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**ADSORPTION ON SILICA IN
Pb- AND Ca-SO₄-CO₃ SYSTEMS**

FERESHTEH RASHCHI

**A thesis submitted to the
Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for
the degree of
Master of Engineering**

**Department of Mining and Metallurgical Engineering
McGill University
Montreal, Canada**

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*In the name of God,
the compassionate, the merciful*

*To my parents, my husband and
my son, Kourosh*

ABSTRACT

Formation of Pb and Ca precipitates on a silica surface in the presence of sulphate and carbonate under neutral to alkaline condition is studied using zeta potential measurements, Scanning Electron Microscopy (SEM), and X-Ray Photoelectron Spectroscopy (XPS). The effect of carbonate on displacing sulphate is discussed.

In the Pb/sulphate system, precipitates of predominantly Pb-oxide/hydroxide formed on the silica surface. In the Pb/carbonate system, the precipitates were predominantly Pb-carbonate/hydroxy carbonate. Precipitates in both the Pb/SO₄ and Pb/CO₃ systems were dispersed by addition of sufficient carbonate, the silica surface eventually becoming free of precipitates. This dispersion was considered to be due to: a high negative surface charge density on both lead carbonate and silica; nucleation being promoted at high concentrations of carbonate, resulting in small precipitates; and increased solubility at high carbonate concentrations.

In the Ca system, calcium sulphate precipitates did not form on the silica particles while calcium carbonate precipitates did. The precipitates were not removed by increasing carbonate concentration. The difference from the Pb system is attributed to a low negative surface charge density on calcium carbonate compared to lead carbonate, leading to less dispersing conditions, and the higher solubility of calcium sulphate compared to lead sulphate.

RÉSUMÉ

La formation de précipités de Pb et Ca sur une surface de silica en présence de sulphate et de carbonate sous des conditions de pH neutre à alcalin est étudiée en utilisant des mesures de potentiel zéta, la microscopie électronique à balayage (SEM) et la spectroscopie photoélectrique à rayons X (XPS). L'effet du carbonate sur le déplacement du sulphate est discuté.

Dans le système Pb/sulphate, des précipités principalement Pb-oxide/hydroxide, sont formés à la surface du silica. Dans le système Pb/carbonate, les précipités prédominants sont Pb-carbonate/hydroxy carbonate. Les précipités des deux systèmes Pb/SO_4 et Pb/CO_3 sont dispersés par l'addition suffisante de carbonate, la surface de silica devenant éventuellement libre de précipités. Plusieurs facteurs ont été considérés pour expliquer la dispersion des précipités par l'addition de carbonates: i) le carbonate de plomb et le silica ont tous deux une densité de charge surfacique fortement négative; ii) la nucléation est favorisée par des fortes concentrations de carbonates, ce qui conduit à la formation de plus petits précipités; iii) une forte concentration en carbonates résulte en une meilleure solubilité des précipités de plomb.

Les résultats relatifs à la formation de précipités de calcium montrent qu'il y a formation de précipités de carbonate de calcium à la surface du silica, mais pas dans le cas du calcium. Ces précipités de carbonate ne disparaissent pas lorsque la concentration en carbonate est élevée.

Les différences observées entre le système avec calcium et le système avec plomb sont

attribuées d'une part par plus faible densité de charges négatives à la surface des particules de carbonate de calcium, entraînant une dispersion plus faible, d'autre part par la plus grande solubilité du sulfate de calcium par rapport au sulfate de plomb.

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CHAPTER 1

INTRODUCTION

1.1 Metal ion adsorption

Surface properties play a critical role in many aspects of mineral processing, in particular, flotation. An understanding the interaction mechanisms between different reagents (inorganic cations and anions, organic collectors, etc.) and mineral surfaces in aqueous solutions is central to the study of flotation chemistry. In the flotation of sulphide ores, flotation response is often altered by the inadvertent presence of ions such as Cu, Pb, Ca, SO_4 and CO_3 .

One source of metal ions is oxidation of sulphide minerals. With certain mineral combinations, oxidation is enhanced by galvanic interactions (Nakazawa and Iwasaki, 1986; Yelloji Rao and Natarajan, 1989; Sui et al., 1995): for example, it is reported that galena,

sphalerite and covellite oxidized 8 to 20 times faster when pyrite was present (Majima, 1969). Pyrite because of its high rest potential, usually acts as the cathode, and other sulphides become the anode. As a result of this enhanced oxidation, more metal ions are expected to be released from anodic minerals than would be the case in the absence of galvanic interaction. This is illustrated by the observation that zinc concentrations derived from sphalerite were higher in the presence of either pyrite (Rao and Finch, 1988), chalcopyrite or galena (Yelloji Rao and Natarajan, 1989).

Released metal ions may remain on the originating mineral or transfer to another, resulting in variation of surface properties, and consequently, mineral floatability. Effects on flotation attributed to metal ions have been reported for galena (Cu ions) (Guy and Trahar, 1985), pyrite (Cu ions) (Gebhardt and Richardson, 1987), quartz (Pb ions) (Fuerstenau et al., 1965; Alexandrova and Nishkov, 1994).

Metal ions may be present on the mineral surface as 'hydroxides' (Shannon and Trahar, 1986; Senior and Trahar, 1991). This suggests they are hydrophilic in nature and decrease floatability. In some cases, metal ion species may induce interaction with xanthate and enhance floatability. Cu ions are often considered to play this role. For example, Cu ions released from Cu-minerals have been shown to result in "accidental" activation of sphalerite (Finkelstein and Allison, 1976; Baldwin et al., 1979), pyrite (Gebhardt and Richardson, 1987; Leppinen, 1990), and non-sulphide minerals (Nagaraj and Brinen, 1995).

In addition to Cu, Pb ions are also believed to be responsible for inadvertent activation of minerals. LIMS (laser ionization mass spectroscopy) analysis by Chrysosoulis et al. (1992, 1994) and Kim et al., (1995) has shown a significant amount of Pb present on sphalerite and pyrite particles in Cu-Pb and Zn flotation concentrates at Brunswick Mining. Kim et al. (1995) and Sui et al. (1995) have shown that Pb ions readily transfer from galena to pyrite when the minerals are in contact in an aqueous medium. Lead ions can also activate non-sulphide minerals (Fuerstenau and Palmer, 1976; Fuerstenau et al., 1965; Alexandrova and Nishkov, 1994).

Calcium is another common ion that can alter the surface properties of minerals. Circuit waters contain high concentration of calcium due to partial dissolution of gangue minerals such as dolomite, and lime addition for pH control. Calcium may, for example activate quartz (Cooke and Digre, 1949; Fuerstenau and Cummins, 1967) and is generally thought to depress pyrite (Fuerstenau and Eligillani, 1968) and possibly sphalerite (Moignard, et al., 1977).

Moignard et al. (1977) indicated that Ca^{2+} adsorption on ZnS is low at pH 7, and increases at higher pH. Even though adsorption densities are low, the zeta potential of ZnS can be altered significantly by Ca^{2+} adsorption and at sufficiently high concentration, 'charge reversal' can occur. They mentioned it is possible that Ca^{2+} adsorption could be associated with decreased sphalerite recovery.

When sulphate ion concentration is high, calcium may precipitate as calcium sulphate

(CaSO_4), and lead as lead sulphate (PbSO_4). If they are present on the mineral surface, either because they formed there or due to heterocoagulation, precipitates can alter flotation response. To illustrate, it is reported that at the Hilton concentrator (Mount Isa Mines Limited, Australia), CaSO_4 and PbSO_4 precipitates decreased recovery of galena (Grano et al., 1995). Surface analysis of samples taken from the galena flotation circuit suggested that under normal operating conditions, an overlayer of precipitated calcium sulphate existed on the surface of sulphide minerals. The precipitate was speculated to deposit due to heterocoagulation and the hydrophilic nature of calcium sulphate was considered to be the cause of the reduced galena flotation. Another illustration is the experience at the Brunswick Mining concentrator, where a persistent concern has been that CaSO_4 precipitates reduce selectivity in sphalerite flotation (Nesset, 1996).

Fuerstenau et al (1987) showed that the surface of PbSO_4 (anglesite) is positively charged at pH above 6. Since galena is negatively charged in this pH range (Fornasiero et al., 1994a), PbSO_4 will tend to heterocoagulate with and coat the surface of galena. Ney (1973) showed that calcium sulphate had two isoelectric points (i.e.p.), at pH ca 2 and ca 10 between which the surface charge was weakly negative. The case for CaSO_4 heterocoagulating with galena therefore, is not clear, although Sun (1943) suggested the possibility of heterocagulation of small particles with low zeta potential values on a particle with high zeta potential regardless of the relative sign.

One approach in flotation circuits to control sulphate precipitates is to replace lime as the pH

modifier with soda ash i.e., to introduce carbonate ions. In the presence of carbonate under alkaline conditions, CaSO_4 and PbSO_4 transform to CaCO_3 and PbCO_3 because the solubility of carbonates is less than the sulphates. In the case of Hilton, the addition of soda ash to the grinding mill significantly improved galena flotation. Analysis revealed a reduced Ca concentration on mineral surfaces and it was speculated that galena and calcium carbonate were mutually repelled.

