DEACTIVATION OF Pb-CONTAMINATED SPHALERITE BY POLYPHOSPHATE

by

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In the name of God

Dedicated to

my parents, my dear husband Navid,

and my children, Kourosh and Soroush

ABSTRACT

Activation of sphalerite by lead ions in the presence of ethyl xanthate was investigated by microflotation, zeta potential measurements, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and extraction by ethylenediaminetetraacetate (EDTA). The source of lead, either from solution or contact with galena particles, proved immaterial. From EDTA extraction data flotation response was determined as a function of surface concentration of Pb ($[Pb]_{surf}$, mg/cm^2). A critical $[Pb]_{surf} \approx 0.5 \times 10^{-4}$ mg/cm^2 causing activation was estimated. By combining with a Pb ion production model from the literature, the possibility of Pb activation for an ore of given Pb grade was explored. Ores with as little as 0.1% Pb are candidates for accidental activation.

A mechanism of lead interaction is proposed: at weakly acidic to mildly alkaline conditions Pb^{2+} and $PbOH^+$ adsorb on sphalerite and react with xanthate to form PbX_2 and $Pb(OH)X$; at high pH, hydrophilic $Pb(OH)_{2(s)}$ precipitates depress flotation.

Various candidate deactivators were compared using microflotation. The reagents were diethylenetriamine (DETA), sodium bicarbonate ($NaHCO_3$), silica sol (SS), sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) and sodium polyphosphate $(NaPO_3)_n$. The latter had the strongest effect and was selected for detailed study. The mechanism of polyphosphate action was investigated by SEM and XPS. The results show that polyphosphate acted to remove Pb ("clean") from the sphalerite by forming soluble complexes.

The polyphosphate (PP) to lead (Pb) ratio in the complexes was determined from conductometric titration of lead nitrate vs. polyphosphate. It was found that initially a precipitate formed with PP/Pb of 1/3. The precipitate dissolved in excess polyphosphate, resulting in a variety of complexes with PP/Pb of 1/2, 1/1, 3/2, 2/1, and 3/1. Knowing the amount of Pb to be removed and taking the lowest PP/Pb ratio, 1/2, the quantity of polyphosphate required to solubilize the Pb can be calculated.

RÉSUMÉ

L'activation de la sphalérite par des ions plombs en présence d'éthyle de xanthate a été étudiée au moyen de la microflottation, de mesures de potentiel zeta, de microscopie électronique à balayage (MEB), de spectroscopie photoélectronique-X (SPX) et de l'extraction à l'acide éthylène-diamine-tétraacétique (EDTA). L'effet des ions plomb est le même, quelque soit leur origine, la solution ou un contact avec les particules de galène. La récupération à la flottation a été déterminé en fonction de la concentration d'ions Pb à la surface ($[Pb]_{surf}$, mg/cm^2), déterminée par extraction avec l'EDTA. Nous avons estimé la concentration critique au-dessus de laquelle il y a l'activation à $[Pb]_{surf}$ _ 0.5×10^{-4} mg/cm^2. En combinant ces résultats avec un modèle de production d'ions Pb tiré d'une publication, nous avons évalué quelle teneur minimum en plomb pouvait causer l'activation de la sphlérite par des ions Pb. Des minerais comportant aussi peu que 0.1% de Pb sont candidats à une activation accidentelle.

Nous suggérons un mécanisme pour l'interaction des ions Pb: sous des conditions moyennement acidiques à moyennement alkalines, Pb^{2+} et $PbOH^{+}$ sont adsorbés sur la surface de la sphalérite et réagissent avec le xanthate pour former du PbX_2 et du $Pb(OH)X$; lorsque le pH est élevé, l'aptitude à la flottation est abaissée par les précipités hydrophiliques de $Pb(OH)_{2(s)}$ qui se forment à la surface.

L'efficacité de plusieurs candidats déactiveurs a été déterminée utilisant la microflottation :

le diéthylènetriamine (DETA), le bicarbonate de soude ($NaHCO_3$), les sols de silice (SS), le phosphate de sodium ($Na_3PO_4 12H_2O$) et le polyphosphate de sodium ($(NaPO_3)_n$). Ce dernier, ayant un effet plus prononcé, fut choisi pour une étude plus détaillée. Nous avons étudié le mécanisme de l'action du polyphosphate par MEB et SPX. Les résultats démontrent que le PP agit en "nettoyant" les ions Pb de la surface par formation de complexes solubles.

