_{2}\rho_{p}\Phi_{p}g + \frac{2\gamma_{h}\cos\theta}{r_{eff}}$$
(5.2)

If Equation (4.13) is substituted for r_{eff} , Equation (5.2) can be rearranged to give;

$$h_{l}(\rho_{l} - \rho_{p}) = h_{2}\rho_{s} + \frac{\gamma_{h} \cos\theta A_{p}}{g(l - \Phi_{p})}$$
(5.3)

However, the simple capillary model of Equation (5.3) would result in close packing of solids. A simple force balance does not provide much insight into the observed nature of refining crusts where Φ_p appears to be much less than the approximate 50% value assumed for random packing.

To reconcile a capillary model with observed solid volume fractions for both silver and bismuth crusts, one could assume certain limiting factors. Specifically, the degree of lead entrainment could be due to two factors, or a combination of the two;

- 1) Hysteresis Effect: As outlined in Section 4.1.1 for non-clay soils⁽⁵²⁾. The bed of particles is prevented from reaching a true equilibrium configuration since the bed is not really bundles of uniform capillaries, but rather a complex network of pores. Local constrictions will result in higher local capillary pressures (as illustrated in Figure 4.2) which prevent further drainage of the system. This will leave pools of liquid metal which will occupy more volume than an idealized capillary bed of particles. Figure 5.17 illustrates the model schematically.
- 2) <u>Viscous Flow of I iquid Metal</u>: The limited rate at which liquid metal can flow through a complex network of pores, can delay the attainment of an equilibrium (balance of capillary and gravitational forces) particle-liquid configuration in practical cases of metal

refining with finite residence time. This is the reverse application of Semlak and Rhines' model for the rate of capillary induced infiltration of powder preforms by liquid metal⁽⁶²⁾.



Figure 5.17 Possible Hysteresis Effect in Intermetallic Crust; local constrictions prevent complete drainage of particle bed.

There is some evidence to support the claim of excess metal entrainment in crust due to a hysteresis effect. For example, silver crust subject to an upgrading process (surface oxidation) is able to drain metal from its system of pores by presumably increasing the contact angle. This will eliminate capillary forces which could prevent liquid flow at critical points in the network where pore diameter is very small. Of course, this model is based on a presumption of change in solid-liquid contact angles, values of which are not available in the literature. Therefore, measurement of contact angles in lead-intermetallic systems is required to confirm this approach.

The possibility of excessive metal entrainment due to the rate of viscous flow of liquid lead can be addressed by applying the Hagen-Poisseuille law for viscous flow in narrow capillaries to the reverse case of liquid drainage due to capillary attraction of intermetallic particles^(65,40). The basic equation for liquid velocity in a narrow capillary is as follows⁽⁴⁰⁾;

$$v = \left(\frac{P_o - P_L}{L} + \rho g\right) \left(\frac{\pi r_{eff}^2}{8\eta}\right)$$
(5.4)

where, v is the average liquid velocity (cm-sec⁻¹),

 P_L and P_o the static pressures of liquid at either end of the capillary, (Pa) L the capillary length (cm), ρ the liquid density (g-cm⁻³), g the acceleration due to gravity (981 cm-sec⁻²), η the liquid viscosity (g-cm⁻¹-sec⁻¹), and r_{eff} the effective capillary diameter (cm).

Bikerman gives the force between two parallel plates (gas-liquid-solid interface) as;

$$f = \frac{\gamma_{lv} l h}{\delta}$$
(5.5)

where; **f** is the force between the plates (g-cm-sec⁻²), **l** the plate width (cm), **h** the height of capillary rise (cm), δ the capillary diameter (cm), and $\gamma_{\rm br}$ the liquid vapour contact angle (g-sec⁻²).

From Equation (5.5) the area term, lh, can be removed giving a pressure exerted by attraction of the two plates;

$$P = \frac{\gamma_{b}}{\delta} \tag{5.6}$$

By substitution of r_{eff} for δ , Equation (5.6) can be used to estimate the pressure at the three phase contact area caused by capillary attraction of particles in a refining crust. The expression can be simplified to the form;

$$P = \frac{\gamma_{b}}{2r_{eff}}$$
(5.7)

Table 5.4 gives calculated values of lead velocity based on capillary forces for a system of intermetallic particles. At 400°C; the surface energy of lead is 447 g-sec⁻², and the viscosity is 0.022 g-cm⁻¹-sec⁻¹. An average pore length of 10 cm has been assumed with average particle diameters of 40 μ m. Applying Equations (4.13), (5.4), and (5.7) one obtains the following data.

Particle Volume Fraction, Φ_{p}	Effective Capillary Radius, r _{err} (µm)	Liquid Pressure due to Attraction, (kPa)	Liquid Metal Velocity (cm-sec ⁻¹)
0.10	120	1.86	4.70
0.15	75	2.98	2.99
0.20	53	4.22	2.11
0.25	40	5.59	1.59
0.30	31	7.21	1.24
0.35	25	8.94	1.00
0.40	20	11.17	0.80
0.45	16	13.97	0.64

Table 5.4 Calculated Velocities of Liquid Lead Due to Particle Attraction (400°C).

From the approximate calculations presented in Table 5.4, it is clear that viscous drag of liquid lead in the capillary pores of intermetallic particles does not limit the rate at which the crust system can drain since practical refining times are in the range of hours, not seconds. Section
4.3.1 discussed the application of a tortuosity factor to the rate equation for capillary rise. A similar factor could have been applied in the above calculations. However, the factor would have to be large indeed to have a great effect on the rate of liquid flow as governed by viscous drag. Furthermore, the relatively large particle size observed in intermetallic crusts, makes the choice of a significant tortuosity term somewhat suspect.

Based on a survey of the available literature, and an investigation of industrial refining crusts, the mechanism of metal entrainment remains undefined. While a hysteresis effect may explain entrainment to some extent, it is clear that viscous drag of metallic lead is not responsible. Therefore, a series of practical experiments were devised to help understand the forces responsible for metal entrainment. These experiments are described in Sections 6 and 7 and hopefully, will shed some light on a fascinating problem.

6. EXPERIMENTAL METHODS TO EXPLORE METAL ENTRAINMENT

The characterization of normal silver and bismuth crusts produced during lead refining raises many questions which have no clear answer in the available literature. Indeed, the physical chemistry of metallurgical drosses containing intermetallic compounds seems to be embodied in the questions raised in this study. Therefore a series of experiments were conducted with the ultimate objective of proposing a coherent explanation for the degree of metal entrainment and some recommendations for reducing this entrainment as a means of improved metal recovery. The strong tendency for the oxidation of CaMg₂Bi₂ intermetallic compound made controlled experiments in the bismuth system impractical. For this reason, laboratory tests focused on metal entrainment in the silver-zinc-lead system. From previous discussions it is clear that the two systems share many features and as such, metal entrainment in refining dross is very likely to be effected by similar forces.

The experimental program was broken into three main phases which attempted to systematically build upon knowledge gained from the previous set of experiments. The main themes were as follows;

<u>Phase 1</u>: Determination of Solid-Liquid Contact Angles

The literature contains no clear references to the solid liquid contact angle between silver-zinc intermetallic compounds and liquid lead. Based on simple capillary models of particle liquid systems, such information is crucial to the development of a coherent theory. Tests used the sessile drop technique to determine if wetting occurred for various silver-zinc intermetallic phases at temperatures of practical importance 400-550°C.

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<u>Phase 2</u>: Liquid Metal Infiltration of Particle Beds

Part 1 - The interaction of synthetic intermetallic particles and liquid lead was studied in shallow particle beds without geometrical constraint. The ability of liquid lead to infiltrate beds of varying average particle diameter and different temperatures were studied. Samples of infiltrated particles were examined under the optical microscope to study particle-liquid interaction.

Part 2 - Similar experiments to Part 1 except that liquid metal could infiltrate columns of particles to a maximum height determined only by surface forces. Again samples were studied to determine the effect of particle size and temperature.

<u>Phase 3:</u> Industrial Scale Experiments to Reduce Metal Entrainment

Conclusions regarding the fundamental nature of the forces giving high liquid metal entrainment in drosses were applied to industrial refining processes in an effort to improve separation efficiency. The full scale work focused on the growth of larger $CaMg_2Bi_2$ intermetallic particles in the Kroll-Betterton process. The experimental procedure and discussion of results for the inplant tests are presented in Chapter 8.

6.1 Sessile Drop Experiments

The ability of liquid lead to wet intermetallic compounds of silver and zinc and $CaMg_2Bi_2$ is of fundamental importance in determining the mechanism of metal entrainment in refining dross. The sessile drop experiment is a common method to determine equilibrium contact angles between solids and liquids at high temperature. This work focuses on the silver-zinc-lead system due to the difficulty in synthesizing, and working with pure $CaMg_2Bi_2$.

6.1.1 Sample Preparation

Two forms of silver-zinc intermetallic compound were prepared in the laboratory by melting appropriate amounts of pure silver and zinc in fireclay crucibles. Special High Grade zinc was obtained from Canadian Electrolytic Zinc (CEZ) Inc. while 99.99% pure silver was obtained from Canadian Copper Refiners (CCR). Approximately 500 gram charges were melted under a molten CaCl₂-NaCl eutectic composition salt phase (33 wt.% CaCl₂, 67 wt.% NaCl) to minimize oxygen transfer to the melt. A temperature of 750°C was required to completely homogenize the liquid alloy. Some stirring was provided to ensure complete mixing. The liquid alloy was cast into 5 cm diameter discs with a nominal 0.5 cm thickness.

Two target compositions were synthesized; the $Ag_5Zn_8 \gamma$ -phase and the $AgZn_3 \epsilon$ -phase. The chemical assay and results of X-Ray Diffraction testing of the two intermetallic phases are given in Table 6.1.

Target Phase	Wt.% Ag	Wt.% Zn	XRD Results
γ-phase	50.8	49.2	confirmed y
e-phase	32.9	67.1	confirmed e
unsaturated Pb	8 (ppm)	< 1 (ppm)	-
saturated Pb	1.09	2.87	-

Table 6.1 Chemical Assay and XRD of Synthetic Ag-Zn Intermetallic and Lead Metal.

The lead used in sessile drop tests was from Brunswick Mining and Smelting Corp. at a nominal purity of 99.99% Pb. Two compositions were used for sessile drop tests; one of pure lead, the other lead already saturated with zinc and silver. The saturated lead sample was prepared by adding small amounts of pure zinc and silver to molten lead at 600°C. Once again, a molten salt of eutectic NaCl-CaCl, was used to prevent oxidation of the alloy prior to casting. The assays

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of the lead used are given in Table 6.1. The two compositions were chosen to investigate the effect of non-equilibrium conditions on the wetting behaviour in the lead-silver-zinc system.

The cast 5 cm discs were easily sectioned into smaller pieces having approximate 2 cm by 2 cm dimensions. The flat surfaces of the intermetallic samples were ground and polished according to the techniques described in Section 5.1.3 to eliminate the effect of a rough surface on the contact angle. Polishing was done just prior to experimentation to avoid excessive oxidation of the intermetallic surface by moisture in air. It is interesting to note that no amount of physical treatment of the surface could eliminate all the effects of an air atmosphere on the surface properties of the samples.

Lead samples were cut from the master alloys using clean shears (the lead was extremely malleable). Samples were cut in the shape of a regular cube and weighed. Nominal weights of 0.5 gram (\pm 0.02 g) were maintained in order to prevent variance in droplet geometry due to gravitational forces. As with silver-zinc intermetallic, the lead samples were prepared just prior to the tests to eliminate cxidation of the metal surface. However, as one might expect, the rate of lead surface oxidation was found to be much less than for the intermetallic compounds.

6.1.2 Sessile Drop Apparatus

Sessile drop tests were conducted in a Lindberg, 4 cm internal diameter, horizontal tube furnace heated by Kanthal resistance elements. The open-ended alumina tube was sealed from the atmosphere at each end by water-cooled caps fitted with neoprene o-ring seals. Plexiglass windows at each end allowed viewing of the experiment in progress. Figure 6.1 gives a schematic diagram of the experimental apparatus.

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Control of gas atmosphere was found to be a crucial variable in the wetting experiments. Trace concentrations of oxygen were found to inhibit wetting of intermetallic substrates. To remedy this situation, great care was taken to provide an essentially oxygen-free environment. The experiments themselves were performed in a 100% hydrogen atmosphere at slightly positive pressure. Linde, ultra-high purity hydrogen was used with a nominal purity of less than 1 ppm O_2 and H_2O . In addition, the hydrogen gas was passed over a Matheson Model 64-1015A oxygen remover (platinum catalyst), to react any residual oxygen with hydrogen, thus producing H_2O . Any residual moisture produced in this way, was then removed by flowing the gas through a Matheson Model 450-B, gas purifier consisting of magnesium perchlorate desiccant. This ensured partial pressures of water below 1×10^{-6} atmospheres. As a final step to ensure low oxygen and moisture in the furnace, several grams of titanium sponge were placed in the hot zone of the furnace for each experiment. From equilibrium considerations, titanium should maintain oxygen partial pressures below 1×10^{-22} atmosphere. The efforts to provide a suitable atmosphere to achieve wetting are not unlike those described by Goetzel and Shaler to achieve metal infiltration of sintered metal powders⁽⁶¹⁾.



Figure 6.1 Schematic Diagram of Sessile Drop Apparatus

To help eliminate moisture, oxygen, and other volatile species from the furnace, Linde ultra-high purity argon (less than 1 ppm oxygen and moisture) was flushed through the system after sealing the water-cooled caps prior to heating. A simple rotary vacuum pump was used to alternately evacuate the system to 100 μ m Hg pressure, and then refill with the high purity argon. The cycle was repeated three times before each experiment. After the final cycle, the dry hydrogen was introduced to the argon filled furnace under a positive pressure. The excess hydrogen was burned as it exited the tube furnace.

6.1.3 Experimental Conditions

Table 6.2 summarizes the sessile drop tests conducted with lead and silver-zinc intermetallic substrates. The main variables of interest were temperature and the potential reactivity of the lead with the substrate. That is, the lead metal composition was altered to represent either saturation or non-saturation with respect to the intermetallic substrate. In all tests the hydrogen flow rate was maintained at 1.0 l/min.

Phase		Temperature	Equilibrium
Intermetallic	Lead	(°C)	Condition
γ	pure	450	non-equil
Υ	saturated	450	n
<u> </u>	pure	450	tt
e	saturated	450	n
γ	pure	550	'n
γ	saturated	550	И
E	pure	550	11
ε	saturated	550	H

 Table 6.2
 Summary of Sessile Drop Tests.