1.2 Objectives

Based on the above it is concluded that:

Lead and calcium may precipitate in the presence of hydroxide/sulphate/carbonate anions in the flotation pulp. Formation of these precipitates on the mineral surface may alter flotation response.

The objective of this thesis is, therefore:

To study the precipitation of sulphates and carbonates of calcium and lead and their interaction with minerals. Silica was chosen as the model substrate since its surface chemistry in aqueous solutions is well known and reproducible. Also, control of silica flotation is important, in some non sulphide (Iwasaki, 1989) and sulphide flotation circuits (Alexandrova and Nishkov, 1994), particularly in the case of zinc (Fairweather, 1996).

1.3 Structure of the thesis

The thesis consists of five chapters. Chapter one introduces the background to the work and the problems encountered in selective flotation of minerals related to calcium and lead species.

In chapter two a review of Ca and Pb effects in flotation is given in both sulphide and non-sulphide systems, along with some examples of the zeta potential work in silica/Pb and silica/Ca systems that has been done previously. The theory of precipitation is also briefly discussed. Finally, precipitation in lead and calcium systems is reviewed.

In chapter 3, the mineral preparation procedure is given in addition to a brief theory, description of the instrumentation used and experimental procedures.

In chapter 4, the results and discussion are presented in the following order for both the Pb and Ca systems: adsorption/precipitation on silica in the presence of the cation (lead or calcium) alone, the cation and sulphate ions, the cation and carbonate ions, and silica in the presence of both, sulphate and carbonate ions. The effect of the order of the addition of ions and the effect of concentration on the morphology of the precipitates are also discussed briefly.

Finally, in chapter 5, conclusions are drawn and suggestions for future work given. The list of references is at the end of the thesis.

CHAPTER 2

REVIEW OF Ca, Pb EFFECTS IN FLOTATION

There is a current focus on the impact of contaminant metal ions in flotation. Lead and calcium ions are two common metal ions that can contaminate both sulphide and non-sulphide minerals (Pb: sulphides (Kim et al., 1995; Sui et al., 1995), non sulphides (Fuerstenau et al., 1965); Ca: sulphides (Moignard et al., 1977), non sulphides (Cooke and Digre, 1949; Fuerstenau et al., 1963)).

They are also important to consider since they precipitate with certain anionic species in a flotation pulp (Pb: Fuerstenau et al., 1987; Ca: Grano et al., 1995).

2.1 Origin of Pb, Ca ions

Lead ions derive primarily from lead minerals, the most common being galena, PbS . This mineral tends to oxidize readily, having about the lowest (electrochemical) rest potential of the common sulphide minerals (Nowak et al., 1984).

There are several oxidation routes: atmospheric oxygen (e.g. during transport from mine to mill); dissolved oxygen; galvanic contact with noble minerals such as pyrite; oxidation by ferric ions released from grinding media and iron sulphide minerals. Less commonly Pb may derive from partially soluble minerals such as anglesite (PbSO_4) and cerussite (PbCO_3).

Calcium can also be derived from minerals in the ore (gypsum: CaSO_4 , dolomite: $\text{Ca.Mg}(\text{CO}_3)_2$ and calcite: CaCO_3). There are however, other sources: notably, the water used and lime added for pH control.

2.2 Origin of SO_4 , CO_3 ions

Sulphoxy species derive from the sulphide minerals as a result of oxidation. Some species are generated when the ore is contacted with water. Others are present in recycle water especially if it is reclaimed from tailings ponds. Sulphate represents the highest oxidation state of sulphur. Some sulphate is added as CuSO_4 activator for sphalerite.

Carbonate may derive from the ore minerals (e.g. dolomite) or from the air (as CO_2). At pH

8.5 dissolved CO_2 may result in ca 1×10^{-4} M (6 ppm) and 3×10^{-3} M (183 ppm) carbonate and bicarbonate respectively. Herra-Urbina and Fuerstenau (1995) investigated the effect of atmospheric CO_2 on the adsorption of lead species in aqueous solution onto quartz. They found, through zeta potential measurements as a function of pH in CO_2 -free and air-saturated water, that in any oxide/aqueous metal system where the metal carbonate precipitates before the corresponding hydroxide, atmospheric CO_2 has a significant affect on interfacial phenomena. They also indicated that lead carbonate is the predominant lead species in the pH range from 6 to 11. Apart from air and gangue mineral, another source of carbonate is deliberate addition of soda ash (Na_2CO_3), an alternative to lime for pH control.

Carbonate affects flotation mainly because insoluble carbonate salts (calcium carbonate and lead carbonate) are formed. In the Hilton concentrator of Mount Isa Mines Limited, Australia, two surveys were conducted, one under standard condition, another after adding soda ash in the SAG mill. Solution analysis showed that the calcium concentration was dramatically decreased from 1.5×10^{-2} M (600ppm) to 7×10^{-4} M (28 ppm) after the addition of soda ash.

2.3 Non precipitating systems

2.3.1 Oxide minerals

The presence of polyvalent metal ions at the oxide/aqueous solution interface is usually a prerequisite for flotation with anionic collectors. This reflects the generally stable bond

between the cation and oxygen in typical oxide minerals (e.g. quartz) making direct interaction with the collector ion unfavourable.

Polyvalent metal ions adsorb specifically on oxides and silicates: this phenomenon is most pronounced when the cation involved undergoes hydrolysis to its first hydroxy complex. Comparison of the pH range over which the zeta potential of quartz is positive in the presence of a metal ion (Figure 2.1) with the distribution diagram for the cation (Figure 2.2) illustrates the connection. For example, in the case of a 1×10^{-4} mole/litre lead chloride solution, PbOH^+ is predominant from pH 6.2 to 10.8. This is exactly the pH range in which the zeta potential of quartz is positive in the presence of 1×10^{-4} mole/litre lead chloride, which is strong circumstantial evidence that adsorption of PbOH^+ is responsible (Fuerstenau et al., 1965; Fuerstenau and Atak, 1965; Fuerstenau and Palmer, 1976).

Figure 2.1 Zeta potential of quartz as a function of pH in the presence of 1×10^{-4} M PbCl_2 (after Fuerstenau, et. al., 1970)

Similar phenomena have been observed in numerous non sulphide systems: ferrous-quartz and magnesium-quartz (Fuerstenau and Palmer, 1976), aluminum-quartz (Fuerstenau et al., 1970; Gaudin and Fuerstenau, 1955b), nickel-quartz (McKenzie and O'Brien, 1969), cupric-chrysocolla (Palmer et al., 1975a), manganous-rhodonite (Palmer et al., 1975a), and ferrous-chromite (Palmer et al., 1975b).

Figure 2.2 Species distribution diagram for 1×10^{-4} M Pb^{2+} (after Latimer, 1952).

Calcium functions similarly to the other cations but at a higher pH. Fuerstenau et al. (1963) found that virtually no flotation occurred at $\text{pH} < 10.9$ at constant concentrations of sulfonate and Ca^{2+} . Increasing the pH to 11.1, however, resulted in complete flotation.

Limited adsorption of calcium ions on quartz, from pH ca 6 to 11, and from solutions as low as 100 ppm in Ca^{2+} ($2.5 \times 10^{-3} \text{ M}$) has been detected (Clark and Cooke, 1968). In the pH range where CaOH^+ is present in significant concentration, namely above about pH 11, extensive adsorption of CaOH^+ occurs (Figures 2.3 and 2.4).

Figure 2.3 Adsorption of calcium species on quartz as a function of pH from solutions 100 ppm in Ca^{2+} (after Clark and Cooke, 1968).

Activation of quartz with calcium ions is influenced by hydrogen ions and sodium ions (Cooke and Digre, 1949). The higher the concentration of these ions, the more calcium is required to activate the quartz. They also proposed that all cations present in the solution tend to adsorb on the surface, and the preferential sequence is H^+ , Ca^{2+} , and Na^+ . To displace adsorbed hydrogen ions to any degree, the calcium concentration in the solution must be more than 10^5 times the hydrogen ion concentration, and the sodium concentration must be more

than 10^9 times the hydrogen ion concentration.

In some circumstances the zeta potential can reverse sign in the presence of metal ions. This means that more charge must be left in the Stern plane than was present prior to adsorption. Three mechanisms of adsorption have been suggested (Palmer et al., 1975a; James and Healy, 1972): (1) water formation by combination of the hydroxyl ion of the hydroxy complex and adsorbed hydrogen ion, (2) hydrogen bonding of the hydroxy complex with the surface, and (3) formation and adsorption of the metal hydroxide on the solid surface.

Figure 2.4 Species distribution diagram for $1 \times 10^{-1} \text{ M}$ Ca^{2+}
(after Clark and Cooke, 1968).

With respect to hydrogen bonding of the hydroxy complex, using quartz as the subject mineral, hydrogen bonding could occur between adsorbed hydrogen ion and the hydroxy complex, such as $\text{Cu}(\text{OH})^+$ in the example below (Palmer et al., 1975a):

An alternative mechanism is the adsorption of the hydroxy complex by the formation and splitting out of water (Palmer et al., 1975a):

Either of these mechanisms would result in more charge in the Stern plane following adsorption. At the present time, it is not possible to state which of these mechanisms is the one acting.