Nous avons déterminé le ratio de polyphosphates/plomb (PP/Pb) dans les complexes solubles à l'aide de titrations conductométriques au nitrate de plomb. Un précipité initial fut formé à un ratio PP/Pb de 1/3. Le précipité est dissout lorsqu'un excès de polyphosphate est ajouté, par la formation d'une variété de complexes avec des ratios PP/Pb de 1/2, 1/1, 3/2, 2/1 et 3/1. Nous pouvons calculer la quantité minimale de polyphosphate requise pour extraire une certaine quantité de plomb de la surface de la sphalérite, en utilisant le plus petit ratio PP/Pb de 1/2.

CONTRIBUTION OF AUTHORS

This thesis was prepared in accordance with article C of the Guidelines Concerning Thesis Preparation of McGill University. This article reads as follows:

> "Candidates have the option of including, as part of the thesis, the text of one or more papers submitted, or to be submitted, for publication, or the clearly-duplicated text (not reprints) of one or more published papers of which the student is the author or co-author. These texts must be bound together as an integral part of the thesis.
> -The thesis must be more than a collection of manuscripts. All components must be integrated into a cohesive unit with a logical progression from one chapter to the next. In order to ensure that the thesis has continuity, connecting texts that provide logical bridges between the different papers are mandatory.
> -The thesis must conform to all other requirements of the "Guidelines for Thesis Preparation" in addition to the manuscripts. The thesis must include: a Table of content, an abstract in English and French, an introduction which clearly states the rationale and objectives of the research, a comprehensive review of the literature (in addition to that covered in the introduction to each paper), a final conclusion and summary.
> -As manuscripts for publication are frequently very concise documents, where appropriate, additional material must be provided (e.g., in appendices) in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.
> -In general, when co-authored papers are included in a thesis the candidate must have made a substantial contribution to all papers included in the thesis. In addition, the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extent. This statement should appear in a single section entitled "Contributions of Authors" as a preface to the thesis. The supervisors must attest to the accuracy of this statement at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to clearly specify the responsibilities of all the authors of the co-authored papers."

The following are manuscripts written by the author and were used in preparation of this thesis. Manuscript 1 comprises Chapter 2, and manuscripts 2, 3, and 4 make up Chapters 4, 5, and 6, respectively.

1. **Fereshteh Rashchi and James A Finch**, "Polyphosphates: A review; Their Chemistry and Application with Particular Reference to Mineral Processing", accepted by *Minerals Engineering*.

2. **Fereshteh Rashchi, Caroline Sui, and James A. Finch**, "Sphalerite Activation and Surface Pb Ion Concentration", to be submitted to *International Journal of Mineral Processing*.

3. **Fereshteh Rashchi, Caroline Sui, and James A. Finch**, "Deactivation of Pb-Contaminated Sphalerite by Polyphosphates", to be submitted to *Colloids and Surfaces*.

4. **Fereshteh Rashchi and James A. Finch**, "Lead-Polyphosphate Complexes", to be submitted to *Canadian Metallurgical Quarterly*.

All of the manuscripts presented above are co-authored by Dr. James Finch in his capacity as research supervisor. Manuscripts 2 and 3 include Dr. Caroline Sui (formerly of the department of Mining and Metallurgical Engineering, McGill University) as co-author, recognising her as the project manager of the "Prevention of Zinc Activation" project and her assistance in the interpretation of the metallurgical aspects of the results. Beyond the contributions of the co-authors mentioned, all of the work presented in this dissertation was performed by the author.

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CHAPTER 1

INTRODUCTION

Activation of minerals in flotation has been the subject of widespread investigation and abundant documentation. To help the reader the following terminology will be used in this thesis. *Activation* is a process whereby the surface of a mineral particle is modified to make it more reactive with a collector. *Depression* is a process whereby the surface of a particle is modified to render it more wettable by water and/or less reactive with a collector. *Deactivation* is a special case of depression whereby the process of activation is reversed. Typically these processes involve addition of a chemical reagent, namely an activator, depressant and deactivator, respectively.