Samples were observed through the plexiglass windows and the change in contact angle noted with time. Due to extensive "spreading" of the liquid metal, back-lit photographs of the sessile drop were not useful in determining the solid-liquid contact angle. Instead, after two hours at temperature, samples were fast cooled by a high flow rate of argon (10 l/min) to preserve droplet geometry. The samples were then sectioned, and examined under the SEM to determine the contact angle, and investigate the nature of the solid-liquid interface.

6.2 Liquid Lead Infiltration of Intermetallic Particle Beds

To help study the mechanism responsible for metal entrainment in intermetallic drosses, the next logical step was to simulate particle-liquid systems under controlled conditions. These experiments were broken into two main parts and constituted the bulk of the experimental work for this study. In part one, pure intermetallic particles of γ -phase silver-zinc were prepared and placed in shallow beds over liquid lead under controlled atmosphere. The experiments were designed to limit the gravitational forces experienced by the infiltrating liquid metal. In part two, a more elaborate experiment was devised where liquid lead could infiltrate a column of γ -phase particles to a maximum height governed by a balance of gravitational forces and capillarity. In each experiment, particle size and temperature were varied.

6.2.1 Part 1: Shallow Bed Infiltration

 Ag_5Zn_8 intermetallic particles were prepared by crushing cast discs (described in Section 6.1.1) in a laboratory ring-mill. The material, as expected, was very brittle and crushed very easily. Size fractions were determined by subjecting the fine product to classification on dry, shaking screens for 10 minutes. The various size fractions were collected and placed in a desiccator to avoid surface reaction with moist air. Despite such precautions, it was found preferable to crush samples no more than one week prior to infiltration tests due to the excessive oxidation of particle surfaces. The various size fractions were characterized in terms of bulk density by volume measurement in graduated cylinders. This method was found to have an experimental error of $\pm 2\%$. Samples of particles were also reserved for characterization of average particle shape and size under the microscope by Image Analysis. Table 6.3 gives the characterization data.

Size Fraction (mesh)	d _{so} (μm)	Average Diameter by I.A. (µm)	Bulk Density (g/cm ³)	Solids Vol. Fraction (%)
20-40 mesh	637.5	321.7	4.52	52.2
40-70 mesh	318	193.6	4.67	53.9
70-100 mesh	181	124.4	4.49	51.8
100-140 mesh	125	104.5	4.44	51.3
140-200 mesh	87.5	76.8	4.3	49.7
200-270 mesh	64	58.6	4.24	49.0
270-325	49	-	3.85	44.5

Table 6.3 Ag₅Zn₈ Particle Data.

In these experiments, the same experimental apparatus (Figure 6.1) and conditions were used as described above. Lead for infiltration was provided by 99.99% pure material from the Brunswick lead smelter. The metal was pre-melted under a nitrogen atmosphere to encourage loss of dissolved oxygen (around 10-15 ppm). Any oxide dross was extracted after melting to produce a clean-charge prior to casting. The low-oxygen lead was then cast into graphite boats in 100 gram bars. These boats served as the test vessels for infiltration experiments.

After casting of the lead buttons, and cooling of the boat (approximately 30 minutes), a 10 gram charge of γ -phase particles were placed on top of the lead button in the graphite boat. The boat was placed immediately in the horizontal furnace and the test started. As discussed above, the gas atmosphere for the tests was controlled in the same way as for sessile drop tests. Infiltrated samples were sectioned, and mounted for metallographic examination and image analysis. Figure 6.2 is a photograph of typical samples produced in the infiltration experiments along with the graphite sample boat.



Figure 6.2 Photograph of a Typical Shallow Bcd Infiltration Sample With the Graphite Crucible.

6.2.2 Part 2: Column Infiltration Tests

The first series of particle infiltration tests were designed to reduce the limitation of the force of gravity on metal infiltration of intermetallic particles of various sizes at different temperatures. The second series of infiltration tests used a column of particles held in a vycor tube which

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allowed lead to infiltrate to a maximum height, not limited by the depth of particles, but rather by a balance of gravitational forces and those forces responsible for infiltration. The tests resembled experiments carried out by Frydrych et al. on the infiltration of cast iron sintered columns⁽⁶⁶⁾. The main difference from previous infiltration experiments is the non-sintered nature of the particle bed. Normally, experiments of metal infiltration have been conducted on sintered pre-forms, where particles have achieved at least random packing density, and cannot move, due to diffusion driven growth at the areas of particle-particle contact. For the current tests, the particles were not joined by solid state bonding, and were therefore free to move within the bed.

Figure 6.3 is a schematic diagram of the furnace apparatus constructed for column infiltration tests. Figures 6.4 and 6.5 are photographs of the apparatus. The experiments were conducted out in a vertical, resistance heated tube furnace with an internal diameter of 4 inches. The tube furnace ends were sealed by water-cooled flanges using neoprene o-rings. Temperature in the furnace hot zone was controlled at ± 0.5 °C by an Omega 9000 programmable controller capable of ramp-and-soak function. A low oxygen, hydrogen gas atmosphere was maintained in exactly the same manner as described in Section 6.1.2 for the sessile drop tests. Once again it was found necessary to use 1 gram of titanium sponge for each run to ensure low oxygen levels.

As shown in Figure 6.3, graphite crucibles (5 cm O/D, 2.5 cm I/D, and 10 cm height) were once again employed to contain the lead charge. Before each run, 99.99% pure lead was melted under nitrogen atmosphere and any dross which formed was skimmed to eliminate as much dissolved oxygen as possible. One hundred grams of lead was then cast in the crucibles and allowed to cool. Eighteen gram charges of intermetallic particles of a particular size range were then added to a ¼" O/D vycor tube, sealed at one end by a stainless steel screen (1 mm²) and held in place by a simple, steel, hose clamp. The addition of steel fittings to the system was not considered a source of contamination, due to the negligible solubility of iron in lead. One gram of 12-20 mesh particles intermetallic particles were added first to each column to prevent finer size

fractions from passing through the screen. Finally, one gram of titanium sponge was added on top of the silver-zinc particles.



Figure 6.3 Schematic Diagram of the Column Infiltration Apparatus.

At the beginning of each experiment the vycor tube was held above the crucible containing the lead by approximately 2 cm. Dried hydrogen was introduced to the system by flowing through the bed of particles. In each run it was necessary to expose the particle bed to hydrogen at

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610°C to render the particle surfaces wettable by liquid lead. The time of exposure needed to achieve wetting varied depending on the average particle size and the gas flow rate. It was found that particles less than 200-270 mesh resulted in too large a pressure drop through the bed to achieve the required flow rate of hydrogen. Therefore, this represented the minimum particle size range tested. The vycor sample holder assembly, containing intermetallic particles, is shown in Figure 6.4.

After sufficient exposure to hydrogen flowing through the particle bed, the gas flow was diverted into the main furnace chamber. The system was allowed to cool to the required test temperature before immersion of the vycor tube in the molten lead. The programmable temperature controller was particularly useful in controlling the overall furnace heating cycle. The tube was immersed by loosening the swagelock fitting (with neoprene o-ring) and sliding the tube downwards to a pre-determined depth of 2 cm in the molten lead. This was sufficient to submerge the 12-20 mesh fraction, and eliminate any possible error from that source. In each run, infiltration was allowed to proceed for 2 hours to ensure an equilibrium configuration. After metal infiltration, samples were allowed to cool to room temperature. The height of metal infiltration was measured and recorded while sections of the infiltrated particle column were prepared for metallographic characterization. Selected samples of the lead bullion reservoir were assayed to determine the dissolved silver and zinc levels after contact with the particle column.



Figure 6.4 Photograph of the Particle Sample Holder Apparatus with a Typical Charge .



Figure 6.5 Photograph of the Column Infiltration Apparatus.

7. DISCUSSION OF RESULTS

This chapter presents the experimental results for sessile drop experiments, and intermetallic particle infiltration tests in the silver-zinc-lead system. A discussion of the results is presented as a means to understand some of the physical phenomena responsible for the high degree of metal entrainment in lead refining crusts produced during silver and bismuth recovery.

7.1 Wetting of Silver-Zinc Intermetallic by Liquid Lead

7.1.1 Establishing a Suitable Gas Atmosphere

Experiments to determine the solid-liquid contact angle between γ and ϵ -phase silver-zinc intermetallic compounds and liquid lead were performed at a number of temperatures. The experiments highlighted the difficulty in simulating conditions within lead refining kettles since it was difficult to eliminate oxygen as a major constituent of the surfaces in question. Indeed, a great deal of effort was expended in providing a gas atmosphere, low in oxygen, which could render the solid intermetallic surfaces wettable by liquid lead. Many researchers in the literature employ high vacuums (less than 1 µm Hg) attained with oil-diffusion pumps, to eliminate oxygen from their systems^(69,72). This was not possible in the silver-zinc-lead system in the temperature range 450-550°C due to the relatively high zinc vapour pressure⁽¹⁸⁾.

After a great deal of experimental work, it was found that a very dry hydrogen atmosphere allowed liquid lead to wet the intermetallic surfaces. Ultra-high purity hydrogen alone (low in oxygen and moisture) was not sufficient, and a platinum catalyst followed by a magnesium perchlorate desiccant were required to give sufficiently pure gas. Titanium sponge in the furnace hot-zone was also found to be a vital component to ensure wetting. However, the titanium was found to react strongly with the gas atmosphere, which complicates the understanding of its role in purifying the hydrogen atmosphere. The important reactions to consider in this system are;

$$PbO \rightarrow H_2(g) \Rightarrow Pb + H_2O(g) \tag{7.1}$$

$$ZnO + H_2(g) \neq Zn_{Ag-2n} + H_2O(g)$$
(7.2)

$$Pb + 1/2O_2(g) = PbO$$
 (7.3)

$$Zn + 1/2O_2(g) \neq ZnO \tag{7.4}$$

$$Ti + O_2(g) = TiO_2 \tag{7.5}$$

$$Ti + H_2(g) \neq TiH_2 \tag{7.6}$$

$$TiH_2 + 2H_2O(g) = TiO_2 + 3H_2(g)$$
 (7.7)

$$TiH_2 + O_2(g) \neq TiO_2 + H_2(g)$$
 (7.8)

If one assumes that the hydrogen entering the system contains approximately 1 ppm $H_2O(g)$, then Table 7.1 can be useful in determining the role of the titanium sponge.

From the thermodynamic data for Equation 7.6 (presented in Table 7.1) it is clear that there is a strong tendency for titanium to react with hydrogen to form titanium hydride (TiH₂(s)). Therefore the system must be considered in terms of the hydride rather than pure titanium. It is also evident from Equation 7.8 that titanium hydride is a powerful oxygen "getter", giving a partial pressure of oxygen around 10^{-52} atmospheres with 1 ppm moisture in hydrogen. Likewise, Equation 7.7 shows titanium hydride to reduce water vapour pressure to approximately 10^{-12} atm. Examining the data for Equations 7.2 and 7.4 (for zinc oxidation), it is clear that titanium hydride is able to provide partial pressures of oxygen and water vapour

below that required to prevent oxidation. It is also probable that the presence of titanium hydride allowed the reduction of zinc or lead oxide layers on the metals. This permitted true contact between the solid and liquid phases without the complication of an intervening reaction layer. The effect of temperature on the ability of the system to reduce oxides would be kinetic in nature such that sufficient temperature was required for reasonable rates of reduction.

Chemical Reaction	k _∞ (500°C)	P_{H2Q} or P_{Q2} (atm)
7.1	<u>2.3</u> 41x10 ⁴	P _{H20} > 1
7.2	3.807x10 ⁻⁵	$P_{H20} = 8.81 \times 10^{-4}$
7.3	<u>3.000x10</u> ⁹	$P_{02} = 1.11 \times 10^{-19}$
7.4	1.845x10 ¹⁸	$P_{02} = 2.94 \times 10^{-37}$
7.5	1.673x10 ⁵⁴	$P_{02} = 5.98 \times 10^{-55}$
7.6	4.169x10 ²	-
7.7	8.137x10 ²³	$P_{\rm H2O} = 1.11 \times 10^{-12}$
7.8	4.014x10 ⁵¹	$P_{02} = 2.49 \times 10^{-52}$

Table 7.1 Gas Phase Equilibria at 500°C⁽⁷³⁾.

- activity of Zn(s) assumed to be 0.1⁽¹⁸⁾.

7.1.2 Sessile Drop Test Results

Table 7.2 summarizes the results from the sessile drop tests. In general, it was found that both phases of silver-zinc intermetallic were well wet by liquid lead in the temperature range 450-550°C. Lower temperatures did not show wetting probably due to the inability of the gas atmosphere to reduce metal oxide layers. As discussed above, this was most likely a kinetic limitation, not due to gas phase purity or an inability of lead to wet the phase at lower temperatures.

Tests were often characterized by an "incubation" period where the contact angle remained greater than 90° for several minutes at the test temperature. This was probably the result of the time required for complete reaction of oxide layers with the gas atmosphere. Higher test temperatures did not require a significant "incubation" period due to faster reduction rates. After incubation, the contact angle was found to change quickly to the point where an angle could no longer be measured by visual inspection. This rapid spreading of the liquid drop over the intermetallic substrate occurred in the case of pure lead and lead saturated with both silver and zinc. Due to the low contact angles during spreading, quantitative measurement of the angles was impossible. However, samples were examined under the SEM to determine the nature of the interface.

Phase		Temperature	Observations
Intermetallic	Lead	(°C)	
Υ	pure	450	spreading
Υ	saturated	450	spreading
<u> </u>	pure	450	spreading
E	saturated	450	spreading
Ŷ	pure	550	rapid spreading
Υ	saturated	550	rapid spreading
<u> </u>	pure	550	rapid spreading
<u>е</u>	saturated	550	rapid spreading

Table 7.2Sessile Drop Test Results.

7.1.3 Examination of Test Specimens

An examination of test specimens underscored the importance of mass transfer at the interface between the solid and liquid as the principle mechanism behind the observed spreading of the liquid. Indeed, in all cases where wetting occurred there was conclusive evidence that the droplet of lead spread in such a way as to cover the entire surface of the intermetallic compound substrate. This was observed for both γ and ϵ -phases at 450 and 550°C. For each example of liquid spreading, samples also showed contraction of the liquid phase back into a single, large, droplet with a solid-liquid contact angle less than 90°.