2.3.2 Sulphide minerals

The presence of lead on the surface of sphalerite has been linked to its flotation with xanthate-type collectors (Mielczarski, 1986; Houot and Raveneau, 1992; von Reeken et al., 1989; Kim and Chrysosoulis, 1996). Kim and Chrysosoulis (1996) using LIMS analysis on Brunswick Mining samples, showed that a significant amount of Pb was present on the surfaces of sphalerite and pyrite particles, and speculated that this Pb had a major influence on the flotation of both minerals. Yelloji and Natarajan (1990) found that the flotation of sphalerite (with collector) was enhanced after contacting with galena in the absence of deliberately added activator.

In plant practice, the Zink-gruvan concentrator of the Vieille Montagne Company in Sweden is an example of sphalerite flotation without intentional activation (Mellberg, 1982). It was assumed that sphalerite floated due to autogenous activation by Pb^{2+} ions, released in the primary grinding stage. Flotation of sphalerite without deliberate Cu addition is usually attributed to accidental activation by Cu or Pb ions.

In the case of pyrite, the effect of lead ions as low as 1 ppm has been investigated (Sui et al., 1995). They found that at pHs 9.2 and 10.5 with lime as pH modifier, uptake of xanthate was promoted by the presence of Pb.

Calcium ions are considered to be readily adsorbed on sulphide minerals over a wide pH range. This may make the surface charge less negative or even result in charge reversal.

Unlike many other cations, calcium ion hydrolysis is not a requisite for adsorption. For example, calcium ion adsorption on sphalerite occurs in the pH range 7.5 to 10.5 where the Ca^{2+} form predominates (Figure 2.4) and results in surface charge reversal at pH 7.5-8 (Moignard et al., 1977). These researchers concluded that the adsorption densities were low, as also concluded by others (Brienne et al., 1993). However, the adsorption of calcium dramatically affected the mineral surface properties (e.g. the zeta potential).

2.3.3 Comparison between the zeta potential of silica and sulphide minerals

In their study of oxidation of galena surfaces, Fornasiero et al. (1994) used quartz to test the validity of the proposed mechanism (section 2.3.3.1) because quartz does not contain any of the atoms present in galena and does not detectably dissolve over the pH range and time used in their study. Therefore, the only surface changes that occur must come from the bulk solution. They also chose quartz as a model since the electrical properties of quartz are similar to those of galena and other sulphide minerals in their non-oxide state.

Figure 2.5 shows zeta potential of silica, galena and pyrite as a function of pH. As it can be seen, they are similar in terms of zeta potential. This partially justifies the choice of silica as a model substrate even for the study of sulphide minerals.

Figure 2.5 Comparison between zeta potential of silica and sulphide minerals, galena and sphalerite (after Vergouw, 1996); pyrite (after Sui et al., 1995)

2.4 Precipitating systems

Significant quantities of ionic species exist in flotation pulps arising from the water source, the minerals involved, and deliberate additions made to control flotation. Some species may combine to form precipitates under certain conditions. In the present context, the precipitates of interest are the sulphates and carbonates of Ca and Pb. Following is a brief discussion of precipitation theory.

2.4.1 Precipitation theory

Precipitation is a heterogeneous process involving creation of a solid/liquid interface. It is also defined as reactive crystallization, i.e. the product of a solid compound out of a solution via a chemical reaction. For reaction

an equilibrium constant can be determined, which is known as the solubility product, K_{sp} . By comparing the K_{sp} of different compounds, the relative solubility is determined. For the above reaction

$$K_{sp} = [A^{n+}]_{eq} [B^{m-}]_{eq} \quad (2-2)$$

Since the K_{sp} corresponds to the molar concentrations of the ions in a saturated solution, if the product of the concentrations is less than the K_{sp} , the solution is below saturation and more solid will dissolve (if any is present). Also, if the product of the concentrations of ions in a given solution is greater than the K_{sp} , the solution is supersaturated and ions will precipitate out until the equilibrium concentrations are reached. The K_{sp} values for the compounds of interest here are given in Table 2.1.

Precipitation of $AB(s)$ is next considered as a general case:

where X^- is the matrix anion and I represents other ionic species present. Simple

thermodynamic analysis (e.g., calculation of the ΔG of the precipitation reaction) might indicate that the formation of the solid product AB is feasible, nevertheless side reactions might occur simultaneously leading to production of additional solid phases. However, not only the formation of more than one crystalline phase but also metastable phases (i.e., phases favoured by the kinetics and not by the thermodynamics) is possible. In other words, in the domain of thermodynamic stability of a compound, a less stable one might form. Usually, this metastable phase forms first, which eventually, given time, should convert to the stable one, e.g., hydroxycarbonate salts (MOHCO_3) tend to form ahead of their carbonate counterparts ($\text{M}_2(\text{CO}_3)_3$) within the domain of stability of the latter.

Table 2.1 Solubility product constant of lead and calcium compounds encountered in this study (Ksp chem. software)

Compound	Formula	K_{sp}
Lead sulphate	PbSO_4	1.6×10^{-8}
Lead carbonate	PbCO_3	7.4×10^{-14}
Lead hydroxide	$\text{Pb}(\text{OH})_2$	1.2×10^{-15}
Calcium sulphate	CaSO_4	9.1×10^{-6}
Calcium carbonate	CaCO_3	2.8×10^{-9}
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	5.5×10^{-6}

2.4.1.1 Supersaturation

According to crystallization thermodynamics, a solid phase forms out of a solution when

$$\Delta G = -RT \ln\left(\frac{a}{a_0}\right) < 0 \quad (2-4)$$

where ΔG : Gibbs free energy of the precipitation reaction

a : activity of the solute in the initial solution and

a_0 : activity of the solute in the final solution (i.e. in equilibrium with the solid phase)

The ratio a/a_0 is defined as saturation ratio, S . To simplify, activities are taken as concentrations, therefore,

$$S = \frac{a}{a_0} = \frac{C}{C_{eq}} \quad (2-5)$$

where C_{eq} is equilibrium concentration.

In the condition of supersaturation, $S > 1$ and $\Delta G < 0$, and supersaturation ratio is defined as:

$$\frac{(C - C_{eq})}{C_{eq}} = S - 1 \quad (2-6)$$

Therefore, supersaturation is the driving force for crystallization.

For the case of reactive crystallization, i.e.,

the saturation ratio is defined as:

$$S = \frac{[A^{n+}]_{(aq)} [B^{n-}]_{(aq)}}{K_{sp}} \quad (2-8)$$

where,

$$K_{sp} = [A^{n+}]_{eq} [B^{n-}]_{eq} = \exp\left(-\frac{\Delta G^0}{RT}\right) \quad (2-9)$$

where, ΔG^0 is the standard Gibbs free energy of the precipitation reaction. Crystallization or precipitation out of a solution involves the nucleation and growth of particles from a supersaturated solution.

2.4.1.2 Nucleation, growth and aggregation

a) Nucleation

The type and rate of nucleation plays an important role in controlling the final precipitate particle size distribution. The most important modes of nucleation that can occur during precipitation are (Dirksen and Ring, 1991):

- Homogeneous nucleation
- Heterogeneous nucleation
- Surface nucleation
- Contact nucleation

Homogeneous nucleation occurs in the absence of a solid surface. When supersaturation

increases, the critical nuclei size decreases and the number of nuclei increases. This means that at high S a large population of ultra fine colloidal particles forms. Homogeneous nucleation can only occur above a minimum S , $S_{cr, hom}$ (Figure 2.6). This graph depicts that for homogeneous nucleation $S_{cr, hom} > 10$ the nucleation rate increases exponentially with S . Since in this work, silica is always present, homogeneous nucleation is probably not the relevant case.

Figure 2.6 Diagrammatic representation of homogeneous nucleation as a function of supersaturation (after Dirksen and Ring, 1991)

Heterogeneous nucleation is induced by surfaces of a different material from the one being precipitated. Nucleation is induced due to the lower surface energy of these surfaces compared to that of a newly formed precipitate particle. The critical supersaturation ($S_{cr, het}$) is lower than the corresponding $S_{cr, hom}$ for homogeneous nucleation but the nucleation rate has the same response as shown in Figure 2.7. Heterogeneous nucleation is the relevant case in this study.

Figure 2.7 Generalized nucleation rate diagram: differences between homogeneous, heterogeneous and surface nucleation (after Dirksen and Ring, 1991)

Surface nucleation occurs in the presence of crystals with the same composition as the material that precipitates. These particles have to be present in suspension and can be added as seed. Surface nucleation occurs at a lower S_{cr} than heterogeneous and homogeneous nucleation, i.e. $S_{cr, surf.} < S_{cr, het.} < S_{cr, hom.}$. This is shown in Figure 2.7.