Sphalerite (Zn,Fe)S is the most important mineral source of zinc. Sphalerite is invariably associated with other sulphide minerals such as galena, chalcopyrite and iron sulphides (pyrite, and pyrrhotite). Sphalerite flotation technology, therefore, has focused on separation from these minerals. A common approach to processing such ores is first to recover chalcopyrite and galena under moderately alkaline conditions, with simultaneous depression of sphalerite and iron sulphides by addition of one or a combination of sulphur dioxide, cyanide, or zinc sulphate. Sphalerite is subsequently activated with copper sulphate in a pulp made alkaline with lime and floated with a xanthate collector. In practice, separation does not always achieve acceptable results. Minerals can be misplaced due to inadequate liberation, mechanical entrainment, entrapment, and true flotation.

Inadequate liberation (locking) in this context refers to composite particles such as galena/sphalerite reporting to a Pb-concentrate. Control of locking requires further size reduction. The ore has to be reduced in size so that the valuable minerals occur as so-called liberated or free particles. Complete liberation is seldom achieved, even if the ore is ground to a size well below the grain size of the desired mineral. An economic optimum degree of size reduction has to be found.

Entrainment occurs when particles enter the froth with the slurry carried in the bubble wake. The mechanism is preferential to fine particles which do not have time to settle out as the bubble rises into the froth. Control of entrainment is usually through use of cleaning stages, froth washing (e.g., as in flotation columns) and feed pulp dilution. Entrainment and locking should be quantified before other misplacement mechanisms are considered.

Entrapment refers to particles trapped in agglomerates which report to the froth product. Sphalerite could, for example, become entrapped in agglomerates containing galena and/or chalcopyrite and thus report to the wrong concentrate.

True flotation refers to direct attachment of particles to bubbles, i.e., particles are hydrophobic. Generally, this involves mineral reaction with collectors. However, hydrophobicity may be imparted without collectors. Some minerals such as molybdenite (MoS_2) are hydrophobic because they have a non-polar structure. The common term for this is natural hydrophobicity (or floatability). Sulphide minerals may become floatable due to build up of oxidation products, so-called collectorless (or self-induced) floatability. Chalcopyrite is the best documented example, including evidence of collectorless flotation under plant conditions (Leroux et al., 1994). Early explanations (Gardner and Woods, 1979; Buckley and Woods, 1982) favoured elemental sulphur as the oxidation product but more recent works have argued for a metal-deficient surface lattice (e.g., Buckley et al., 1985, 1989; Buckley and Walker, 1988) or a polysulphide (Kartio et al., 1996) as the cause of hydrophobicity. Sphalerite usually does not exhibit collectorless floatability although there is some evidence after Cu-activation (Harris and Richter, 1985; Prestidge et al., 1994; Lascelles et al., 2000).

Sphalerite does not normally respond to collectors like short-chain xanthates. The usual practice is to activate by addition of Cu ions. Other metal ions, notably Pb and Fe(II), can activate as well (Finkelstein, 1997, 1999). The possibility of "accidental activation" by metal ions, therefore, is often suspected when sphalerite reports to the wrong concentrate. Activation by contaminant ions is readily demonstrated under laboratory conditions (Houot and Raveneau, 1992) and there is circumstantial evidence from plant surveys (Kim and Chryssoulis, 1996).

Contaminant metal ions may come from recycle and process waters, from impurities in the sphalerite lattice (Finkelstein and Allison, 1976; Mielczarski, 1986), or from oxidation of and subsequent transfer from other minerals (e.g., Cu from chalcopyrite and Pb from galena).

When sulphide minerals are exposed to oxygen and water during mining and processing various surface species are formed. Some are detected as released metal ions in the pulp but the bulk are hosted on mineral surfaces and become evident only through direct surface analysis, e.g., X-ray photoelectron spectroscopy (XPS), or indirect analysis such as extraction by chelating agents, for example ethylenediaminetetraacetate (EDTA). The species are mobile, indiscriminately spreading to and contaminating most mineral surfaces.