The spreading effect is illustrated by a series of SEM photo micrographs for a particular sample. Figures 7.1 through 7.4 present images for an ϵ -phase substrate with pure lead metal tested at 450°C. In Figure 7.1 an image with secondary electrons (SE), giving topography, shows a raised portion of the cample surface which is the lead droplet after exposure to the substrate. However, Figure 7.2 shows the same image with back-scatter electrons (BSE) giving good atomic number contrast. In this micrograph the lead phase (light phase) has indeed covered the entire sample surface (grey shade) before contracting to its equilibrium configuration. This follows Aksay's description of non-equilibrium wetting where the substrate is soluble to some extent in the liquid phase⁽⁴²⁾. Here, mass transfer proceeds at the solid-liquid interface resulting in a localized decrease in the solid-liquid surface energy as described in Section 3.2.2. Rapid spreading occurs as a result, until the point where the bulk of the liquid phase becomes saturated with the soluble component of the substrate. At this time, equilibrium between the two phases has been reached, and the liquid phase contracts to assume a final equilibrium contact angle between solid and liquid. Figure 7.3 gives the final equilibrium contact angle (approximately 21°) while showing the residual pockets of liquid lead which have remained on the substrate after contraction of the droplet. This too is consistent with the description of non-equilibrium wetting proposed by Aksay. The evidence of mass transfer is provided by Figure 4.4 where an e-phase, intermetallic particle, has precipitated from the liquid solution upon cooling due to saturation of the liquid phase at 450°C.

Mass transfer from the liquid phase to the solid was also found to cause spreading of the liquid droplet on the intermetallic substrate. Figures 4.5 and 4.6 show γ -phase intermetallic exposed to saturated (with respect to silver and zinc) lead at 450°C. Here, the liquid phase is initially super-saturated with respect to the solid phase. Due to super-saturation, growth of silver-zinc intermetallic is expected. Not surprisingly, the substrate provides the lowest energy site for such growth. Figure 7.5 confirms this, where intermetallic compound growth is clearly evident along the solid-liquid interface. Electron microprobe analysis of the growth layer confirmed that the new phase was the silver-rich, β -phase (on a γ -substrate). This is not what one would predict given the temperature and composition of the liquid phase (1.09% Ag and 2.87% Zn; see Figure 2.3). However, it is probable that some zinc could have been lost from solution (due to the high vapour pressure of zinc) thus rendering the melt high in silver, and hence in equilibrium with the β -phase. From Aksay's argument, the growth of the intermetallic phase at the solid-liquid interface would give a localized decrease in the solid-liquid surface energy due to the minimization of Gibbs energy associated with crystal growth. Rapid spreading will result, due to the sudden decrease in interfacial surface energy. Figure 7.6 shows the final equilibrium contact angle. Again the image reveals a pocket of lead remaining on the substrate after contraction of the droplet once chemical equilibrium had been attained.

Finally, Figure 7.7 shows the result of tests without proper control of oxygen and moisture. Here a lead droplet has reacted with a γ -phase substrate at 550°C. While reaction has taken place at the solid-liquid interface, the droplet has not spread or achieved a true solid-liquid contact angle due to surface oxidation of the substrate. It is interesting to note that even with the scanning electron microscope, it is impossible to positively identify the oxidation layer. This would suggest that the layer may be very thin indeed. In may be possible that there is no oxidation product, but rather a thin layer of adsorbed oxygen. In any case, it is clear that interaction of the solid intermetallic with an oxidizing atmosphere results in a non-wetting surface.



Figure 7.1 SEM Photo Micrograph of an ϵ -Phase Substrate Wet by Lead at 450°C; SE image shows the equilibrium droplet configuration.



Figure 7.2 SEM Micrograph of Figure 7.1 Sample; BSE image shows the extent of lead spreading (light phase).



Figure 7.3 SEM Micrograph of a Cross-Section from the Sessile Drop Specimen Shown in Figure 7.1; BSE image shows equilibrium contact angle and residual lead remaining after contraction (light phase).



Figure 7.4 Higher Magnification SEM Micrograph of Figure 7.3; BSE image shows ϵ -phase precipitate (grey crystal) in lead due to saturation of the liquid phase.



Figure 7.5 SEM Micrograph of a Cross-Section from a γ -Phase Sessile Drop Specimen with Super-Saturated Lead; the solid-liquid interface shows β -phase crystal growth from solution (BSE image).



Figure 7.6 SEM Micrograph of Specimen Shown in Figure 7.5 at Lower Magnification; shows the equilibrium contact angle and residual lead after spreading (BSE).



Figure 7.7 SEM Micrograph of a γ-Phase Sessile Drop Specimen in a Slightly Oxidizing Atmosphere at 550°C; dissolution of the substrate has occurred, but no spreading (BSE).

7.1.4 Implication of Non-Equilibrium Wetting

From the series of sessile drop tests it was clear that under conditions of intimate atomic contact, liquid lead wets γ and ϵ -phase silver-zinc intermetallic compounds. Therefore, refining crusts containing crystals of silver-zinc must be effected by the surface chemistry of the system where low contact angles (less than 45°), can result in strong capillary forces. These capillary forces are presumed to influence the entrainment of metal amongst the crystals. The difficulty experienced in promoting the wetting of substrates even without visible oxidation products, confirms the role of oxygen in the current process of upgrading silver crusts discussed in Section 5.2.3. It is clear that any surface oxidation of silver-zinc particles (visible or not) will prevent wetting, and thereby eliminate capillary forces as a means of metal entrainment in refining dross.

Perhaps the most significant finding of the sessile drop tests was the role of "reactive wetting". It was found that mass transfer at the solid-liquid interface led to spreading of the liquid phase and strong wetting of the substrate. For lead refining, it is presumed that the intermetallic crystals containing silver or bismuth are constantly surrounded by super-saturated lead since the metal bath is continuously cooled. The implication therefore, is that crystals may be in a state of perpetual non-equilibrium wetting, due to the existence of a mass transfer boundary layer; a necessary result of crystal growth from super-saturated solution.

7.2 Particle Infiltration Tests

The results from sessile drop tests on silver-zinc substrates confirmed a common-sense supposition that intermetallic crystals growing from solution during metal refining must be wet by liquid lead. Here, a minimum equilibrium solid-liquid contact angle of 90°, would constitute wetting, and result in capillary forces. However, the tests also showed that a non-equilibrium state could effect the wetting behaviour by reducing the solid-liquid surface energy, γ_{sl} , due to mass transfer at the solid-liquid boundary. This promoted spreading, where contact angles were reduced effectively to zero.

The concept of non-chemical equilibrium wetting when applied to intermetallic particle beds, may help explain the degree of metal entrainment in crusts. Therefore, particle infiltration tests focused on establishing conditions where metal infiltration could be driven by capillary wetting under conditions of mass transfer at the solid-liquid boundary. Particles were arranged in random packing, without sintering, to allow free movement of individual particles with respect to their neighbours. In this sense the experiments were novel in the field of liquid metal infiltration of fine powders.

7.2.1 Shallow-Bed Infiltration

The furnace described in Section 6.2 for sessile drop tests, was again employed to investigate infiltration of silver-zinc intermetallic particles by liquid lead. The γ -phase intermetallic was chosen for the tests since it was brittle, and easily crushed and classified into appropriate size fractions. Unfortunately, the ductility of the ϵ -phase made particle synthesis from this material impractical and this precluded test work with the ϵ -phase.

The greatest experimental difficulty in achieving liquid metal infiltration of a shallow particle bed was control of the gas atmosphere. As discussed in Sction 7.1.1, even freshly prepared intermetallic surfaces needed exposure to a sufficiently reducing atmosphere to microscopically "clean" the metal of any adsorbed oxygen or oxide coatings. For fine particle size fractions (100 μ m and below), the gas atmosphere was unable to sufficiently react with particles deeper in the bed. This often resulted in infiltration from the lead surface over the surface of the particle bed, trapping some "un-wet" particles in the centre of the bed. This phenomenon unfortunately prevented the gathering of data for particles fractions smaller than 200-270 mesh.

Test temperatures were limited to a minimum temperature of 475°C for similar reasons as discussed above; ie. for temperatures lower than 475°C, it was found that the kinetics of particle "cleaning" by the gas phase were too slow, and resulted in the wetting of only particles directly exposed to the gas atmosphere at the top of the bed.

Figure 7.8 is an optical micrograph of a typical infiltration sample. Samples were evaluated using image analysis techniques which allowed the determination of average particle volume fraction, aspect ratio, and inter-particle spacing. The data has been summarized in Figures 7.9 through 7.11. From the curves for particle volume fraction versus particle diameter, a trend emerges where infiltrated samples show a marked decrease in solid fraction compared to measurements of random packing for solid particles of the same average diameter. However,

while volume fraction does show a slight decrease with particle size for dry powders, this phenomenon can be explained by the changing aspect ratio of the particles as average diameter decreases. Figure 7.12 shows a lowering of the aspect ratio with decreasing average particle diameter. From this data it would appear that a reduction in the particle aspect ratio at lower average particle sizes, leads to slightly lower packing densities.

From the experimental data, there is no clear effect of temperature. However, this is not surprising considering the consistent wetting behaviour observed during sessile drop tests. Nevertheless, the pronounced expansion of the particle bed at average particle diameters less than 100 μ m poses some interesting questions regarding the nature of metal entrainment in refining crusts.



Figure 7.8 Optical Micrograph of a Typical Shallow Bed Infiltration Sample with a 110 µm Average Particle Size; note the lack of particle contact (50x).

From a simple capillary model point of view, a particle bed will allow surface forces to draw liquid into the bed pores to a height determined by the effective pore radius, r_{eff} , and other variables such as liquid density, and solid-liquid contact angle. Sessile drop experiments suggest that lead may wet silver-zinc intermetallic phases sufficiently to allow capillary induced infiltration of silver-zinc particle beds. However, the same surface forces will have the effect of maintaining random packing density, or perhaps as Bikerman suggests, to help increase solids volume fraction by promoting more efficient particle arrangement due to strong forces of particle attraction^(38,40,52). Therefore, from a capillary point of view, the γ -phase particle beds should have maintained, or increased, in solid volume fraction, during lead infiltration.

In Chapter 5 the characterization of silver and bismuth crusts considers the situation where particle volume fractions are observed to be much lower than random crystal packing would predict. In general, volume fractions of 10-20% are observed in industry, compared to approximately 50 vol.% for random packing. It is reasonable then to suggest that the observed entrainment may be caused by a hysteresis effect (as Suggested in section 5.4) or by slow rates of metal drainage from the bed due to viscous drag in narrow pores. In Section 5.4 calculations of typical capillary attraction forces, and their effect on liquid velocity in a narrow capillary, would tend to discredit the viscous drag mechanism as a possible explanation. Similarly, the hysteresis effect, as described by Yong for soil drainage, is not very credible given that crystals will tend to pack due to buoyancy forces as described by Equations (5.1) through (5.3)⁽⁵²⁾.

The data presented in Figures 7.9 through 7.11 would also tend to discount a hysteresis effect as the principle mechanism of entrainment. Since infiltration tests started from a condition of particle-particle contact (random packing), not liquid saturation, it seems clear that the observed reductions in particle volume must be caused by other forces. In this sense, metal entrainment appears to be a "reversible" phenomenon for intermetallic compounds. Furthermore, the test duration (2 hours) would suggest that the volume fraction changes are due to sustained forces rather than the transient effects of initial solid-liquid contact during infiltration. The shallow bed tests were characterized by the ability of particles to re-arrange depending on surface, and other forces. In addition, the shallow nature of the bed also limited the magnitude of the gravitational forces to counter capillary forces. For this reason it was decided to conduct similar infiltration experiments of particle columns, to allow infiltration limited only by a balance of forces; gravitational and capillary.



Figure 7.9 Experimental Plot of Average Particle Volume Fraction vs. Average Particle Size for Shallow Bed Infiltration Tests at 475°C. Data for Random Packing is Shown.



Figure 7.10 Experimental Plot of Average Particle Volume Fraction vs. Average Particle Diameter for Shallow Bed Infiltration Tests at 500°C.



Figure 7.11 Experimental Plot of Average Particle Volume Fraction vs. Average Particle Diameter for Shallow Bed Infiltration Tests at 550°C.



Figure 7.12 Particle Aspect Ratio vs. Average Particle Diameter.

7.2.2 Column Infiltration Results

The shallow bed infiltration tests were a good simulation of conditions in a refining kettle since both capillary and buoyancy forces were acting on the floating particles. However, analysis of surface forces was made more difficult due to this complexity. For this reason, column infiltration tests were performed, where particles were suspended above the melt, thus eliminating the mass of the particles as a variable in the infiltration.

In normal instances of metal infiltration into sintered beds of particles, the liquid will rise to a level determined by the capillary pressure. From Buckingham's early experiments in soil water infiltration, it was observed that the complex network of pores would give an uneven front of infiltration since certain pores would resist infiltration (due to widening), while others would allow liquid passage at similar heights⁽⁵²⁾. For lead infiltration into columns of γ -phase intermetallic particles, the infiltration fronts were found to be quite uniform, and well defined. This was probably the result of a relatively uniform particle size used in each experiment, giving consistent effective pore diameters.

Figures 7.13 and 7.14 present infiltration data for the two test temperatures used. As expected, the height of liquid infiltration (measured as height of infiltration front above the liquid lead level) increased with decreasing average particle size. The curves are compared to theoretical predictions of capillary induced rise (Equation (3.8)) calculated using an effective pore radius as defined in Equation (4.13). The calculation of r_{eff} requires the assumption of cubic crystals and a constant particle volume fraction; assumed to be approximately 50%. From the two figures, it is clear that capillary rise, while observing theoretical trends, does not follow the magnitude of the theoretical liquid rise predictions. It is interesting to note that the deviation from predicted rise is more significant for smaller particles. This is curious, and will be discussed in detail shortly. In addition, lower infiltration temperature was found to reduce the measured height of liquid rise as compared to theoretical prediction.

Figures 7.15 and 7.16 present image analysis data for cross-sections of infiltrated columns sampled at the limit of infiltration (top) and near the liquid metal level (bottom). As with shallows beds of particles, the volume fraction of solids was found to decrease significantly as the average particle diameter decreases. This bed "swelling" was observed at the top and bottom of each sample column, without any discernable trend based on location in the column. The reduction in particle bed volume is surprising in the column experiments since capillary theory predicts strong forces will tend to compact the particle bed as metal infiltration proceeds. As with shallow particle beds, the data shows that low solid volume fractions attained during infiltration match observations of actual metal refining crusts. Since the process of bed swelling appears to occur during infiltration as well as draining (during actual lead refining), the idea of a hysteresis effect being responsible for high levels of metal entrainment does not appear to be convincing.