Contact nucleation involves the plastering of freshly formed particles on the walls of the reactor. This is very important in industrial crystallization systems. An empirically derived equation shows that the rate of contact nucleation, $J_{cont. nucl.}$, depends on the stirrer rotation speed (RPM), particle mass density or solids loading (M_t) and the supersaturation (Dirksen and Ring, 1991).

$$J_{cont,nuct} \propto (S - 1)^b (M_t) (RPM)^h \quad (2-10)$$

$$0.5 < b < 2.5 \quad \text{and} \quad 2 < h < 4$$

Since the silica suspension was held in a beaker, contact nucleation may occur in this study.

b) Growth

After the nuclei form they grow into particles either through deposition and incorporation of new solute material (controlled by the growth kinetics) or by aggregation of individual nuclei (Figure 2.8). Supersaturation has a qualitative effect on a final crystal morphology. At higher levels of supersaturation, nucleation rate increases and consequently many small nuclei form.

c) Aggregation

Aggregation is common in aqueous precipitation systems; it is favoured by compression of the electrical double layer surrounding the individual particles. This is achieved by having a high ionic strength or via specific adsorption of ionic surfactants or via polymer-induced flocculation. Aggregation will not be considered in this study.

In conclusion, knowing the different dependency of nucleation and growth rates on supersaturation can be exploited to induce a precipitation process favouring crystallinity and growth. This is demonstrated in Figure 2.9. By controlling the supersaturation below $S_{cr, hom}$ and using seed, production of well formed crystalline solids is favoured. On the contrary, under the regime of homogeneous nucleation, metastable (amorphous) phases tend to form

ahead of the stable crystalline phases.

Figure 2.8 Growth vs aggregation

Growth and aggregation are competing mechanisms: with the degree of supersaturation the selectivity, particle size distributions and morphology are controlled .

Figure 2.9 The two different types of precipitation

2.4.2 Review of previous work on precipitating systems

2.4.2.1 Lead precipitates

The lead precipitates encountered in flotation are primarily hydroxides, hydroxy carbonates, carbonates, and sulphates. In solution, open to the air, lead carbonate and/or lead hydroxy carbonate seem to be the dominant lead species found on the surface (Fornasiero et al., 1994a):

As the total carbonate concentration increases the various oxide lead phases transform to $Pb_3(OH)_2(CO_3)_2$, consuming all the added carbonate. Lead carbonate forms at high carbonate concentration (Grano et al., 1995). The zeta potential versus pH of cerussite, $PbCO_3$, is negative (Figure 2.11) and similar to that of lead hydroxy carbonate.

In many cases, the interaction between these precipitates and minerals is believed to be electrical in nature. The zeta potential vs pH for lead precipitates, collected from various sources, is shown in Figure 2.10. Recalling the general trend in zeta potential for sulphide minerals (Figure 2.5), it is apparent that hetero coagulation with sulphides is possible. The pH range for hetero coagulation for each precipitate suggested by the available data is given in Table 2.2. The table suggests that under typical flotation conditions, lead hydroxy

carbonate and lead carbonate are probably dispersed from sulphide minerals at alkaline pH.

Fornasiero et al. (1994a), proposed a mechanism for the dissolution of lead from a galena surface followed by its readsorption as lead hydroxide to explain the changes in the zeta potential of galena during oxidation. They used zeta potential measurements to study the oxidation process. At high pH values and in the presence of N_2 , lead hydroxide forms colloidal particles which increase in size with time and eventually form visible precipitates. These lead hydroxide particles are positively charged for pH values lower than 12 (Figure 2.10), and thus may heterocoagulate with the negatively charged galena.

Figure 2.10 Zeta potential as a function of pH of anglesite and cerussite (after Fuerstenau, M.C. et al., 1987); lead hydroxide and lead hydroxy carbonate (after Fornasiero et al. 1994a)

Table 2.2 Suggested pH range for hetero coagulation of lead precipitates with pyrite, sphalerite and galena

Sulphide Mineral	Lead Precipitate	pH Range
Pyrite	Pb(OH)_2	<11.6*
	PbSO_4	2-4.2 & 5.7-10.9
	PbCO_3	2-4
	$\text{Pb}_3(\text{OH})_4\text{CO}_3$	4.3-6
Sphalerite	Pb(OH)_2	<11.6
	PbSO_4	3.8-4.2 & 5.7-10.9
	PbCO_3	3.8-4
	$\text{Pb}_3(\text{OH})_4\text{CO}_3$	4.3-6
Galena	Pb(OH)_2	<11.6
	PbSO_4	2.2-4.2 & 5.7-10.9
	PbCO_3	2.2-4
	$\text{Pb}_3(\text{OH})_4\text{CO}_3$	4.3-6

* At low pH, Pb(OH)_2 is soluble.

Herrera-Urbina and Fuerstenau (1995) studied the electrokinetic behaviour of the quartz/ Pb/CO_3 system and suggested the presence of lead carbonate on the surface. They also found that the zeta potential was virtually restored to that of quartz at elevated carbonate concentration (i.e., above stoichiometric to form PbCO_3). They attributed this to specific adsorption of HCO_3^- , which is the dominant species in the pH range 6.3 to 10.3, on the lead carbonate-coated quartz. They showed that the zeta potential of PbCO_3 in excess HCO_3^- did shift towards that of quartz (Figure 2.11). The reverse trend of the zeta potential above pH

10) was attributed to hydrolysis of the lead carbonate precipitate, which is unstable at high pH (Herrera-Urbina and D.W. Fuerstenau, 1995).

Figure 2.11 Zeta potential of synthetic lead carbonate as a function of pH in 10^{-3} M KNO_3 , in the absence and presence of 10^{-4} M K_2CO_3 (after Herrera-Urbina and D.W. Fuerstenau, 1995).

The lead carbonate was synthesized by precipitation from solution of potassium hydroxide in an air-saturated solution of lead nitrate. Although they did IR and found characteristic bands of lead carbonate, comparing the lead carbonate curve in Figure 2.11 with the lead hydroxide curve in Figure 2.10 suggests that lead hydroxide may also have been formed. This may be because insufficient carbonate was present from the air alone.

Sui et al. (1995) investigated the effect of lead ions on pyrite/xanthate interaction by cyclic voltametric and ex situ spectroelectrochemical techniques. At pHs 9.2 and 10.5 with lime as pH modifier, uptake of xanthate was promoted by the presence of Pb. With soda ash as pH modifier, the effect of lead was suppressed, and no dixanthogen peak appeared on the voltammogram, and the height of the two characteristic dixanthogen peaks in the IR spectrum was much reduced. They suggested that lead carbonate formed and because of its low solubility, tends to coat and passivate the pyrite surface against xanthate interaction. No direct evidence of lead carbonate on the surface was given.

In an XPS study of the oxidation of galena, Fornasiero et al. (1994b) revealed a small amount of PbSO_4 on the surface. This was in agreement with thermodynamic calculations which showed that in the presence of sulphur, lead forms PbSO_4 in neutral to acidic solutions (Fornasiero et al., 1994b; Garrels and Christ, 1965). It is also evident in the stability diagram of the anglesite-water system (Figure 2.12).

However, the zeta potential versus pH of PbSO_4 reported by Fuerstenau D.W. et al. (1985) resembled that of galena conditioned at a high pH value in the presence of Pb, i.e. with $\text{Pb}(\text{OH})_2$ on its surface. Fuerstenau, M.C. et al. (1987) found the same result when they measured the zeta potential of anglesite: they attributed it to lead oxide formation rather than lead hydroxide (Figure 2.10), by reference to the Eh-pH diagram (Figure 2.12).

Lead sulphate (anglesite) is sparingly soluble and most of the lead sulphate formed during

galena oxidation will go into solution at low pH values. At high pH values, due to its lower solubility, solid $\text{Pb}(\text{OH})_2$ will form and may be present on the galena surface.

Figure 2.12 Eh-pH diagram of the anglesite-water system at $P_{\text{CO}_2}=0$ atm. and 25°C (after Fuerstenau et al., 1987).

2.4.2.2 Calcium precipitate

The calcium precipitates encountered in flotation are calcium sulphate and calcium carbonate.

The zeta potential of these precipitates are given in Figures 2.13 and 2.14.

Somasundaran and Agar (1967) determined the zero point of charge to identify the potential determining ions and to propose a mechanism for the creation of the surface charge on calcite.

The zeta potential of calcite as a function of pH for various intervals of mixing is given in Fig.

2.13. The continuous change in zeta potential and pH with mixing (Fig. 2.13) was explained on the basis of different hydrolysis reactions which give rise to a net charge on the surface. For example, at low pH reactions (2-13) and (2-14) proceed in the forward direction and reactions (2-15) and (2-16) in the reverse direction, whereas at high pH the reverse is true.

The zero point of charge of calcite, as measured by the streaming potential technique, shifted gradually from an initial pH of 10.8 towards 9.5 as equilibrium was approached. They obtained an isoelectric point of 8.2. Somasundaran and Agar (1967) observed that zeta potential and pH of the system gradually changes for several days, indicating there are slow stages in the reactions developing the change at the interface.

As discussed for lead precipitates, hetero coagulation of calcium precipitates with sulphides is possible. Recalling the general trend in zeta potential for sulphide minerals (Figure 2.5), the suggested pH range for hetero coagulation for calcium sulphate is given in Table 2.3. Because of the changing pH and zeta potential of calcium carbonate with time it is hard to predict the corresponding pH range for that precipitate.

Table 2.3 **Suggested pH range for hetero coagulation of calcium sulphate with pyrite, sphalerite and galena**

Sulphide Mineral	pH Range
Pyrite	>10.5
Sphalerite	2-3.8 & >10.5
Galena	>10.5

The metallurgical performance of lead roughers and scavengers is sometimes characterized by a low flotation rate of galena, which reduces the concentrate grade. Surface layers of calcium sulphate may be present resulting from poor circuit water quality and/or rapid dissolution of gangue minerals (Grano et al., 1995). They suggested that these hydrophobic layers can reduce the exposure of "clean" galena surfaces to collector and inhibit galena flotation. Samples were extracted from the lead-zinc circuit of Mount Isa Mines and analysed by XPS. Soda ash was then added to the circuit and the analysis was repeated. There was a concomitant improvement in the galena flotation rate. From the results they suggested that the level of sulphate was reduced when soda ash was present, whilst more sulphide was exposed, allowing more extensive interaction with collector.

Smart (1991) used three surface-sensitive techniques, XPS, scanning Auger microscopy and analytical scanning electron microscopy, to study the surface layers on metal sulphides as single minerals, mixed minerals, synthetic ores and real ores from eight Australian concentrators. The results from application of these techniques suggested that the surface layers on base metal sulphide minerals were dominated by hydroxides but also contain, in

specific cases, other chemical species that can alter flotation response and selectivity. Among these other species were carbonates and sulphates. XPS evidence of three different chemical forms of hydroxide precipitates on sulphide surfaces was presented in the study. It was concluded that the surfaces of minerals in complex sulphide ores are normally dominated by hydroxides, carbonates and minor sulphate concentrations.

Figure 2.13 Zeta potential of calcite in equilibrium with aqueous solutions and air as a function of pH and mixing (after Somasundaran and Agar, 1967)

Figure 2.14 Zeta potential of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as a function of pH (after Ney, 1981)

CHAPTER 3

EXPERIMENTAL METHODOLOGY

3.1 Mineral preparation and reagents

Silica, - 400 mesh ($\sim 38 \mu\text{m}$), was prepared by wet screening and leaching in warm 23% nitric acid solution for one hour following the procedure recommended by Kulkarni and Somasundaran, (1977). The mineral was then washed with distilled water till the pH of the solution approached the natural pH of the mineral-distilled water system, and stored in cleaned polypropylene bottles at a pH of 1.6 until use. The pH 1.6 is close to the isoelectric point of silica and was used for storage following the recommendation of Somasundaran (1970).

All the reagents used are listed in Table 3.1.

Table 3.1 Reagents used in the study

Reagent	Purity, %	Source	Remarks
PbSO ₄	98	Aldrich	
PbCO ₃		Aldrich	
CaSO ₄ .2H ₂ O		A&C American chemicals	
CaCO ₃	99.5	J.T.Baker chemical co.	
Pb(NO ₃) ₂		Anachemica chemicals	Source of lead ions
Ca(NO ₃) ₂ .4H ₂ O	99	B&A	Source of calcium ions
Na ₂ SO ₄		BDH Inc.	Source of sulphate ions
NaHCO ₃		Fisher Scientific	Source of carbonate ions
KNO ₃			0.001 M. electrolyte for zeta potential
NaOH		Anachemica	pH-modifier

3.2 Experimental Techniques

Zeta potential measurements, scanning electron microscopy and x-ray photoelectron spectroscopy were used to analyze the response of silica in the following sequence of tests:

- Silica alone
- Silica in the presence of the cation (lead or calcium)
- Silica in the presence of the cation and sulphate ions
- Silica in the presence of the cation and carbonate ions

- Silica in the presence of the cation, sulphate and carbonate ions

For comparison, the zeta potential of specimens of lead carbonate, lead sulphate, calcium carbonate and calcium sulphate were also measured.

3.2.1 Zeta potential measurements

3.2.1.1 Basic theory

When a solid particle is in water, a surface charge develops. As the particles move with respect to water, there is a surface of shear on the water-side of the interface (Figure 3.1). The region between the particle surface and this plane of shear is not fully understood except that it is a region of rapid change. The plane of shear is represented here by the wavy line a short distance from the Stern plane. It is at this shear plane that the zeta potential measurements are made.

If one applies an electric field across a suspension of small particles, the particles will tend to move toward either the anode or the cathode depending on whether the solid surface carries a positive or negative charge. The migrating speed (electrophoretic velocity) of the particles is directly proportional to the magnitude of the surface charge or zeta potential.

The electrophoretic velocity U is directly proportional to the applied field strength. An equation proposed by Smoluchowski relates the mobility to the zeta potential:

$$U = \zeta \epsilon / \eta \quad (3-1)$$

Figure 3.1 Diagrammatic interpretation of the electric nature of the water-solid interface

The electrophoretic velocity U has units of $LT^{-1}V^{-1}L$ (e.g. $\mu m.s^{-1}$ per $V\ cm^{-1}$). The zeta potential, ζ , is usually quoted in mV. Assuming the dielectric constant, ϵ , and viscosity of water, η , to be their normal values, $\zeta = 12.8\ U$ (at $25^\circ C$).

The zeta potential does change with ionic strength. Therefore, the ionic strength of the solution should be constant. This is achieved by using a background electrolyte, e.g., NaCl or KCl. The latter is often preferred since the radius of the K^+ and Cl^- ions is the same, therefore, they move in solution with the same speed. The background electrolyte (type and concentration) is chosen according to the type of the experiment to be performed. In this study, KNO_3 was used to avoid the possible formation of $PbOHCl$ (the nitrate anion is too big to form a similar compound). The concentration used was $10^{-3}\ M$.

The pH at which there is zero charge at the surface of the particle is known as the point of zero charge or pzc. There is also a pH of zero zeta potential, known as the isoelectric point (iep). In many cases, the iep and pzc are equal.

3.2.1.2 Instrumentation

A LASER ZEE meter (Model 501, Penkem, Inc., Figure 3.2) was used to measure the zeta-potential of particles suspended in an electrolyte. The suspension is inserted into the cell (Figure 3.3).

Figure 3.2 Detail of the cell used

Inside the instrument a prism takes an image, rotates a few degrees, flips back and repeats the cycle. The image causes the microscope inside the instrument to scan in one direction and then reset. The rate and direction of the prism motion is adjusted so that the apparent motion caused by the prism exactly matches the particle velocity caused by the electric field. This makes the particles appear stationary and the zeta potential is then displayed on the readout.

Experimental values of zeta potential are generally between $\pm 100\text{mV}$. Typically measurement

takes approximately one minute. The claimed accuracy is $\pm 5\%$ or ± 1 mV (Penkem, 1995).

Figure 3.3 Penkem Laser Zee Meter, Model 501

3.2.1.3 Experimental procedure

One-half gram of silica was added to a solution of 10^{-3} M KNO_3 (background electrolyte) to obtain a suspension of 0.01% solid. The suspension was mixed for 5 minutes followed by introducing a given concentration of ions, and mixed again for 5 minutes. A sample of the suspension (30 mL) was transferred to the cell for zeta potential measurements. The measurements were repeated twice for each set of conditions (reproducibility was ± 2 mV for most of the pH range). Between measurements, the beaker was sealed by a paraffin film to restrict access to atmospheric CO_2 .

3.2.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is widely used to examine surfaces: resolution down to a few thousand angstroms is possible, depending on the nature of the sample. Scanning electron microscope images characteristically have a wide range of contrast: that is, detail can be seen both in very dark and in very light areas. The images also have great depth of focus: they are sharp at both very low and very high points of the surface. The result is that even quite rough surfaces show in revealing clarity with an impression of depth.

3.2.2.1 Basic theory

The SEM uses a beam of electrons focused by electromagnets onto a spot on the specimen surface. The electron beam is created by passing a current through a filament (usually tungsten) and heating it to a point where electrons are given off. The electrons are accelerated by an electric field and acquire kinetic energy. When the beam strikes the surface of the sample, this energy is dissipated and this yields several signals that are gathered by various detectors in the specimen chamber.

The three main types of signals emitted by the electron beam-sample interactions are:

- 1) Secondary Electrons. These ejected electrons are low energy, weakly bound electrons. Due to their low energy, they cannot travel far before they are recaptured: therefore, they can only be detected if they have escaped from or near the surface of the sample. Because of this, the secondary electron signal only carries topographic

information about the sample.

- 2) **Backscattered Electrons.** If a primary electron (an electron from the source beam) strikes the nucleus of a sample atom, an elastic collision may occur. The rebounding electron is termed a backscattered electron. Backscattered electrons have more energy than secondary electrons and can escape from deeper within the sample. Because materials with high atomic numbers scatter more electrons than materials with low atomic numbers, the backscattered signal provides compositional information.
- 3) **Characteristic X-rays.** When a beam electron ejects an inner shell atomic electron from its orbital, outer shell electrons jump in to fill the vacancy. The energy associated with this jump is emitted as an X-ray, whose energy is characteristic of the atom from which it came. This type of signal provides elemental information about the sample.