Figure 7.13 Experimental Data Showing Capillary Rise Height vs. Average Particle Diameter for Column Infiltration Tests at 550°C; data is compared to theoretical rise height based on random packing of particles.



Figure 7.14 Experimental Data Showing Capillary Rise Height vs. Average Particle Diameter for Column Infiltration Tests at 450°C; data is compared to theoretical rise height based on random packing of particles.


Figure 7.15 Average Volume Fraction of Solid Particles vs. Average Particle Diameter; column infiltration experiments at 550°C.



Figure 7.16 Average Volume Fraction of Solid Particles vs. Average Particle Diameter; column infiltration experiments at 450°C.

Discussion of Results

Figures 7.17 through 7.20 give a series of optical micrographs of expanded column beds after infiltration. Without the benefit of image analysis, it is still possible to see the effect of lower particle diameters on the bed expansion, where Figure 7.20 with an average diameter of $77\mu m$ shows more metallic lead than Figure 7.17, with an average particle diameter of $194 \mu m$.

As mentioned above, temperature was found to influence the overall height of infiltration, where samples at 450°C do not attain the same height of infiltration as identical samples at 550°C. Similarly, Figure 7.16 shows that the decrease in solid volume fractions were greater for identical size fractions at the lower temperature. This is consistent with lack of rise, since an expanded bed will have a greater effective pore radius, and hence a reduced capillary pressure. Thus, temperature seems to have the effect of promoting bed expansion.

The effect of particle bed swelling is illustrated in Figure 7.21. In this graph, the inter-particle spacing (as measured through IA) has been plotted against average particle diameter. The data are compared to the theoretical particle spacing calculated by assuming random packing, and applying Equation (4.13). While a linear relationship can be observed, the significant finding is that the magnitude of deviation from predicted spacing remains almost constant as the average particle size decreases. This means that as particle size decreases, the relative inter-particle spacing increases. One way of explaining this constant deviation is to picture a boundary layer of constant thickness surrounding each particle and preventing actual particle contact. As average particle diameter is reduced, the effect of the boundary layer on inter-particle spacing will become more pronounced. This concept in illustrated in Figure 7.22 where schematic (a) shows the interparticle distance to be large compared to the boundary layer thickness. In diagram (b), the same boundary layer thickness could comprise a much greater component of the interparticle spacing.



Figure 7.17 Optical Micrograph of a Column Infiltration Sample with an Average Particle Diameter of 194 μm (40-70 mesh); 550°C. (100X)



Figure 7.18Optical Micrograph of a Column Infiltration Sample with an Average Particle
Diameter of 124 μ m (70-100 mesh); 550°C. (100X)



Figure 7.19 Optical Micrograph of a Column Infiltration Sample with an Average Particle Diameter of 104 μm (100-140 mesh); 550°C. (100X)



Figure 7.20 Optical Micrograph of a Column Infiltration Sample with an Average Particle Diameter of 77 μm (140-200 mesh); 550°C. (100X)



Figure 7.21 Inter-Particle Distance vs. Average Particle Diameter; column infiltration test data at 450 and 550°C.



Figure 7.22 Mass Transfer Boundary Layers Surrounding Intermetallic Particles; (a) large diameter relative to δ_{c} , (b) shows the effect upon small particles.

Figure 7.21 suggests that the normal effective capillary radius between particles, r_{eff} , may be augmented by a constant value which may correspond to a type of boundary layer. If we consider the basic form of the capillary rise equation, a constant boundary layer term can be included which reflects the observed bed swelling. Therefore the capillary rise equation can be modified to include a constant term, r_b , the capillary radius due to a boundary layer effect. In this case r_{eff} is still calculated based on random packing density, even though the bed has expanded. The capillary rise equation can be written as;

$$h = \frac{2\gamma_{b} \cos\theta}{\rho g(r_{eff} + r_{b})}$$
(7.9)

Since it is probable that infiltration (due solely to capillary forces) may experience a hysteresis effect, and not attain the full infiltration height due to local changes in effective radius, one can include a constant term, H, in Equation (7.9). It seems reasonable that the hysteresis constant will be different for each situation. Therefore the complete expression for height of capillary rise in an expanding bed of particles can be written;

$$h = \frac{2\gamma_b \cos\theta}{\rho g(r_{eff} + r_b)} - H$$
(7.10)

In Figures 7.23 and 7.24, Equation (7.10) has been used to predict the measured height of infiltration. In each, the calculated height of infiltration gives good agreement with the experimental data. For each temperature a boundary layer radius of 25 μ m was used. This was baced on the average interparticle spacing offset of 50 μ m, shown in Figure 7.21. Table 7.3 gives the constant values used in plotting equation (7.10). It should be pointed out that while the interparticle spacing offset is a measured quantity, the constant H has been chosen to match the experimental data. In this sense it is not surprising that the calculated curves agree with the data.

Temp (°C)	r _ь (μm)	H (cm)
450	25	5
550	25	3

 Table 7.3 Constant Values for Capillary Rise Calculations.



Figure 7.23 Equation 7.10 Predictions of Capillary Rise at 550°C.



Figure 7.24 Equation 7.10 Predictions of Capillary Rise at 450°C.

The boundary layer concept described above, is the same as that observed for clay soil particles and discussed in detail in Section 4.1.2. However, in the case of clay particles in aqueous solution, the effect is limited to very small particle diameters (sub-micron) since the thickness of the diffuse ion layers is in the order of tens of Angstroms. The observed swelling of intermetallic particle beds during metal infiltration appears to occur at much larger particle sizes, and is obviously not the result of diffuse ion layers since we are dealing with a metallic solution. Nevertheless, there are certain similarities in the systems. In the case of colloidal particles, attractive forces due to liquid surface tension (which become stronger as particles approach) are balanced by very strong repulsive forces (osmotic pressures) which increase greatly upon close particle contact. The same mechanism appears to exist for liquid metals and reactive particles since a narrowing of effective pore radius due to capillary attraction is obstructed at low particle sizes.

7.3 Reactive Particle Bed Swelling in Liquid Metals

7.3.1 Mass Transfer in Particle-Metal Systems

The clay soil analogy to intermetallic particle bed swelling is intriguing because in this analogy, as particle size is reduced relative to the thickness of the boundary layer surrounding each particle, increased overlap of the boundary layers gives rise to forces of repulsion between individual particles which counteract capillary forces with the result that the particles are forced apart. Since the effect appears to become significant in liquid metal at particle sizes less than approximately 100 μ m, then the boundary layers in question are likely to be of a similar size range.

Sessile drop results described earlier in this chapter, illustrate the powerful effect of mass transfer on the wetting characteristics of intermetallic substrates. Indeed, the data suggests that "spreading" can be induced by mass transfer from the liquid phase to the solid (crystal growth from super-saturated liquid solution), or solid dissolution into a relatively pure liquid phase. In each, experimental results show liquid spreading until chemical equilibrium has been reached, as described by Aksay⁽⁴²⁾.

For intermetallic crusts in lead refining (both silver and bismuth) the crystals in the crust will continue to grow from super-saturated solution as the bath continues to cool. This implies continued mass transfer at the crystal surfaces, and one would expect the continuation of strong forces of wetting as measured in the sessile drop experiments. Similarly, particle bed infiltration experiments have simulated this behaviour as mass transfer at the crystal boundaries will occur due to liquid phase solubility of the intermetallic in the pure lead. Therefore, for either dissolution or growth, mass transfer is a key component of intermetallic-liquid metal systems with respect to the condition of the solid-liquid interface.

The present experimental work has only considered intermetallic particles which model lead refining systems; namely the silver-zinc-lead system. However, any system of solid particles which can react with liquid metal would be a possible candidate to experience swelling due to an overlap of mass transfer boundary layers. This could include oxide particles where oxygen solubility in metal is significant, sulphide particles, or ceramic particles with appreciable solubility in the liquid phase. In this sense an overall system can be described where "reactive" wetting of the particle could lead to the bed swelling observed in lead refining. This could be termed "Reactive Particle Repulsion".

An excellent example of this phenomenon was recently experienced at the Noranda Technology Centre⁽⁷⁴⁾. Small scale crucible experiments investigating the rate of reaction between SO_2 bubbles and zinc metal in dilute solution with lead-bismuth alloy (0.5 wt% Zn) at 200°C resulted in the entire liquid phase becoming a mass of viscous metal-dross. Subsequent chemical analysis of the dross phase detected only 0.02 wt.% S suggesting a limited quantity of solid reaction

product between zinc and SO₂. Metallographic examination of the dross could not detect the presence of any solid reaction particles. This suggested that the average particle size must have been in the order of 1 μ m (or less) and hence easily obscured by the soft lead-bismuth alloy during polishing. Based on the above theory, limited solubility of ZnS in the alloy system could result in mass transfer occurring at the particle-liquid interface. Very large mass transfer boundary layers relative to the tiny particles could explain the dramatic effect of such as small quantity of solid reation product.

7.3.2 Effect of Temperature on the Mass Transfer Boundary Layer

As discussed in Section 2.3.2, mass transfer in liquid metal systems will result in the creation of a mass transfer boundary layer, δ_c . The magnitude of the layer thickness will be determined by factors such as solute diffusivity, D_A , liquid phase viscosity, and the liquid metal velocity. In general, boundary layers in liquid metals are surprisingly large at low temperatures with minimal liquid velocities. Table 2.3 gives an interesting "order-of-magnitude" calculation for mass transfer boundary layer thickness for bismuth in lead (based on Equations 2.26 through 2.28) at 400°C assuming the growth of CaMg₂Bi₂ crystals. For crystals with an average diameter of 50 µm, and a low liquid velocity of 0.1 mm-sec⁻¹, the boundary layer thickness would be approximately 300 µm. Such a thickness is obviously much greater than the particle diameter, and will involve considerable overlap of boundary layers in the case of a refining crust comprising such crystals. It is interesting to note that the boundary layer thickness remains relatively constant (360 µm at 550°C) with increasing temperature. This is due to a balance of higher diffusivities but lower liquid viscosity in this narrow temperature region; both of which obey Arrenhius type relationships.

7.3.3 Mechanism of Reactive Particle Repulsion

For colloidal particles such as clays or mineral particles, the forces resulting in water retention are based on an osmotic pressure. The osmotic pressure increases as particles are drawn together by capillary forces. Eventually a balance of forces (osmotic and capillary) is reached which determines the final interparticle spacing. The forces are relatively easy to understand since the diffuse ion layer thickness remains constant with respect to the pore water salt concentration. In this sense, the system is at chemical equilibrium and does not involve mass transfer. The osmotic pressure balances the localized drop in solvent vapour pressure to preserve the overall equilibrium in terms of Gibbs energy. Since no mass transfer takes place, the system can be considered to be in thermodynamic equilibrium at all times.

The osmotic pressure analogy with respect to reactive solid particles in liquid metal is not so simple. However, it is a useful analogy in visualizing a possible mechanism to explain the observed particle bed swelling because it introduces the concept of a pressure term to counter capillary attraction. Since particle repulsion in colloidal systems involves the interaction of boundary layers (diffuse ion layer), it is not unreasonable to suggest that proximity of boundary layers in metal-particle systems could give rise to similar forces of repulsion; expressed as static pressures.

The key difference between the two systems is that one exists at chemical equilibrium, while the other is defined by non-equilibrium conditions. Similar to the boundary layer Gibbs energy minimization described by Aksay et al., one may picture the forces at work to be transient in nature, determined to a large extent by the maintenance of continued reaction. In much the same way as dynamic spreading of a reactive liquid on a solid surface will cease upon attainment of chemical equilibrium, it is reasoned that repulsion should persist only so long as reaction continues to maintain a mass flux. The completion of this reaction will be limited by rates of mass transfer in the system. Unfortunately, apart from nucleation and growth theory, the

literature does not provide much insight into such non-equilibrium systems, particularly reaction between liquid metals and solids.

Due to the lack of sufficient basic theory, it remains to speculate as to the exact mechanisms surrounding the observed reactive particle repulsion in liquid metal. However, based on the osmotic pressure analogy, it seems clear that a static pressure term must be introduced which balances the capillary forces which tend to compact the particle bed during infiltration or crystal growth.

Thus, for a system of particles which are separated by some distance, one can express a static pressure term in the liquid caused by surface energy (capillarity) as being equal to the capillary pressure when the bed has expanded to an effective pore radius, r_{eff} (as defined by Equation 5.4) including the potential energy term for the height of the liquid;

$$\Delta P_{c} = \frac{\gamma_{b}}{2r_{eff}} + \rho g h - \frac{2\gamma_{b}}{r_{eff}}$$
(7.11)

where, ΔP_c is the static pressure due to capillarity.

In a static system with no change in interparticle distance, one can consider a balance of pressures, such that;

$$\Delta P_c + \Delta P_s = \frac{\gamma_b}{2r_{eff}} + \rho g h - \frac{2\gamma_b}{r_{eff}} + \Delta P_s = 0 \qquad (7.12)$$

where, ΔP_{s} is the swelling pressure.

Since at a stable height of capillary rise one can say that the basic equation of capillarity is satisfied (that is $\rho gh=2\gamma_{\mu}/r_{eff}$), one can simplify the pressure for swelling as;

$$-\Delta P_{s} = \frac{Y_{b}}{2r_{eff}}$$
(7.13)

The difficulty for a dynamic system is defining the swelling pressure in terms of the mass transfer boundary layer. There is no precedent in the literature which gives insight into this dilemma. However, a tentative answer may lie in the work of Aksay et al., where they defined a localized minimization of Gibbs energy at the solid-liquid boundary in the case of non-equilibrium wetting. They argued that the energy minimization is local since mass transfer rates, to and from the boundary are finite. For wetting, Aksay describes a drop in γ_{d} and γ_{b} , due to the reduction in Gibbs energy. This idea may be used to consider the effect of a local reduction in Gibbs energy in terms of the molar vapour pressures in the liquid phase.

In defining a Gibbs energy change at constant temperature and volume, one can write;

$$d\overline{G} = VdP \tag{7.14}$$

and,

$$\int_{\overline{G'}}^{\overline{G}} \frac{d\overline{G}}{F} = RT \int_{P}^{P} \frac{1}{P} dP$$
(7.15)

According to the above expression, a spontaneous reduction in Gibbs energy can result in a lowering of the system pressure, P. This is similar to the osmotic pressure and could represent the "missing" term to offset capillary pressures.

The effect of particle proximity can be explained due to the localized nature of the chemical reaction. Since the Gibbs energy minimization is restricted to the mass transfer boundary layer, then overlap of these layers will allow the pore liquid to become part of the effective volume where reaction occurs. Therefore, this volume will have a reduced pressure compared with the bulk liquid metal below. In much the same way as overlapping diffuse ion layers reduce pore water vapour pressure, it can be said that the overall pressure of the liquid metal is reduced by non-equilibrium conditions.