Images from backscattered electrons were used in this work. A backscattered image of the sample can be obtained rapidly and provides sufficient compositional information to distinguish mineral phases. The different phases appear as different shades of grey.

The photograph, more correctly referred to as a scanning electron micrograph, reproduces the image observed on the visual screen. The magnification used in this work is 600 times

unless otherwise stated.

3.2.2.2 Instrumentation

The SEM (Figure 3.4) consists basically of four components:

- 1) The illuminating/imaging system produces the electron beam and directs it onto the sample.
- 2) The information system includes the data released by the sample during electron bombardment and detectors which discriminate among and analyze these information signals.
- 3) The display system consists of one or two cathode-ray tubes for observing and photographing the surface of interest.
- 4) The vacuum system removes gases from the microscope column which would otherwise interfere with high-resolution imaging.

3.2.2.3 Experimental procedure

Sample preparation was the same as for the zeta potential measurements except that the suspension was left for a 24 hour period to let the precipitate particles grow. The suspension was filtered and the solids washed several times with distilled water and left to dry in air. A small portion of the solids was mounted on double-sided tape (carbon tape) or on conductive silver paint. Finally, a thin coating of gold was applied using a sputter technique. Back-scattered (BS) electron images were taken.

Figure 3.4 The JSM-840 scanning electron microscope

3.2.3 X-ray Photoelectron Spectroscopy (XPS)

The technique of X-ray photoelectron spectroscopy is relatively new to the field of surface analysis. It is a surface sensitive technique, capable of revealing the elemental and chemical composition of the surface and near surface up to a maximum depth of about 50-100 Å.

The first information obtained is a qualitative analysis in which atoms present on the surface of the sample are identified. Each electronic level for each atom is characterized by a binding energy for which tables exist (Briggs, 1977).

The second observation is of the shift in the peak position resulting from changes in the structure and oxidation state of the chemical compound. In this work, the first information (identifying the atoms) was used.

3.2.3.1 Basic theory

The basis of the XPS technique is shown schematically in Figure 3.5. When an X-ray irradiates matter, the incident photon is absorbed, giving up its energy in expelling and imparting kinetic energy to an inner orbital electron. Therefore, the bound electrons are ejected from the atoms. This process is termed photoelectric absorption, and the ejected electron is a photoelectron (Figure 3.6).

Figure 3.5 Schematic representation of XPS experiment

Figure 3.6 Schematic representation of photoelectron generation in XPS

These ejected electrons have energies which are characteristic of the elements present in a sample, and investigation of electron-energy spectra gives chemical information. If the incident photons have low energy, only outer-shell electrons are ejected, but if they have high energy, inner-shell (K, L, M) electrons may be ejected as well. The disciplines concerned with study of these electron spectra are known as 'electron spectroscopy for chemical analysis' (ESCA) or X-ray photoelectron spectroscopy (XPS).

The energy of the photoelectron is related to that of the incident primary photon as follows

$$E_{\text{e-ray}} = h\nu = E_k + E_b + \phi \quad (3-2)$$

where

- $E_{\text{e-ray}}$: the energy of the incident photon;
- E_b : the energy required to expel an electron (binding energy);
- E_k : the kinetic energy of the free photoelectron;
- ϕ : the energy required to remove an electron from the specimen surface.
- h : Plank constant
- ν : frequency of the photon

All energies are in electron volts. Since ϕ is only a few electron volts, the above equation is

simplified as

$$E_k = E_{\text{vac}} - E_b \quad (3-3)$$

This equation allows the E_b of a particular energy level of a given atom to be calculated, which helps to determine the electronic structure of the solid. Although core electrons are not involved in chemical bonding, the core energy levels of atoms in a solid are sensitive to structure and bonding. The value of the core level binding energy is determined by the type of atoms present in the solid, and the chemical shifts give information on the chemical bonds of the elements, (e.g., the oxidation state and molecular environment). Moreover, quantitative information on the atomic ratio between element and environment is given by the measurement of the peak area.

Only electrons close to the surface can escape from the solid, those electrons dislodged deeper in the solid are retarded by the material and are unable to escape. Therefore, XPS is a surface sensitive technique with an effective sampling thickness of about 50-100 Å. This value is smaller for electronic conductors than for non-conductors.

3.2.3.2 Instrumentation

The XPS-ESCALAB 220i-XL used in this study (Figure 3.7) consists basically of six components:

- 1) Source of X-rays (that interact with the sample)
- 2) Two chambers, preparation chamber with a pressure of 1×10^{-9} torr and analysis

chamber with a pressure less than 1×10^{-9} torr.

- 3) Transferring system, brings a specimen on a support from the preparation chamber to the analysis chamber.
- 4) Vacuum system, to provide desired pressure.
- 5) Monitor, to see the sample transferring correctly.
- 6) Computer with Eclipse program

Figure 3.7 The XPS-ESCALAB 220i-XL

3.2.3.3 Experimental procedure

A portion of the samples prepared for the SEM was used for XPS measurements. X-ray photoelectron spectra were obtained on an ESCALAB 220i-XL spectrometer with an Al K_{α}

anode ($h\nu=1486.6$ eV) at a normal take off angle. The x-ray was monochromated and the instrument was calibrated against the $\text{Ag}_{3d5/2}$ band-pass energy of 20 eV corresponding to an energy resolution of 0.6 eV. The powder samples, placed on a copper tape, were maintained under a background pressure of 1×10^{-9} Torr for ~ 1 hr in the sample chamber before spectra acquisition.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Lead system

4.1.1 Pb^{2+}

Zeta potential of silica as a function of pH and different concentrations of lead (as lead nitrate) is presented in Figure 4.1. The i.e.p. of silica alone is ca pH 1.8 (or $\text{pH}_{\text{iep}} \sim 1.8$). In the presence of 10^{-5} M (2 ppm) and 5×10^{-5} M (10 ppm) Pb^{2+} , zeta-potential increases but remains negative. In the presence of 10^{-4} M (20 ppm) Pb^{2+} ions over the pH range 7-11, the zeta-potential reverses giving two additional pH_{iep} , ca 7 and 11. By comparison with the solution species distribution diagram (Figure 2.2), the dominant adsorbing species appears to be PbOH^+ .

The SEM BS image (Figure 4.2) shows evidence of a precipitate on the silica surface. From the phase stability diagram (Figure 2.2), at pH 10 the probable species is PbO .

Figure 4.1 Zeta potential as a function of pH for silica alone and in the presence of Pb^{2+}

Figure 4.2 SEM (BS) micrograph : Silica in the presence of 10^{-4} M Pb^{2+} at pH 10 (NaOH)

4.1.2 $\text{Pb}^{2+} / \text{SO}_4^{2-}$

Figure 4.3 gives the zeta potential for lead sulphate and for silica alone and in the presence of 10^{-4} M Pb/SO_4 ions. Lead sulphate showed a pH_{iep} ca 6 and was weakly positively charged from pH 6 to 10, a result similar to that of Fuerstenau et al., (1987) (Figure 2.10). On addition of sulphate ions the zeta potential of silica became similar to that of PbSO_4 . The SEM-BS micrograph at pH 10 (Figure 4.4) shows evidence of a precipitate. Heterocoagulation over the pH range 6-10, possibly contributes to the presence of precipitates on the surface. This is in agreement with the suggested pH range for heterocoagulation of lead sulphate with pyrite, sphalerite and galena in Table 2.2.

Figure 4.3 Zeta potential of silica as a function of pH in the presence of 10^{-4} M Pb^{2+} and SO_4^{2-} and zeta potential of lead sulphate

Figure 4.4 SEM (BS) micrograph : silica in the presence of 10^{-4} M Pb^{2+} and SO_4^{2-} at pH 10 (NaOH)

Above ca pH 8 PbSO_4 is unstable with respect to PbO (Figure 12). Figure 4.5 (c) shows the XPS survey spectra of silica in the presence of lead and sulphate ions and reveals no sulphur (characteristic peak at 168-171 eV for sulphate group). The spectra, in fact is similar to that for silica and Pb with no sulphate (Figure 4.5 (b)).

Figure 4.5 Survey XPS spectra from silica surface: (a) Silica alone pH=10 (NaOH); (b) treated with 10^{-4} M lead nitrate; (c) surface (b) treated with 10^{-4} M sodium sulphate; (d) treated with 10^{-4} M lead nitrate and 10^{-2} M sodium bicarbonate; (e) treated with 10^{-4} M lead nitrate, 10^{-2} M sodium bicarbonate and 1M bicarbonate; (f) surface (c) treated with 10^{-4} M bicarbonate; (g) surface (f) treated with 10^{-2} M bicarbonate.