Another way of expressing the effect of mass transfer boundary layer overlap is to consider the rate of Gibbs energy minimization. It is well understood that the existence of a mass transfer boundary layer implies that the overall system is tending towards a lower Gibbs energy state. The rate at which the system can attain equilibrium is governed by the rate of mass transfer through the boundary layer. Therefore one can define a rate of Gibbs energy minimization, dG/dt, which is at a maximum in a system without conflicting boundary layers. However, when particle proximity causes overlapping mass transfer boundary layer thickness. This will have the effect of reducing the overall rate of Gibbs energy minimization. In other words, the system attempts to maximize the rate at which it can minimize its overall Gibbs energy. A liquid flow term may be the ultimate effect of the system's attempt to shorten the mass transfer path length which can only be satisfied by the particles moving and remaining apart.

8. INDUSTRIAL APPLICATIONS

The purpose of the current study of metal entrainment in lead refining dross, was to develop an understanding of the physical variables controlling the degree of metal loss. Chapter 7 discusses in detail the findings of the work. However, some of the important conclusions can be summarized as follows;

<u>Non-Equilibrium Wetting</u> - plays a key role in metal entrainment. Reaction between solid particles and liquid metal gives strong wetting as expressed by the solid-liquid contact angle. Without wetting, capillary forces would not tend to retain metal in floating particle beds. The ability of the liquid metal to wet solid particles ensures entrainment of at least 50 vol.% metal. For non-wetting surfaces, the degree of entrainment can fall considerably.

<u>Crystal Size</u> - has a strong effect on the degree of metal entrainment. Experimental work confirms observations made in industry, that smaller crystal size, particularly below 100 μ m diameter, gives metal entrainment greater than the 50 vol.% predicted by random packing of particles.

Inter-Particle Repulsion - appears to exist in systems where crystal growth or dissolution (mass transfer) is taking place. The forces of repulsion are more significant as average particle size is reduced. The effect is most pronounced for crystals below 50-100 μ m, which matches the magnitude of mass transfer boundary layers for such systems.

<u>Particle Bed Depth</u> - will have a beneficial effect in reducing overall entrainment by increasing the forces (buoyancy) bringing particles together.

The above parameters can be manipulated, in certain situations, to reduce the overall entrainment of liquid metal. In this chapter, two examples of process modifications based on this fundamental knowledge, are presented. In each, metal entrainment has been reduced. It is presumed that these techniques could be applied to a range of other processes (or industries) where metal loss to a dross phase is undesirable.

8.1 Continuous Agitation During Debismuthising

The idea to continuously stir bismuth refining kettles during crystal precipitation to enhance the grade of bismuth in the crust is relatively simple, yet has never been practiced in industry. The concept was based on an attempt to increase average $CaMg_2Bi_2$ crystal diameter by "seeding" the molten bath with the first crystal nuclei to form. Based on the current experimental work, a modest increase in average diameter could have a significant effect on crust grade. Normal bismuth crusts have an average crystal diameter of 45 µm, which gives lead entrainment in the order of 90 vol.%. (around 4.5 wt.% Bi). It was estimated that an increase in diameter to 65-70 µm, could have the effect of reducing entrainment to only 70-80 vol.%, giving crust grades in the order of 10-15 wt.% Bi.

8.1.1 Experimental Procedure

Instead of testing the concept of continuous agitation on the laboratory scale, it was decided to proceed directly to the full-size production vessel; here a 230 tonne capacity kettle at the Brunswick Mining and Smelting Ltd., Belledune refinery (BMS-S). The key to pursuing the experiments lay in modifying the power supply for a kettle agitator to enable variable speed control. This was considered a necessary prerequisite since normal agitators operating at (one speed only) full speed, would create a sizable vortex in the molten lead, drawing in oxygen, and promoting the rapid oxidation of reagent metals such as calcium and magnesium. In order to minimize oxidation it was clear that the agitator would have to be reduced in speed such that crystals could be suspended in the bulk liquid with a minimum of vortex formation.

To accomplish the goal of reduced agitator speed, a Variable Frequency Controller was purchased and installed at BMS-S. The control for agitator speed resembles a domestic rheostat switch to dim lights in a home. Through plant scale trials it was found that a setting of 2.5 (out of a possible 10) gave a suitable agitator speed to keep a molten crust layer in suspension without vortex formation. The impeller shaft was found to turn at 72 rpm. It was recognized that the chosen agitator speed was only optimized relative to Brunswick's kettle and impeller design.

In total, three full-scale tests were undertaken under control conditions. Since that time, the practice of continuous agitation during debismuthising has been adopted at the Brunswick refinery as normal operating procedure due to the encouraging nature of the preliminary results. Therefore, despite the limited number of measured tests, a great deal of plant data has been used to help verify the study findings. In each plant test, a full 230 tonne charge of lead bullion was bailed into one of two debismuthising kettles. The temperature was measured, and a sample of bullion taken and quickly analyzed (by XRF techniques) to give an initial bismuth, calcium, and magnesium assay to determine the amount of calcium-magnesium alloy to add in order to reach the desired bismuth removal at 320°C. In all three tests the final target bismuth content was 15 ppm bismuth.

The reagent metal additions were made by over-head crane in the form of 15 kg ingots. Bath temperature was maintained above 480°C before reagent addition, to ensure easy dissolution of reagents and keep equilibrium conditions above supersaturation. Generally, the Ca-Mg alloy shattered due the thermal shock induced by addition to molten lead. The broken ingots were stirred into the hot lead at high agitation speed. The creation of a vortex (and the drawing of reagent metal into the vortex) was responsible for the rapid dissolution of the solid alloy into the molten lead. The lead temperature was found to increase approximately 10°C after dissolution due to the heats of solution of both calcium and magnesium. After complete solution of the reagent, the agitator speed was returned to the low value to keep any crust which had formed in solution. In two of the three runs, special care was taken to agitate the full kettle and raise

any remaining crystals of CaMg₂Bi₂ from the previous charge, thereby minimizing the population of crystal nuclei.

In the three experiments, one was allowed to cool simply by normal heat loss from the kettle (without burners), while the last two used cooling fans around the base of the kettle to increase convective heat loss from the kettle walls. In normal debismuthising practice, the cooling fans are employed to speed cooling, and increase productivity from the kettle.

Lead bullion samples were taken at various intervals during the cooling. The time and bath temperature were recorded for each sample. The slow speed agitation made sampling of bullion during cooling considerably more accurate than normal practice since the top layer of crust did not contaminate the sample spoon. The bullion samples were carefully cast into small discs and quickly solidified. The samples were "faced" by a lathe (removing several millimetres as discussed in Section 5.1.1) prior to assaying metal shavings by atomic absorption (AA) spectroscopy. The facing of the sample discs eliminated error due to entrained crystals which tended to float to the sample surface prior to solidification. XRF analysis of supersaturated bullion samples was found to give erroneous results due probably to the fine intermetallic crystals formed during sample cooling. The intermetallic phase evidently caused problems with the calibration of the XRF unit since the minor elements of interest were now present in a different matrix (intermetallic instead of lead).

The continuous agitation was stopped at 350°C. Since the impure lead bullion for each test contained approximately 4000-5000 ppm Bi, Figure 2.8 predicts that the majority of bismuth has been removed at this temperature. The agitator was removed by over-head crane, and a crust layer allowed to form. After 15-30 minutes, crust samples were taken from the kettle surface at various locations. The samples were combined into one composite sample for chemical analysis by AA.

8.1.2 Continuous Agitation Results and Discussion

As a general comment, slow speed continuous agitation during debismuthising was found to be a simple and easy technique to implement on the plant scale. The long cooling times allowed operators to set the initial agitator speed and ignore the process until 350°C. This was found to be an improvement over the semi-continuous skimming employed under normal operation. Furthermore, the crust which formed at 350°C was found to be dense, and easily skimmed in large slabs. Normal crusts, due to near continuous skimming at higher temperature, tend to remain very fluid and hence more labour intensive to skim.

Figure 8.1 presents analytical data for the three crusts compared to average crust assays as a function of skimming temperature. In all three instances a great improvement in crust grade was achieved. The grade continues improvement for Tests #1 through #3. This corresponds to a more rigorous attempt to dissolve any prior crystals in the lead bath before cooling. Figure 8.2 gives the time temperature profiles for the three tests compared to normal operation. It can be seen in Test #2 and especially Test #3, the bath temperature increase prior to cooling. For these two tests, kettle heating and agitation was employed as a crystal dissolution operation before calcium and magnesium additions. The data would suggest that initial crystal population is important in improving overall grade. Figure 8.2 also indicates that kettle cooling rates with agitation are considerably higher than normal cooling without agitation (fans only). From the point of view of refinery productivity, this is very encouraging. From the data it is estimated that a typical charge can be completed in 8 hours versus 12; a 50% increase in productivity.

A low initial crystal population giving higher grade crusts, agrees with the proposition that bath seeding, with a limited number of crystals, should result in the preferred growth of the crystals. This is provided that crystal growth rates are sufficiently high to prevent significant supersaturation (for a given cooling rate), favouring nucleation over growth. Micrographs of bismuth crust presented in Chapter 5 show well defined crystal interfaces indicating ionic bonding, but also crystal growth limited by mass transfer in the bulk solution, characteristic of

quiescent melts. Agitation will significantly increase liquid velocity, and therefore decrease the thickness of the mass transfer boundary layer. Under these conditions, crystal growth rates should increase since they are no longer as limited by diffusion in the bulk liquid. Figure 8.3 gives a comparison of momentum and mass transfer boundary layer thickness for various liquid velocities for the case of $CaMg_2Bi_2$ crystal growth from lead at 400°C. As in Table 2.3, crystal diameter is presumed to be approximately 50 µm and the flat crystal face model outlined in Equations (2.21), (2.27) and (2.28) are again used. Continuous agitation was estimated to give a liquid velocity in the range of 10-100 cm-sec⁻¹.



Figure 8.1 Bismuth Crust Grade vs. Skimming Temperature; historical data is compared to results obtained with continuous agitation.



Figure 8.2 Temperature Profile for Continuous Agitation During Debismuthising; data is compared to normal operation with fan cooling.



Figure 8.3 Momentum and Mass Transfer Boundary Layer Thickness for CaMg₂Bi₂ Crystal Growth from Lead at 400°C.



Figure 8.4 Optical Micrograph of Bismuth Crust Produced During Continuous Agitation; crystal interface shows irregular habit. (200 X)



Figure 8.5 Optical Micrograph of a Large Dendritic CaMg₂Bi₂ Intermetallic Crystal Produced During Agitation; crystal length approximately 1000 µm. (200 X)

Figures 8.4 and 8.5 present optical micrographs of CaMg₂Bi₂ crystals produced during continuous bath agitation. The crystal morphology is in direct contrast with the faceted crystal interfaces in Chapter 5. As discussed in Chapter 3, the reduction in mass transfer boundary layer thickness leads to the possibility of unstable growth interfaces since a protuberance at the solid-liquid interface could extend into areas of greater supersaturation, favouring localized growth. This type of crystal growth results in the classical dendritic structure observed in Figure 8.5. Figure 8.4 shows that the majority of crystals have the same diameter (approximately 50 μ m) as normal bismuth crusts. However, Figure 8.5 confirms that some crystals grow much larger than the average. From an understanding of the effect of crystal size on metal entrainment, it seems evident that improved crust grades are due to the favoured growth of certain crystals to very large sizes. Since many other factors affect metal entrainment (temperature, crust thickness, etc.) it is virtually impossible to quantify the effect of larger crystals. However, it can be said that the trend towards larger particles should favour higher grades. The effect of crystal habit (dendritic) on metal entrainment is unclear and would require further investigation.

Figure 8.6 compares measured liquid assays with equilibrium curves for Ca-Mg-Bi saturation of lead. Calcium, magnesium, and bismuth levels in lead were used to calculate the CaMg₂Bi₂ solubility product, k_{ap} , according to Equation (2.7). The k_{ap} values were plotted versus the bullion temperature. In each test, the offset of the cooling curve from the equilibrium saturation curve indicates the degree of supersaturation in the bath. Faster cooling conditions (Test #2 and Test #3) give greater supersaturation. Table 8.1 summarizes the supersaturation, expressed as a ΔT , as a function of average cooling rate of the bath.

Condition	Cooling Rate	Supersaturation
Namel Or	12.8	25
Normai Op.	12.8	
1est #1	15.7	8
Test #2	18.5	25
Test #3	16.9	15

Table 8.1 Continuous Agitation During Debismuthising - Supersaturation Data.



Figure 8.6 Solubility Product for Lead Bullion During Continuous Agitation Compared to the Equilibrium Curve.

It is interesting that while Test #2 has the highest supersaturation, Test #3 gave the highest grade crust. For continuous agitation, it would appear that the degree of supersaturation does not affect grade as much as the initial crystal population. However, one can predict that high supersaturation will eventually lead to greater nucleation driving force, with or without agitation. From Table 8.1, the high supersaturation for normal cooling (at relatively slow cooling rates) reflects the slow crystal growth mechanism imposed by a quiescent melt. Crystal growth rates, controlled by solute diffusivity in the bulk liquid, and indeed solute diffusion through the pore liquid of the crust under normal operation, will tend to favour more supercooling, and hence nucleation.

The data presented in Table 8.1 can be used to illustrate the probable mechanism of bismuth crust formation. Essentially, the bath will be supercooled to the point where intermetallic crystals nucleate (probably heterogeneously) and grow slowly, controlled by the rate of solute diffusion in a quiescent melt. As the crystals reach a critical diameter they will float to the top of the kettle and join the "wet" crust layer. Growth will continue in the crust but at slower rates due to the increased solute diffusion path length. The slow growth mechanism will allow substantial supercooling to be maintained, permitting additional crystals to be nucleated in the bulk liquid. In this manner, crusts with relatively small, and uniform crystals are formed. From an understanding of entrainment mechanisms, the characteristic small crystal size will ensure high metal entrainment in the refining crust.

8.2 Low Temperature Salt Treatment of Silver Crust

Silver crust is currently treated in many industrial operations by a high temperature liquation process. The process is briefly described in Chapter 2. A molten chloride salt (NaCl-CaCl₂) or more recently, borax (Na₂O:2B₂O₃) is used to provide an oxygen transfer barrier while silver crust is heated to $750^{\circ}C^{(7)}$. At this temperature the intermetallic phase melts and forms an

immiscible metal layer floating on lead. The resulting triple alloy (Ag-Zn-Pb) is tapped and further treated to recover silver.

As mentioned above, the action of the molten salt is presumed to be one of a barrier to rapid oxidation, and to some extent a "flux" to absorb any oxide particles which would tend to form a "dry" dross. However, sessile drop tests conducted in this study showed aggressive wetting of Ag-Zn intermetallic phases by molten chloride salts. The wetting was attributed to reaction at the solid-liquid interface (non-equilibrium wetting) and the inherently low surface energy of molten chloride salts; see Table 3.2. It was decided to exploit the tendency for chloride salts to preferentially wet Ag-Zn intermetallic particles as a means of reducing metal entrainment in crusts <u>in situ</u>, avoiding the costs of a dedicated, high temperature, liquation vessel. The study was undertaken through laboratory scale experiments.

8.2.1 Process Concept

The preferential wetting of intermetallic particles by a second phase should have the effect of eliminating the strong forces entraining metallic lead. From a process point of view it is critical that the "fluxing" medium should have two important qualities;

- <u>Reactivity</u> with respect to the three metals should be minimized in order to maintain recovery.
- Melting Point should be low enough to make processing in the primary desilverising kettle feasible; 420-450°C.

The prevention of significant reaction between the wetting phase and silver, zinc, or lead requires the use of reactive metal chlorides. While many common systems exist which would not react (such as NaCl-CaCl₂ eutectic) with the metals, it was difficult to identify an appropriate system with a sufficiently low melting point. Eventually it was decided that the eutectic KCl-ZnCl₂ offered the best compromise between chemical properties and cost. The ZnCl₂ component offered the additional benefit of some limited reaction with zinc in the intermetallic. Based on Aksay's work, mass transfer will improve wetting by reducing the solid-liquid interfacial energy, $\gamma_{al}^{(42)}$. Figure 8.8 shows the binary phase diagram for the potassium chloride-zinc chloride system.



Figure 8.8 Binary Phase Diagram for the System KCl-ZnCl₂⁽⁷⁵⁾.

The process concept was to introduce some salt to the primary desilverising kettle after formation of the silver crust, but prior to skimming. It was envisioned that a rake type apparatus, attached to an standard agitator shaft, could be used to provide intimate mixing of the salt phase with the metal crust. The wetting action of the salt would free a large portion of the entrained lead, which could then drain back into the lead phase. A salty crust could then be skimmed and further processed for silver recovery. Figure 8.9 illustrates the basic process.



Figure 8.9 Schematic Diagram of Low Temperature Crust Treatment on the Industrial Scale; primary desilverising kettle with rake attachment on agitator shaft.

8.2.2 Experimental Procedure

Samples of silver crust were obtained from the primary desilverising kettle at Brunswick Mining and Smelting Corp. Ltd. The silver crust starting assay was determined by taking a composites sample of the material prior to testing. Several composite samples gave an average assay of 4.25% Ag and 10.49% Zn.

Approximate 1.5 kg charges of silver crust were placed in a 316 stainless steel crucible having an internal diameter of 12 cm and a height of 15 cm. The vessel was placed in a circular furnace heated by means of Kanthal electric resistance elements. Temperature was measured by a stainless steel sheathed, chromel-alumel (type K) thermocouple placed in the crust charge. Test conditions were maintained at 400 and 500°C using a Omega Engineering CN-9000 programmable temperature controller. Control was maintained at $\pm 1°$ C.

Once crust had attained the desired test temperature, reagent grade KCl and anhydrous $ZnCl_2$ were added. Salt levels of 5, 10, and 20 wt% of crust were investigated. A fixed salt mixture of 40 wt.% KCl and 60 wt.% $ZnCl_2$ was used in all tests. Agitation of the system was provided by a six-bladed, 45° pitch impeller with a rake-like attachment on the shaft as illustrated in Figure 8.10. The system was agitated at 20 rpm for one hour. Some fuming of $ZnCl_2$ was noted, particulary at 500°C.



Figure 8.10 Schematic Diagram of Laboratory Apparatus Used to Test Low Temperature Crust Treatment.

After one hour of reaction time the agitator was removed from the mixture. The salty-crust was skimmed from the metal surface by means of a perforated stainless steel spoon. The resulting liquid lead phase (free of crust or dross) was cast from the crucible into small moulds. Both product phases were weighed after cooling. It was particularly important to weigh the crust phase containing chloride salts since the $ZnCl_2$ proved to be hygroscopic, quickly absorbing moisture from the atmosphere.

The product phases were sampled and assayed to determine the recovery of lead, zinc, and silver. Bullion samples were taken from the bottom and top of the cast metal to investigate the possibility of some entrained Zn-Ag crystals. Metal samples were taken by collecting drill shavings. Sampling method, and subsequent analysis of digested metal by atomic absorption spectroscopy, were considered to be reliable and accurate. The salty-crust proved to be a much more difficult phase to sample and assay reliably. Chlorine was found to interfere with normal silver digestion techniques while the inhomogeneous nature of the crust made sampling difficult. Eventually, silver, zinc, and lead deportment to the crust phase was determined by difference since charge masses, and those collected in the bullion phase were well known and trusted. Low vapour pressures of silver and lead gave credibility to the technique of mass balance by difference.

8.2.3 Low Temperature Salt Liquation Results and Discussion

The use of at least 10 wt.% of crust, KCl-ZnCl₂ eutectic mixture, was found to give excellent removal of lead from silver crust without losing significant quantities of silver and zinc to the bullion phase below. Recovery of lead to bullion improved with more salt and higher temperatures. However, sufficient recovery of lead from crust was found at 400°C, to make treatment in the primary kettle (420-450°C) a workable concept.

Figures 8.11 and 8.12 show the elemental recovery of lead and silver from the crust treated with various quantities of salt at both 400 and 500°C. From the data, it would appear that better liberation of lead from the system of intermetallic crystals, is achieved with greater amounts of molten salt. Since the salt is presumed to preferentially wet the crystals, it is presumed that a minimum volume is required to completely wet the high surface area of the crystals. Based on a density of approximately 1.8 g-cm³ for the molten salt, and a density of 8.26 g-cm⁻³ for ϵ -phase

crystals, and assuming a maximum packing of 50 vol.% solids, one would require at least 18 wt.% salt (relative to the intermetallic crystal mass) to form a continuous liquid phase.

The silver crust used in the tests contained approximately 14 wt.% crystals; %Ag+%Zn. If one assumes that 100% of the molten lead was rejected during mixing with the molten salt, the volume fraction of intermetallic crystals and molten salt can be calculated. At salt additions of 5, 10, and 20 initial crust wt.%, the give volume fractions of molten salt have been calculated as 62.1, 76.6, and 86.8 vol.% respectively. Clearly the salt additions used were more than enough to wet the entire particle bed in such a way as to replace all the lead as a continuous matrix. However, the data shows that a large excess was required to achieve near complete liberation. It could be that similar expansionary forces are experienced in the case of a continuous salt phase thereby requiring liquid volume fractions in the order of 70-80 vol.%.



Figure 8.11 Recovery of Lead to the Bullion Phase at Various ZnCl₂-KCl Salt Addition Levels.


Figure 8.12 Recovery of Silver to the Bullion Phase for Low Temperature Salt Treatment of Silver Crust.

The unavoidable recovery of some silver to the separated bullion phase is not high enough to cause an undue silver recycle in an industrial application. From Figure 8.12, the silver recovery appears to be more a function of temperature than amount of salt used. This follows based on the increased solubility of Ag-Zn in lead bullion at higher temperatures.

The low temperature molten salt separation of Ag-Zn crystals from a lead matrix once again illustrates the critical role of surface interactions in intermetallic dross systems. Strong surface wetting, aided by mass transfer in non-equilibrium systems, prevent the easy removal of liquid metal from the crystals. However, a second phase, exhibiting a greater potential to wet the solid crystals (such as a reactive salt) will be able to intervene between the solid and liquid metal, thereby allowing separation. In much the same way as oxygen appears to allow lead to drain from industrial silver crusts, phases such as molten salts can act as surface active agents to influence the forces causing entrainment.

The simple laboratory scale tests investigating silver crust liquation can serve as the basis for a new industrial process to treat silver skimmings in the lead industry. Figure 8.13 gives a tentative flowsheet based on the results. Essentially, salt can be added to the primary desilverising kettle to effect near 90% removal of liquid lead from the Ag-Zn crystals. The salty-dross can be skimmed from the kettle into a crust treatment vessel (a steel kettle). Additional chlorine can be added to the system in the form of ammonium chloride (NH_4Cl) or chlorine gas. This additional chlorine will react with the zinc in the intermetallic particles according to the following;

$$AgZn_{1} + 3Cl_{2}(g) \neq Ag + 3ZnCl_{2}$$

$$(8.1)$$

The metallic silver will combine with lead carryover (or lead added deliberately to collect silver), and form a very high grade lead-silver alloy for subsequent upgrading. The high ZnCl₂ salt thus

formed, could be returned to the primary kettle for re-use while some could be bled from the system to maintain the overall KCl-ZnCl₂ balance. The salt bleed could be treated in a lead blast furnace or similar vessel to avoid stockpiling an environmentally sensitive by-product. Naturally, the economic viability of such a process would depend on the price of zinc since reagent zinc is not regenerated in this process, and the ability of a smelter to work with chlorine and its salts.



Figure 8.13 Schematic Diagram of an Industrial Process Using Low Temperature Salt Treatment During Primary Desilverising.

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9. CONCLUSIONS AND RECOMMENDATIONS

9.1 Findings and Conclusions

 Silver and bismuth refining drosses produced at Noranda's, Brunswick Lead Smelter, have been characterized in terms of intermetallic phase, average particle size, and degree of metal entrainment.

Silver Crust - is composed mostly of the ϵ -phase (AgZn₃) with average particle size approximately 50 µm. Liquid lead entrainment is in the order of 80 volume percent.

Bismuth Crust - is composed entirely of $CaMg_2Bi_2$ crystals exhibiting a regular crystal habit and average diameter of 45 µm. Lead entrainment is approximately 90 volume percent.

- 2. A simple capillary model of metal entrainment in silver and bismuth crust was developed and compared to data collected from industrial silver and bismuth crusts. Overall the model was found to be inadequate. According to this model, capillary forces will tend to reduce the observed metal entrainment by seeking random packing of solid dross particles at approximately 50 volume percent. Observations to the contrary cannot be explained by slow rates of liquid metal drainage under the applied capillary pressure. Calculations of liquid metal velocities in dross pores suggest that in reality rates of liquid flow are high enough to permit the attainment of an equilibrium configuration of solid particles in a matter of seconds. This does not agree with intermetallic dross samples where hours of possible drainage time do not produce a significant decrease in metal entrainment.
- 3. Sessile drop experiments in the lead-silver-zinc system revealed that liquid lead wets silver-zinc intermetallic substrates; γ and ϵ -phases. Reaction between the solid substrate

and the liquid lead was found to produce conditions of reactive spreading due to a localized reduction in the solid-liquid interfacial energy, γ_{al} . Liquid spreading occurred during the mass transfer process, allowing liquid lead to cover the entire solid substrates at an effective solid-liquid contact angle, θ_{al} , of zero degrees. Eventual attainment of chemical equilibrium (no concentration gradient) resulted in an increased solid-liquid interfacial energy, and the establishment of an equilibrium solid-liquid contact angle. Liquid metal was found to retract to the equilibrium configuration after spreading.

- 4. Infiltration of γ -phase (Ag₅Zn₈) particles by liquid lead was found to obey the form of a capillary rise prediction where the height of liquid rise increased with decreasing particle spacing. The liquid was found to resist attaining the full height predicted due to swelling of the particle bed during infiltration. The swelling effect increased with decreasing average particle size.
- 5. It was concluded that experimental infiltration data could be used to develop an expression predicting height of metal rise in intermetallic particle beds. Data from image analysis of infiltrated particle beds gave a constant increase in interparticle spacing of 50 µm. The constant increase in effective pore radius allowed the development of a simple capillary model with the following form;

$$h = \frac{2\gamma_b \cos\theta}{\rho g(r_{eff} r_f)} - H$$

 It was concluded that the constant increase in interparticle spacing was due to a swelling pressure term which is equal and opposite to the capillary pressure which tends to force particles to random packing;

$$\Delta P_s = \frac{\gamma_b}{2r_{eff}}$$

- 7. It was concluded that the observed swelling is caused by mass transfer at the solid-liquid interface of the intermetallic crystals giving a reduced static pressure due to a localized minimization of Gibbs energy. The static pressure change (swelling pressure) has been attributed to an overlap of mass transfer boundary layers where the mid-point static liquid metal pressure is less than the pressure in the bulk liquid. For systems with low liquid metal velocities, mass transfer boundary layers have been estimated in the order of 100 µm. This magnitude of boundary layer matches the observed constant increase in interparticle spacing.
- 8. Two new processes have been tested to reduce liquid lead loss in intermetallic dross:
 - Continuous Agitation During Debismuthising has been tested on the full-scale at Brunswick Mining and Smelting. Agitation of the metal bath during cooling promotes CaMg₂Bi₂ crystal growth. The larger crystal diameters render the effect of mass transfer boundary layer overlap less significant, and hence reduce the volume fraction of entrained lead.
 - 2) Molten Salt Liquation of silver crust has been tested in the laboratory. Limited reaction between Ag-Zn intermetallic particles and a molten KCl-ZnCl₂ salt permits preferential wetting of the crystals by the salt phase. Once wet by salt, the system of solid particles can no longer retain liquid lead by capillary forces. Results show over 90% removal of lead from industrial silver crusts after mixing with the molten salt.

9.2 Recommendations for Future Work

The theory developed in this work relates mass transfer between a solid-particle and liquid metal as the main force causing metal entrainment beyond that expected for random packing of solid particles. The example of lead refining was used. It seems reasonable to extend the experiments to other related systems such as iron-zinc intermetallic particles in zinc baths, or iron-zinc particles in liquid aluminum, to determine if the same relationships can be observed. This would provide substantial confirmation of the model.

Experimental techniques prevented the evaluation of intermetallic particle infiltration with very small diameters relative to the mass transfer boundary layer (particles less than 50 μ m). However, other experimental work at the Noranda Technology Centre has suggested that reactive particles in lead with diameters as low as 1 μ m can cause massive metal entrainment in the order of 99.5 volume percent. It would be valuable (in terms of model validation as well as industrial metallurgical practice) to extend experiments to very small particles in order to follow-up the trends observed in the current study.