4.1.3 $\text{Pb}^{2+} / \text{CO}_3^{2-}$

The zeta potential of PbCO_3 (Figure 4.6) shows a moderate negative charge over the pH range 7-11. The increase in zeta potential above pH 10 may indicate formation of Pb hydroxy species which are positively charged at this pH (Figure 2.10). The zeta potential of silica in 10^{-4} M Pb and CO_3^{2-} is similar to that of lead carbonate or lead hydroxy carbonate (Figure 2.10), suggesting the presence of these compounds on the surface. Increasing the carbonate concentration tends to return the zeta potential to the original values in the absence of lead.

Figure 4.6 Zeta potential of silica as a function of pH in the presence of 10^{-4} M of Pb^{2+} and different concentrations of CO_3^{2-}

SEM micrographs of the silica at pH 10 in the presence of 10^{-4} M to 1 M CO_3^{2-} are given in Figures 4.7 and 4.8 (a) and (b). Compared to 10^{-4} M and 10^{-2} M, it is evident that at 10^{-1} M carbonate, the silica surface is practically free of precipitates and at 1 M CO_3^{2-} entirely free. The restoration of the original Pb-free silica zeta potential at high $[\text{CO}_3^{2-}]$ may be related to dispersion: the $\text{PbCO}_3/\text{Pb}_2(\text{OH})_2\text{CO}_3$ and silica are mutually repelled and the surface is cleaned of precipitates. This is a different explanation to that of Herrera-Urbina and Fuerstenau (1987) who argued that HCO_3^- specifically adsorbs on PbCO_3 -coated silica which therefore becomes more negative as $[\text{CO}_3^{2-}]$ increases (Figure 2.11).

Rather than electrical effects, another explanation might be that by increasing the carbonate ion concentration, nucleation becomes more important than growth thus promoting generation of lots of nuclei and resulting in small precipitates. The precipitates were visibly smaller at high $[\text{CO}_3^{2-}]$ (Figure 4.2) and may consequently be readily dispersed.

A third possibility may be an effect of concentration on the solubility of the precipitate. At high carbonate concentration, concentrations should be replaced by activities in the K_{sp} equation, i.e.,

$$K_{sp} = a_{\text{CO}_3^{2-}} \cdot a_{\text{Pb}^{2+}} = [\text{CO}_3^{2-}] f_{\text{CO}_3^{2-}} \cdot [\text{Pb}^{2+}] f_{\text{Pb}^{2+}} \quad (4-1)$$

The higher the concentration of carbonate, the higher is the ionic strength, I , and the lower is the activity coefficient, f , which decreases exponentially with I (Skoog and Leary, 1992).

At very high carbonate concentration, both activity coefficients become considerably lower

than unity. As K_{sp} is a constant, $[Pb^{2+}]$ will be greater than what is expected from eq. (2-2) and therefore the solubility increases.

In Figure 4.5, XPS surveys (d) and (e) show the spectra of silica in the presence of lead and 10^{-2} M and 1M carbonate, respectively. Spectrum (d) shows the $4f_{7/2}$ and $4f_{5/2}$ peaks of lead (at 135 and 140 eVs, respectively) with a lower intensity than in spectra (b) and (c) which means some of the lead-containing precipitate has gone. Spectrum (e), shows no characteristic peak for lead, i.e. the surface has been cleaned in agreement with the SEM micrographs.

4.1.4 $Pb^{2+} / SO_4^{2-} / CO_3^{2-}$

Figure 4.9 shows the zeta potential of silica in the presence of lead and sulphate ions and 10^{-4} M CO_3^{2-} . The zeta potential is almost identical to that of $PbCO_3$ or lead hydroxy carbonate (Figure 2.10). This implies that lead sulphate has been transformed to either of these compounds, which is expected from their relative solubilities (Table 2.1). By adding carbonate in excess of the stoichiometric requirement (to form $PbCO_3$), the zeta potential value moved closer to that of silica alone as was the case in Figures 4.7 and 4.8. Again, with high $[CO_3^{2-}]$ the surfaces became cleaned of precipitates.

Figure 4.5 (f) shows that the lead peaks are present in the system with 10^{-4} M carbonate but in spectrum (g) with 10^{-2} M carbonate, there is no lead peak. These observations are consistent with the SEM and zeta potential results.

(a)

(b)

Figure 4.7 SEM (BS) micrograph of silica at pH=10 (NaOH): (a) in the presence of 10^{-4} M Pb^{2+} and CO_3^{2-} , (b) in presence of 10^{-4} M Pb^{2+} and 10^{-2} M CO_3^{2-}

(a)

(b)

Figure 4.8 SEM (BS) micrograph of silica at pH=10 (NaOH): (a) in the presence of 10^{-4} M Pb^{2+} and 10^{-1} M CO_3^{2-} , (b) in presence of 10^{-4} M Pb^{2+} and 1M CO_3^{2-}

Figure 4.9 Zeta potential of silica in the presence of 10^{-4} M of Pb^{2+} and SO_4^{2-} and 10^{-4} M of CO_3^{2-}

4.2 Calcium System

4.1.2 Ca^{2+}

Zeta potential of silica in the presence of calcium ions (from $\text{Ca}(\text{NO}_3)_2$) is shown in Figure 4.10. At pH above ca 6, the zeta potential increases, and at 10^{-2} M Ca^{2+} above pH ca 10, the sign of the charge reverses. The principal adsorbing species is probably Ca^{2+} by reference to the stability diagram (Figure 2.4).

Figure 4.10 Zeta potential of silica in the presence of different concentrations of Ca^{2+} at pH=10 (NaOH)

4.2.2 $\text{Ca}^{2+} / \text{SO}_4^{2-}$

Figure 4.11 gives the zeta potential vs pH for CaSO_4 , and for silica alone and in the presence of 10^{-2} Ca and SO_4^{2-} . The zeta potential of CaSO_4 confirms the two pH_{iep} values (ca 2 and 10) reported in the literature (Figure 2.14). After addition of 10^{-2} M calcium and sulphate ions the zeta potential of silica approached that of CaSO_4 (Figure 4.11), although the SEM micrograph did not show evidence of any precipitate formation (Figure 4.12a).

The experiment was repeated at higher concentration of ions. At 2×10^{-2} M again, no precipitate was evident. At 5×10^{-2} M, as seen in Figure 4.12b, needle shaped precipitates of

calcium sulphate formed, but the surface of silica remained clean.

Figure 4.11 Zeta potential of silica as a function of pH in the presence of 10^{-2} M Ca^{2+} and SO_4^{2-}

One possible reconciliation between the zeta potential measurements, implying adsorption of a Ca-related species, and the surface remaining clean is that Ca is present as the same species as in the absence of SO_4 , i.e. probably Ca^{2+} . Comparison of Figures 4.10 and 4.11 (Figure 4.13), does reveal it is difficult to distinguish the zeta potential in the Ca only case, from the Ca/ SO_4 system. Other possibilities are that a film of CaSO_4 formed which is not detected by the SEM image, or the sample preparation procedure for the SEM removed the Ca species.

(a)

(b)

Figure 4.12 SEM (BS) micrograph of silica at pH=10 (NaOH): (a) in presence of 10^{-2} M Ca^{2+} and SO_4^{2-} . (b) in presence of 5×10^{-2} M Ca^{2+} and SO_4^{2-} .

Figure 4.13 Comparison between zeta potential of Ca, Ca/SO₄ and CaSO₄

Figure 4.15 (c), (d) and (e) show the XPS surveys in the presence of different concentrations of calcium and sulphate ions. At low concentration (surveys c & d), there is no Ca_{2p_{3/2}} peak at 348 eV (Ca in CaSO₄), suggesting that calcium sulphate was not present on the surface, consistent with the SEM results. At higher concentration (5×10^{-2} M) the silicon peaks are gone (Figure 4.15e). This may suggest a coating but given the large amount of calcium sulphate precipitate formed compared to the quantity of silica present (Figure 4.12 b), the absence of silicon peaks may simply mean the CaSO₄ is the dominant solid in the sample.

The XPS results therefore, are not conclusive but are consistent with the suggestion that calcium precipitates are not present on the silica. The tentative conclusion at this stage is that

a Ca species, probably, Ca^{2+} , enters the double layer but does not adsorb on the surface as it is neither potential determining nor specifically adsorbed.

4.2.3 $\text{Ca}^{2+}/\text{CO}_3^{2-}$

The zeta potential of silica in the presence of $2 \times 10^{-2} \text{ M}$ of Ca^{2+} and CO_3^{2-} ions (Figure 4.14) shows values similar to calcium carbonate. Some caution is required in making the comparison as the zeta potential of calcium carbonate is known to depend on factors such as aging and mixing conditions (Figure 2.13). The SEM micrograph (Figure 4.16) shows precipitates on the surface, and Figure 4.15f shows both 'carbon in carbonate' and calcium peaks that confirm the presence of calcium carbonate on the surface.

Figure 4.14 Zeta potential of silica as a function of pH in the presence of $2 \times 10^{-2} \text{ M}$ Ca^{2+} and CO_3^{2-}

Figure 4.15 Survey XPS spectra: (a) Silica alone pH=10 (NaOH); (b) treated with 10^{-1} M calcium nitrate; (c) treated with 10^{-2} M calcium nitrate and sodium sulphate; (d) treated with 2×10^{-2} M of the previous salts; (e) treated with 5×10^{-2} M of the previous salts; (f) treated with 10^{-2} M of calcium nitrate and sodium bicarbonate; (g) treated with 10^{-2} M of calcium nitrate and sodium sulphates and 10^{-1} M bicarbonate.