The two processes developed to reduce lead entrainment in bismuth and silver crusts were not tested and developed rigorously. Further work should be undertaken to fully evaluate the technical and economic implications of these activities. As a note, the continuous agitation of bismuth crusts has been adopted on the industrial scale. Future work should be directed towards a patent application.

CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

Mass transfer at the solid-liquid interface has been identified as the mechanism behind the high degree of lead entrainment in silver and bismuth crusts produced during the pyror retal urgical refining of lead. Reaction at the interface has been linked to a static pressure term in the liquid metal resulting from the overlap of mass transfer boundary layers. The static pressure prevents the intermetallic particles from attaining random packing densities. The effect is most pronounced for systems of particles whose average diameter approaches the thickness of the mass transfer boundary layer.

The theory advanced in this thesis can be extended to other metal-dross systems where mass transfer between the solid and liquid occurs. This is particularly true for systems where intermetallic particles have precipitated from the liquid metal.

The thesis goals are unique since this is the first time liquid metal entrainment in dross phases comprising intermetallic particles has been studied in detail. This is particularly true for silver and bismuth crusts produced during pyrometallurgical lead refining. The theory, experimental techniques, and industrial processes which have emerged are new to this area of metallurgy.

The characterization of silver and bismuth crusts with respect to intermetallic phase, crystal morphology, and degree of metal entrainment has never been attempted in the literature. Results show that a simple capillary model of metal entrainment does not adequately explain the high degree of liquid metal entrainment.

The role of mass transfer in defining the nature of the solid-liquid contact angle for molten lead and Ag-Zn intermetallic crystals is novel. Theoretical predictions of dynamic liquid spreading, caused by a transient decrease in the solid-liquid interfacial energy, were confirmed. The observation that all intermetallic drosses experience non-equilibrium wetting since they exist in supersaturated solutions, helps resolve the issue of whether the solids are well wet by liquid metal.

The experimental results showing swelling of Ag-Zn intermetallic particles infiltrated with liquid lead have allowed the development of a new understanding of metal entrainment. A constant increase in interparticle distance appears to be caused by an overlap of mass transfer boundary layers surrounding each particle. A novel mechanism has been proposed where localized minimization in Gibbs energy, due to a mass flux, can give rise to a local static pressure drop in the liquid phase. The pressure drop is responsible for the repulsion between particles, and the increase in interparticle distance. The effect becomes extreme when average particle diameters are small enough to begin approaching the thickness of the mass transfer boundary layer. For silver and bismuth crusts, swelling is evident at particle diameters less than 100µm since repulsive forces are able to expand interparticle distances by approximately 50µm.

Two unique processes have been proposed to reduce metal loss in intermetallic crusts based on the new fundamental understanding. For bismuth crusts, constant slow speed agitation during the cooling will promote intermetallic crystal growth by seeding the melt. The degree of swelling is less pronounced for larger particles, and hence metal entrainment is reduced. Silver crust metal entrainment has been dramatically reduced by employing a molten salt phase to preferentially wet the intermetallic crystals. This allows lead metal to drain from the particle bed since capillary forces are no longer at work. A step has been proposed which recovers the silver from the intermetallic crystal-salt mixture, while allowing the salt to be re-used in the process.

REFERENCES

- 1. S. Lavoie, G. Dubé, "A Salt-Free Treatment of Aluminum Dross Using Plasma Heating", Journal of Metals, Feb. 1991, pp. 54-55.
- K.B. Chaudhuri, G. Melcher, " How Kivcet Lead Smelting Compares With Other Direct Reduction Processes for Lead", European Mining Journal, April 1978, pp. 88-91.
- 3. E. Muller, "How KIVCET CS Shaft Furnace Simultaneously Smelts Pb-Zn", World Mining, April 1977, pp. 46-50.
- 4. M. Schmidt, P. Fischer, "The First Commercial-Scale QSL Plant; Results of the Commissioning", Proc. TMS Sym. Lead-Zinc 90, Ed. T.S. Mackey, R.D. Prengamon, Feb. 1990, pg. 885.
- 5. S. Jananshahi, R.L. Player, "Process Chemistry Studies of the Isasmelt Lead Reduction Process", Aus. IMM Non-ferrous Smelting Sym., Port Pirie, September 1989, pp. 33-39.
- 6. J.G. Palmer, "Battery Recycling A Solution in Peril", Proc. CIM Sym., Primary and Secondary Lead Processing, Ed. M.L. Jaeck, Pergamon Press, August 1989, pp. 113-118.
- 7. W. Hofmann, <u>Lead and Lead Alloys</u>. Eng. Trans. of 2nd Ed., Springer-Verlag, Berlin: 1970.
- 8. J.D. Esdaile, G.W. Walters, "Lead Purification by Crystallization and Reflux", Australian I.M.M. Conf. Proc., South Australia, June 1975.
- 9. J.D. Esdaile, G.W. Walters, "Tin Refining by Crystallization and Reflux", Australian I.M.M. Conf. Proc., South Australia, 1975.
- 10. H.E. Hirsch, "The Recovery of Metallic Arsenic in Cominco's Lead Operations", Proc. TMS AIME Sym. Lead-Zinc-Tin 80, Ed. J.M. Cigan, T.S. Mackey, T.J. O'Keffe, 1980, pp. 360-372.
- 11. T.R.A. Davey, "The Physical Chemistry of Lead Refining", Proc. TMS AIME Sym. Lead-Zinc-Tin 80, Ed. J.M. Cigan, T.S. Mackey, T.J. O'Keffe, 1980, pp. 477-507.
- 12. T.R.A Davey, "The Physio-Chemical Principles of Refining Metals", International Symposium on Fifty Years in Metallurgy, Banaras Hindu University, Varanasi, Dec. 1973, pp. 29-50.

- 13. R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, K.K. Kelly, <u>Selected Values of</u> <u>Thermodynamic Properties of Metals and Alloys</u>. ASM, Ohio: 1973.
- 14. T.R.A. Davey, "Desilverising of Lead Bullion", Trans. AIME, 200 (1954), pp. 838-848.
- 15. T.R.A. Davey, B. Bied-Charreton, "The Davey Desilverising Process at Penaroya's Noyelles-Godault Lead Refinery", TMS Paper # A83-17, 1982.
- 16. K.R. Barrett, R.P. Knight, "Improvements in Silver Recovery From Lead at Britannia Refined Metals, Ltd., England", British IMM Conf., 1989, pp. 307-316.
- 17. T.R.A. Davey, "Desilverising and Debismuthising of Lead", Erzmetall, <u>10</u> (1957), pp. 53-60.
- Z. Wang, <u>Metal Vapour Condensation at Reduced Pressures</u>. M.Eng. Thesis, McGill University, 1990.
- 19. P.J. Hancock, Z. Wang, P.G. Evans, R. Harris, "Vacuum Dezincing of Silver Crusts", Canadian Metallurgical Quarterly, Vol. 30, No. 1, 1991, pp. 7-14.
- 20. <u>Intermetallic Compounds</u>. Ed. J.H. Westbrook, John Wiley and Sons, New York: 1967.
- 21. International Centre for Diffraction Data; Powder Diffraction File. Pub. by JCPDS; 1992.
- 22. M Hansen. <u>Constitution of Binary Alloys</u>. McGraw-Hill Book Company, Inc., New York: 1958.
- 23. B.D. Cullity. <u>Elements of X-Ray Diffraction</u>. 2nd Edition, Addison-Wesley Publishing Co., Inc., Don Mills: 1978.
- 24. T. Banytis, P.G. Wiltshire, "Refining Developments at BHAS, Port Pirie", Australian I.M.M., Port Pirie Conf., 1990, pp. 88-93.
- 25. V.F. Leferrer, "Vacuum Dezincing of Parkes Crust", Journal of Metals, Trans. AIME, November 1957, pp. 879-883.
- J.E. Casteras, C. DiMartini, "Method of Treating Debismuthising Dross to Recover Bismuth", Proc. TMS AIME Sym. Lead-Zinc-Tin 80, Ed. J.M. Cigan, T.S. Mackey, T.J. O'Keefe, 1980, pp. 348-359.
- 27. D.R. Blaskett, D. Boxall, Lead and Its Alloys. Ellis Horwood Ltd., London: 1990.

- 28. P. Hancock, R. Harris, "Solubility of Calcium-Magnesium-Bismuth Intermetallic in Molten Lead", Canadian Metallurgical Quarterly, Vol. 30, No. 4, pp. 275-276.
- 29. A.J. Spring-Thorpe, B.R. Pamplin, Journal of Crystal Growth, 3, 4, 1968.
- 30. <u>The Growth of Crystals From The Melt</u>. Ed. E.P. Wohlfarth, John Wiley and Sons Inc., New York: 1965.
- 31. A. VanHook, <u>Crystallization Theory and Practice</u>. Reinhold Publishing Corp., New York: 1961.
- 32. R.F. Strickland-Constable. <u>Kinetics and Mechanism of Crystallization</u>. Academic Press Inc., London: 1968.
- 33. A.W. Verre. <u>Crystal Growth: Principles and Progress</u>. Plenum Press, New York: 1987.
- 34. A.G. Walton. <u>The Formation and Properties of Precipitates</u>. Interscience Publishers, New York: 1967.
- 35. D. Elwell, H.J. Scheel, <u>Crystal Growth from High Temperature Solutions</u>. Academic Press Inc., London: 1975.
- 36. G.H. Geiger, D.R. Poirier. <u>Transport Phenomena in Metallurgy</u>. Addison-Wesley Series in Metallurgy and Materials, Addison-Wesley Publishing Company, Don Mills: 1973.
- 37. R.B. Bird, W.E. Stewart, E.N. Lightfoot. <u>Transport Phenomena</u>. John Wiley and Sons Inc., New York: 1960.
- A.W. Adamson. <u>Physicl Chemistry of Surfaces</u>. 5th Ed., John Wiley and Sons, Inc., New York: 1990.
- 39. T. Young, Phil. Trans. Royal Society London, 95 65, 1805.
- 40. J.J. Bikerman. <u>Surface Chemistry</u>. Academic Press Inc., New York: 1958.
- 41. R.E. Johnson, "Conflicts Between Gibbsian Thermodynamics and Recent Treatments of Interfacial Energies in Solid-Liquid-Vapour Systems", Journal of Physical Chemistry, 63, Oct. 1959, pp. 1655-1658.
- 42. I.A. Aksay, C.E. Hoge, J.A. Pask, "Wetting Under Equilibrium and Nonequilibrium Conditions", Journal of Physical Chemistry, Vol. 78, No. 12, 1974.
- 43. J.A. Pask, R.M. Fulrath, "Fundamentals of Glass-to-Metal Bonding: VIII, Nature of Wetting and Adherence", Journal of the American Ceramic Soc., Vol. 45, 1962, pp.

592-596.

~

- 44. J.D. McDermid. <u>A Thermodynamic Approach to Brazing Silicon Carbide</u>. Ph.D. Thesis, McGill University, 1992.
- 45. <u>Handbook of Chemistry and Physics</u>. 64th Edition, Ed. R.C. Weast, The Chemical Rubber Co. Press Inc., 1983.
- 46. K.S. Yeum, R. Speiser, D.R. Poirier, "Estimation of the Surface Tensions of Binary Liquid Alloys", Metallurgical Transactions B, Vol **20B**, No. 10, pp. 693-703.
- 47. H.R. Thresh, D.W.G. White, J.O. Edwards, J.W. Meier, "Properties of Molten Zinc and Zinc Alloys Part III; Surface Tension", Canadian Dept. of Mines and Technical Surveys; Mines Branch, Report No. PM-R-64-28, Oct. 1964.
- 48. J.M. Blakeley. Introduction to the Properties of Crystal Surfaces. Pergamon Press Ltd., London: 1973.
- 49. <u>The Surface Chemistry of Metals and Semiconductors</u>. The Electrochemical Soc., Ed. H.C. Gatos, John Wiley and Sons, Inc., New York: 1960.
- 50. H.A. Barnes, J.F. Hutton, K. Walters. <u>An Introduction to Rheology</u>. Elsevier Science Publishers B.V., Amsterdam: 1989.
- 51. J.M. Dealy, K.F. Wissburn, "Melt Rheology and its Role in Plastics Processing: Theory and Applications. Van Nostrand Reinhold. New York: 1990.
- 52. R.N. Yong, B.P. Warkentin. <u>Introduction to Soil Behaviour</u>. MacMillan Series in Civil Engineering; G.E. Nordby Ed., Collier-MacMillan Canada, Ltd., Toronto: 1966.
- 53. B.H. Mahan. <u>University Chemistry</u>. Addison-Wesley Publishing Company, Manila: 1975.
- 54. B.P. Warkentin, R.K. Schofield, "Swelling Pressure of Na-Montmorillonite in NaCl Solutions", Journal of Soil Science, Vol. 13, 1962, pg. 98.
- 55. C.C. Mwaba, <u>The Influence of Surface Phenomena on the Filtration and Dewatering</u> of <u>Mineral Suspensions</u>. Ph.D. Thesis, University of London (1987).
- 56. C.C. Mwaba, "Surfactant-Enhanced Dewatering of Graphite and Hematite Suspensions", Minerals Engineering, Vol. 4, No. 1, pp. 49-62, 1991.
- 57. S.K. Nicol, "The Effect of Surfactants on the Dewatering of Fine Coal", Proc. of the Australian IMM., 260, pp. 37-44, (1976).

- 58. H.B. Gala, S.H. Chiang, W.W. Wen, "Surfactant Enhanced Dewatering of Fine Coal", Proceedings of the Third World Filtration Congress, The Filtration Society, London, pp. 754-761 (1982).
- 59. A.F. Baker, "Hot Surfactant Solution as A Dewatering Aid During Filtration", Proc. of the 2nd Symposium on Coal Preparation, Louiseville USA, 1976, pp. 175-186.
- 60. J. Versluys, "Die Kapillaritat der Boden", Internat. Mitt. Bodenk., 7, 1917, pp. 117-140.
- 61. C.G. Goetzel, A.J. Shaler, "Mechanism of Infiltration of Porous Powder-Metallurgy Parts", Journal of Metals, Vol. 16, No. 11, Nov. 1964, pp. 901-905.
- 62. K.A. Semlak, F.N. Rhines, "The Rate of Infiltration of Metals", Trans, Met. Soc. AIME, vol. 212, June 1958, pp. 325-331.
- 63. S. Banerjee, R. Oberacker, C.G. Goetzel, "Mechanism of Capillary Induced Infiltration of Iron Skeletons with Cast Iron", American Powder Metallurgy Institute, Vol. 20, No. 4, pp. 325-341.
- 64. L.R. White, "Capillary Rise in Powders", J. of Colloid and Interface Science, Vol. 90, No. 2, Dec. 1982, pp.534-538.
- 65. E. W. Washburn, "The Dynamics of Capillary Flow", Phys. Review, Vol. 17, 1921, pp. 273-283..
- 66. J. Frydrych, J. Lezanski, W. Rutowski, "An Experimental Study Concerning Some Effects Occurring During Skeleton Infiltration with Liquid Metals", Modern Developments in Powder Metallurgy, Vol. 3, 1966, pp. 69-79.
- 67. J.R. Ligenza, R.B. Bernstein, "The Rate of Rise of Liquids in Fine Vertical Capillaries", Journal of the American Chemical Society, Vol. 73, 1951, pp. 4636-4638.
- 68. C. Toy, W.D. Scott, "Ceramic-Metal Composite Produced by Melt Infiltration", Journal of American Ceramic Soc., Vol. 73, No. 1, 1990, pp. 97- 101.
- 69. Daniel Muscat. <u>Titanium Carbide/Aluminum Composites by Melt Infiltration</u>. Ph.D. Thesis, McGill University, May 1993.
- A.A. Kurilko, G.A. Kurshev, V.A. Rudyuk, Y.V. Naidich, "Kinetic Laws of Infiltration of Porous Ti by Pb and In Melts", Poroshk. Metall. (Eng. Trans.), Vol 9, 261, 1984, pp. 35-38.

- 71. <u>Chemical Engineer's Handbook</u>. 5th Edition, Ed. R.H. Perry, C.H. Chilton, McGraw-Hill Book Co. Inc., New York: 1973.
- 72. T. Lebeau, <u>Wetting of Alumina Based Ceramics by Aluminum Alloys</u>, McGill University, M.Sc. Thesis, 1993.
- 73. O. Kubaschewski, C.B. Alcock, P.J. Spencer, <u>Materials Thermochemistry</u>. 6th Edition, Pergainon Press Ltd., New York: 1993.
- 74. R. Li, "Reaction Rates Between SO₂(g) and Liquid Metals", internal memorandum, Noranda Technology Centre, December 29, 1993.
- 75. <u>Phase Diagrams for Ceramists</u>. Ed. M.K. Reser, The American Ceramic Society, Columbus, Ohio: 1964.

APPENDIX I

Typical output from an X-Ray Diffraction (XRD) pattern data search conducted at the Noranda Technology Centre. This data was compared to measured diffraction angle data for principle phase determination of silver crust samples and intermetallic phases synthesized in the laboratory. A typical diffraction pattern showing a strong peak for Ag_3Zn_8 is given in Figure A1.1.

29-1155	JCPOS-ICO	DD Copyright (c) 1990	Qua.	litv: C				
AgZn						A D	i Int.	n k l
۰ ۰ ۰۰ ۲						1 3 156		100
Silver Zinc				*******		2.251 1.222 1.5779	100	
Rad: ÇuKal Çutoff: Ref: See comm	Lambda: 1 Int: Calc lents box for	1.54050 Filt culated I/Ic r primary powder patt	er: or: 21.00 ern reference	d-9	sp: Calculated	1.2003 1.1157 0.9979	1 22 1 22 1 6 1 9	$ \begin{array}{c} 2 & 1 & 1 \\ 2 & 2 & 9 \\ 3 & 1 & 0 \end{array} $
Sys: Cubic a: 3.150 A: Ref: Ibid.	b: 8:	S.G.: Pm3m (221) c: C:	A: Z:	1	C: mp:	·' 0,8434 ! ! !	15 	321 1 1
0x: 9.152	Om:	SS/FON: F9=74(.00	9.13)				1	1 L
ea: Ref:	nw8:	ey:	Sign:	24:			1 1	1
Peak height i pattern refer Grant-in-Aid Metall., 10 9	intensities. rence: Techn Report, (19 935 (1962).	CsCl type. PSC: cP isch Physische Dienst 76). Additional unit Mwt: 173.25. Volume	2. To replac , Delft, Nett cell referen [CD]: 31.43.	e 8-222 Nerlands Nce: Grr	. Primary , JCPDS , Rovel, Acta			
						1 i	 •	

Data	for	β-phase	AgZn.

Strong lines: 2.23/X 1.29/2 1.58/1 0.84/2 1.00/1 3.16/1 1.12/1 1.82/1

-1156 JCPDS-ICO	O Copyright (c) 1990	Quality:	<u>c</u>			. Int.	h- k- l
AgZn Silver Zinc					3.818 2.820 2.594		
Rad: CuKal Lambda: 1 Cutoff: Int: Calc Ref: See comments box for	.54050 Filter: ulated I/Icor: primary powder pattern	d reference.	-sp: Calcula	ted I	2.268 2.204 2.146 1.8704	12 100 96 20 11	2 1 0 1 1 1 3 0 0 2 0 1 2 1 1
Sys: Hexagonal a: 7.635 b: A: B: Ref: Ibid. Dx: 9.093 D m :	S.G.: P-3 (147) c: 2.820 C: SS/FOM: F28=243(.003	A: Z: 4.5	C: .3694 mp:	 	1.8340 1.7366 1.5808 1.5374 1.5170 1.4261	1 1 21 1 21 1 2 1 1 1 1	3 1 0 3 0 1 2 2 1 3 1 1 3 2 0 4 0 1
ea: nw8: Ref: Peak height intensities.	ey: Ag3Zn type, PSC: hP9,	Sign: 2V: To replace 7-3	72. Primary		1.4100 1.3790 1.3360 1.3227 1.2970	4 1 10 2 1	0 0 2 1 0 2 3 2 1 1 1 2 2 0 2
pattern reference: lechni Grant-in-Aid Report, (197 Netall., 10 935 (1962).	sch Physische Dienst, D 6). Additional unit ce Mwt: 173.25. Volume[CC	olit, Metherland il réference: Or j: 142.36.	s, JLPUS T, Rovel, Ac	ta 	1.2846 1.2726 1.2496 1.2280 1.1974 1.1878	14 8 3 2 4 13 13	4 1 1 3 3 0 4 2 0 2 1 2 5 0 1 3 0 2
d A ¦ Int.; H	ki da	Int. h	k 1	 d A	Int.	1 1 	1
1.1341 1 2 1.1178 2 3 1.1021 4 6	2 2 1 2 0 0			 			

Data for ζ -phase AgZn.

Strong lines: 2.27/X 2.20/X 1.58/2 2.15/2 1.28/1 1.19/1 2.50/1 1.87/1

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26-956	JCPDS-ICD	D Copyright (c) 1990	Qual	ity:			
Ag Zn	•••••				d A	Int.	n k 1
5 8 Silver Zinc					3.81 3.30 2.70	10 5 10	
Rad: ČuKal Čutoff: 10.0 Ref: See comme	Lambda: 1 Int: Visu nts box for	.54056 Filt Ial I/Ic primary powder patt	er: Ni or: ern reference.	d-sp:	2.50 2.20 1.99 1.91 1.71	100 100 10 10 10	3 3 0 3 3 2 4 2 2 5 2 1
Sys: Cubic a: 9.3407 A: Ref: Ibid.	b: 8:	S.G.: I-43m (217) c: C:	A: Z: 4	C: 4 mp:	1.56	20 10 10	5 0 0 5 1 1 6 2 2
0x: 0.659	De:	SS/FOM: F11=6(.08	1,21)		۱ ۱		
ea: Ref:	nw8:	ey:	Sign:	2V:	+		
Made from weig temperatures, Cu5Zn8 type.	hed pieces the lowest PSC: c152.	reacted at 720 C an one being 150 C. A Mwt: 1062.38. Volu	id annealed at ictual composi ime[CD]: 814.9	several tion Ag5Zn7.90. 6.			

Data for γ -phase Ag₅Zn₈.

Strong lines: 2.20/X 1.56/2 3.81/1 2.70/1 1.99/1 1.91/1 1.71/1 1.52/1

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25-1325	JCPDS-ICDD C	opyright (c) 199	0 Quality:	; į			
AgZn					d A	Int.	h k l
3					2.434	12	100
; Silver Zinc					2.212	35 100 1	
Rad: CuKal	Lambda: 1.54	056 Fil		d-so:	1.411	50	
Cutoff: , Ref. See commen	Int: Diffrac nts box for pr	tometer 1/1 imary powder pat	cor: tern reference.		1.265	40 25 5	1 0 3 1 1 2 2 0 1
Sys: Hexagonal a: 2.8227 A: Ref: Ibid.	b: 8:	S.G.: P63/mmc (1 c: 4.427 C:	94) 4 A: Z: 0.5	C: 1.5685 ∎p:	ł 		4 1 1 1
Dx: 8.262 ()=:	SS/FON: F8=11(.0	84,9)		 		· · · · · · · · · · · · · · · · · · ·
ea: Ref:	nw8:	ey:	Sign: 2V:	:	 		
Annealed at van portions of Ag Primary pattern Private Communi Handbook of Lat	rious temperat and Zn. Actu n reference: C ication, (1973 ttice Spacings	ures down to `15 al composition A ook, Jr., Gould I). Additional u , (1958). Mwt: :	0 C. Reacted ~720 gZn2.94. Mg type. Laboratories, Cleve nit cell reference 304.01. Volume[CD]	C from weighed PSC: hP2. eland, Ohio, USA, : Pearson,]: 30.55.			
						i	; ;

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Data for ϵ -phase AgZn₃.

Strong lines: 2.14/X 1.41/5 1.27/4 2.21/4 1.64/4 1.19/3 2.43/1 1.18/1

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Figure A1.1 Typical XRD Output for Ag₅Zn₈.



APPENDIX II

Wavelength Dispersive Spectroscopy (WDS) was used to help determine the phases present in samples of industrial silver crust. The following is a typical output from a quantitative analysis using ZAF correction software.

Symmetry For Run : SEM706 00.00 FV TILT= .00 ELEV.=35.00 AZIM.= .00 COSINE=1.000 %11 elmts analysed, NORMALISED 👘 means 🕮 sigma ZnK AgL FeK THERE, #7360 71.6 28.2 .04 1207014. 47360 71.4 28.6 . Ø 7%7865, #7145 66.1 33.8 .Ø< TYTEST, #7145 FREE PARTI. 65.9 34.1 Ø 2MT768, #7145 65.9 33.9 .Ø< TYTESS, #7145 DARK IN GREY 76.1 20.1 3.8 MTE610, M7145 DARK IN GREY 77.3 19.1 3.6 TYT063. #7350 75.7 29.8 .0< 297064, #7360 74.7 30.Ø 8 EM70611, #7146 78.7 21.3 .Ø EMT0612, #7146 77.1 22.9 **.**Ø 5070613, #7146 76.8 23.Ø .Ø< EMTRA14, #T146 DARK IN GREY 87.1 8.7 4.2 ENT0615, #7144 52.6 47.4 . Ø . 51.7 48.3 TMT0616, #7144 • Ø -Y70617, #7144 51.5 48.5 .Ø 770611, #7146 92.7 25.1 ø 0470612. 47146 86.0 25.5 . Ø mean= 72.2 29.4 . 6 RMSD= 11.7 10.6 1.5

1

APPENDIX III

Image Analysis (as described in Section 5.1.4) was used extensively to measure the fraction of entrained lead in industrial crusts and laboratory samples produced during infiltration tests. The following is typical output from the analysis of an infiltrated particle bed. Here the starting size fraction was nominally 100-140 mesh screen size.

LECO IMAGE ANALYSIS REPORT

Pb Dross Samples

Carrie t pro	oram: L2001 Ver	rsion 2.02 Beta R29		
Company nam	e : HTC		Date	:18-
ປະສະດີ ກະທີ່ສໍ	: P. Hanco	⊳ k	Mao.	:503
So time nam	e : PRDROSS		Calic.	
Sample id	: 54140200			
		Statistic data		
		Number of fields: S		
Statistics:	instruction #	3 - plane 6, Particle		
Current Uni	t : mic			
	Area %			
Run Value				
Average	34.9717			
Std Dev.	0.4586			
Minimum	34.3903			
ที่สุหมักแก	35.5683			
,		Statistic data		
		Number of fields: 5		
Statistics:	: instruction #	5 - plane 8. Inter Partu:le		
Current Un:	it : mic	_ , ,		
	Length			
Run Value	-			
Avenage	100.9410			
Std Dev.	89.9643			
stinimum	4.0699			
Макілип	681.7509			

/

Statistic data Number of fields: 5

Statistics: instruction #7 - plane 6, Particle Current Unit : mic

Asp. ratio

Run Value	
Average	1. 596 🕶
Sta Sev.	0.4090
Minimum	1.0000
ปละเตนก	4.1025

Statistic data Number of fields: 5

Statistics: instruction #9 - place 0, Particle Current Init : mic

Length

Run Value -	
ਸੰਯੂ ਹਨ 8 ਤੁੰਦ	95.1529
Std Dev.	27.5010
មានក្នុង៣៤៣	24.0242
Макіпцп	288.8431

.

Statistic data Number of fields: 5

Statistics: instruction #11 - plane 6, Particle Current Unit : mic

Width

	44.6.00.041
Run Value -	
Average	58x 5208
Std Dev.	22.1177
Minimum	15.7480
Masinum	138.3782

1.



2

Ø

100.0000 %

1275

2

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:

Undersized

Percentage accepted :

Oversized

Accepted

54140200. Inter Particle - Count vs Length distribution

217

APPENDIX IV

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X-Ray Diffraction was performed on Bismuth Crust samples at Lakefield Research, a division of Falconbridge Ltd., located in Lakefield, Ontario. The following table is a summary of typical output identifying a $CaMg_2Bi_2$ intermetallic compound in a lead metal matrix.

Sample #	Sample # Pb with Intermetallic Phase							
2 theta angle	d Angstroms	Intensity	Identification					
25.25	4.09		CaMg2Bi2 Int 23					
27.00	3.83		CaMg2Bi2 Int 25					
28.65	3.61		CaMg2Bi2 Int 100					
31.80	3.26							
32.90	3.16							
33.30	3.12							
36.45	2.86	***1	Pb					
37.20	2.80		CaMg2Bi2 Int 32					
41.70	2.51							
42.35	2.47	**2	Pb					
44.35	2.37		CaMg2Bi2 Int 36					
48.65	2.17		CaMg2Bi2 Int 31					
52.70	2.01							
52.90	2.01		CaMg2Bi2 Int 22					
61.50	1.75	**3	РЬ					
63.80	1.69							
73.70	1.49	**3	Pb, CaMg2Bi2 Int 9					
76.90	1.44		CaMg2Bi2 Int 9					
77.60	1.43	*5	Ръ					