(a)

(b)

Figure 4.16 SEM (BS) micrograph: silica in the presence of 10^{-2} M Ca^{2+} and CO_3^{2-} at pH=10 (NaOH), (a) 600 times magnification, (b) 2000

4.2.4 $\text{Ca}^{2+} / \text{SO}_4^{2-} / \text{CO}_3^{2-}$

Figure 4.17 shows the zeta potential of silica in the presence of all three ions. The zeta potential is almost identical to that in the Ca/CO_3 system, suggesting the same species, CaCO_3 , is present (as anticipated from the relative solubilities of CaCO_3 and CaSO_4 (Table 2.1). This result was supported by SEM (Figure 4.18), which suggested the presence of the same precipitate as in Figure 4.16, and confirmed by XPS which showed no evidence of sulphur (Figure 4.15).

Figure 4.17 Zeta potential of silica as a function of pH in the presence of 10^{-2} M Ca^{2+} and SO_4^{2-} and 2×10^{-2} M CO_3^{2-}

Figure 4.18 SEM (BS) micrograph: silica in the presence of 10^{-2}M Ca^{2+} and SO_4^{2-} and $2 \times 10^{-2}\text{M CO}_3^{2-}$ at $\text{pH}=10$ (NaOH)

The zeta potential of silica in the presence of excess carbonate ions is presented in Figure 4.19. As can be seen, the surface charge was insensitive to $[\text{CO}_3^{2-}]$. The SEM confirmed that CaCO_3 precipitates remained on the surface (Figure 4.20) and they became more crystalline compared with precipitates formed at lower carbonate concentration (Figure 4.18). Figure 4.15g reveals calcium and 'carbon in carbonate' peaks, which further support the SEM and zeta potential results.

Figure 4.19 Zeta potential of silica in the presence of 10^{-2} M Ca^{2+} and SO_4^{2-} and increasing concentrations of CO_3^{2-}

Figure 4.20 SEM (BS) micrograph: silica in the presence of 10^{-2} M Ca^{2+} and SO_4^{2-} and 5×10^{-2} M CO_3^{2-} at pH=10 (NaOH)

4.3 Morphology of calcium carbonate precipitates

Increasing the concentrate of carbonate ions changes the morphology (shape) of the precipitates. Figure 4.21 shows carbonate precipitates in the presence of 10^{-1} and 1M CO_3^{2-} . Comparing with Figures 4.18 and 4.20, it can be seen that at $2 \times 10^{-2}\text{M}$ CO_3^{2-} (Figure 4.18), the precipitates are approximately spherical, while at $5 \times 10^{-2}\text{M}$ (Figure 4.20), they become more cubic which remains the case upto 1M . Figure 4.21 also shows clearly that from 10^{-1} to 1M the precipitate size decreases, probably reflecting the effect of concentration discussed in section 2.4.1.2b.

4.4 Changing the order of adding SO_4^{2-} and CO_3^{2-}

Figure 4.22 shows the SEM micrograph of silica in the presence of carbonate with subsequent addition of sulphate ions. From XPS, the precipitates do not contain any sulphur, therefore, the concentration of carbonate was enough to keep the calcium as calcium carbonate. It can be concluded that the most important parameter is the solubility of the salts, and the order of the ion addition is not important with regard to chemical composition. Figure 4.22b shows that the shape of precipitates are different from that in Figure 4.16b with the same magnification. This might be due to changing the order of adding reagents, since kinetic growth factors can be affected by the presence of other substances as Dirksen and Ring (1991) indicate in the case of ionic and non-ionic surfactants.

(a)

(b)

Figure 4.21 SEM (BS) micrograph: silica in the presence of 10^{-2} M Ca^{2+} and SO_4^{2-} and
(a) 10^{-1} M CO_3^{2-} , (b) 1M CO_3^{2-}

(a)

(b)

Figure 4.22 SEM (BS) micrographs of silica in the presence of 10^{-2} M calcium and carbonate and then 10^{-1} M sulphate ions (a) 600 times magnification, (b) 2000, (c) 5000

Figure 4.22 (c)

4.5 Significance to flotation

The practical drive behind this study was to try to interpret the interaction between sulphate precipitates and minerals and the effect of adding carbonate. The immediate observation is that the Pb and Ca systems are different in two ways: precipitates form on silica in the Pb/SO₄ system but not in Ca/SO₄ case; and addition of sufficient carbonate “cleans” the surface of precipitates in the case of lead but not in the case of calcium. This introduces some new insight into the possible effect of these precipitates on flotation.

The conventional explanation of the effect of adding carbonate is to remove sulphate coatings and create dispersing conditions, for example as discussed in the analysis of the Hilton circuit (2.4.2.2). The hypothesis appears to hold for lead but not for calcium. The work here on silica has shown that calcium sulphate is not present on the surface while calcium carbonate

is and that the system is not notably dispersed at elevated carbonate levels. The positive effect on flotation of adding carbonate in some systems, however, is well recognized. The following interpretation is offered. The species having the effect on flotation is the calcium ion itself. Calcium sulphate is sufficiently soluble ($\sim 2\text{g/L}$) that even when it forms several hundred ppm of calcium remains in solution. The zeta potential results show it is not easy to distinguish the effect of Ca alone from when CaSO_4 is present. In contrast, calcium carbonate is much less soluble. The effect of adding carbonate, therefore, may be to form a precipitate which collects most of the calcium, effectively removing it from solution and eliminating any interaction with the mineral. That some carbonate precipitates remain on the surface may not be as important as the fact that the rest of the surface has been "cleaned" of calcium leaving it free to interact with flotation agents. To test if this hypothesis is a general one, it will be necessary to examine a sulphide substrate. In translating the results to flotation practice since in many sulphide systems both lead and calcium are present, it will be necessary to distinguish between these two species as they appear to respond differently to the presence of sulphate and to the addition of carbonate.

If depression of silica is the target, increasing carbonate levels could be advantageous, as possible activating metal ions may become dispersed as carbonate precipitates. Any calcium carbonate precipitates that remain on the surface would act as hydrophilic sites and tend to depress the silica.

CHAPTER 5

CONCLUSIONS AND SUGGESTIONS

FOR FUTURE WORK

5.1 Conclusions

5.1.1 Pb System

- 1) Over the pH range 6-11, lead sulphate is slightly positively charged, lead carbonate moderately negatively charged.
- 2) The zeta potential and SEM results show that both carbonate/hydroxy carbonate and sulphate precipitates form on silica, but at pH=10 the sulphate precipitates are unstable and transform to oxide/hydroxide, as confirmed by XPS.
- 3) At pH=10, the precipitate in the presence of lead and sulphate is the same as in the presence of lead alone (lead oxide/hydroxide).

- 4) Lead oxide/hydroxide precipitates are replaced by carbonates/hydroxy carbonates, and at high $[\text{CO}_3^{2-}]$ the precipitates become sufficiently negatively charged to disperse and the silica surface becomes clean. There may be other contributing factors for precipitate removal at high $[\text{CO}_3]$ related to generation of nuclei rather than precipitate growth being favoured and increased solubility of lead precipitates.

5.1.2 Ca system

- 1) For the experimental conditions here, calcium sulphate and carbonate have similar zeta potentials, with a maximum around -20 mV.
- 2) In the Ca/SO_4 system, the results suggest adsorption of calcium ions as in the absence of SO_4 ; the surface remained free of CaSO_4 precipitates. The zeta potential of Ca and Ca/SO_4 are also similar.
- 3) In the Ca/CO_3 system, CaCO_3 precipitates formed on the silica surface, and unlike the Pb/CO_3 case, did not all disperse at high $[\text{CO}_3^{2-}]$.
- 4) In the $\text{Ca}/\text{SO}_4/\text{CO}_3$ system, with sufficient CO_3 the results were the same as for the Ca/CO_3 system.
- 5) In the calcium system, from 10^{-1} to 1M the precipitate size decreases, i.e., the high initial supersaturation leads to a high nucleation rate.

5.2 Suggestions for future work

- 1) A study of lead and calcium sulphate precipitates should be performed in sulphide

mineral systems

- 2) More work needs to be done on investigating the role of Ca and/or CaSO_4 in these systems, to define the effect on flotation.
- 3) The role of pulp potential should be included to help further determine the ionic species present and determine any contribution to the adsorption mechanism.
- 4) Beside Pb and Ca, studying the effect of other cations, e.g., Mg is suggested.
- 5) It has been observed (Baker and Judd, 1996) that magnetic and electric fields can affect the morphology of CaCO_3 , and this may open a new method of fundamental study, and perhaps even of control in practice.
- 6) A study of the size distribution of precipitates by laser diffractometry is also suggested.

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1653 East Main Street
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Phone: 716/482-0300
Fax: 716/288-5989

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