A common potential activating ion is Pb released during oxidation of (mainly) galena (Rey and Formanek, 1960; Houot and Ravenau, 1992; Basilio et al., 1996). Lead ions are readily produced from oxidation of fine galena, a process enhanced by galvanic interaction with noble metal sulphides, particularly pyrite (Sui et al., 1995; 1999a). For example, Sui et al (1999a) found that for particles < 10 μm more than 10% of Pb relative to the bulk Pb in galena became EDTA extractable (a measure of lead ion production). This experience mirrors that in the plant. Kant et al. (1994) in a survey of Cu rougher flotation, Greet et al. (1994) on Pb roughers, and Sui et al. (1999a) on Zn roughers all indicate that high Pb ion production is the rule rather than the exception. However, the connection between the amount of Pb ion produced and the amount of Pb ion which can cause activation remains to be explored.

Little emphasis is placed on lattice impurities in accidental activation. Recently, Zielinski et al. (2000) investigated the influence of lattice-iron on sphalerite misplacement. They studied lead flotation circuit products from three concentrators, Red Dog, Sullivan and Polaris. They found that the iron content in liberated sphalerite reporting to the lead concentrate was lower than that of the feed. They considered the possibility that high-iron sphalerite was more readily oxidized which could lead to formation of potential metal ion adsorption sites, while less oxidizable low-iron sphalerite could still adsorb activating metal ions. That is, accidental activation was still considered the probable cause of misplacement but the phenomenon appears to be sensitive to the Fe-content of the sphalerite.

There are two main ways, in principle, that accidental activation could be countered: prevention and treatment. Prevention could involve preventing either metal ion generation or subsequent adsorption, and treatment could involve either removing the ions from surfaces (a "cleaning" action) or forming a reaction product with the metal ion that prevents reaction with collector (a "blocking" action).

Preventing lead ion generation suggests the use of reducing reagents early in the process, for instance in the grinding stage. The addition of sulphite to create reducing conditions and consume oxygen thereby retarding sulphide oxidation is one possibility. Another is to sequence grinding and flotation to remove galena early in the process and thus limit the extent of size reduction and exposure to air. Both strategies have been used to effect (Nesset, 2000).

To remove (or "clean") contaminating species from surfaces, the methods can be divided into two groups, mechanical and chemical. The former include sonication and attrition (e.g., as in high intensity conditioning), and the latter, the addition of certain reagents.

At sufficient concentration carbonate seems to work by a cleaning action through formation of metal carbonates which are negatively charged and disperse from the surface (Rashchi et al., 1998; Sui et al., 1998). An example of a complexing agent in a cleaning role is diethylenetriamine (DETA). It is employed in the depression of pyrrhotite and partly functions by removing copper and nickel ions from the surface (Marticorena et al., 1995; Xu et al., 1997; Yoon et al., 1995). (This action is not general, however; Sui et al. (1997) found that Pb was not removed from the surface of pyrite by DETA.) Adapting water treatment agents to this role, e.g. activated carbon and silica sols, suggests another option, but such agents must be able to remove adsorbed species to function as "cleaning" agents. Cyanide is employed to deactivate copper activated sphalerite through the formation of soluble copper(I) cyanide complexes, e.g., $Cu(CN)_3^{2-}$ (Gaudin et al., 1959; Prestidge et al., 1997). Prestidge et al. proposed a mechanism for cyanide deactivation of copper(II) activated zinc sulphide. The mechanism depended on the form of copper at the activated zinc sulphide surface which, in turn, was controlled by the activation mechanism. They suggested that cyanide removes copper hydroxide and copper polysulphide species from the surface of copper (II) activated zinc sulphide, as no surface cyanide complexes were detected.

The process where a reagent forms a surface species that is hydrophilic and prevents subsequent reaction with collector is referred to as a blocking action. Cyanide depression of pyrite may fall in this category through formation of iron cyanide species on the surface (Elgilliani and Fuerstenau, 1968). Another process exploiting a blocking mechanism would be to elevate pH and form metal oxide/hydroxide layers. These products are hydrophilic and their presence reduces the number of sites for xanthate adsorption. For example, as the pH is increased above 10.7, oxidation of galena to plumbate ($HPbO_2^-$) is favoured over that of lead xanthate formation. Several researchers have suggested that when zinc sulphate is added, hydrophilic zincate ions, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$, adsorb on sphalerite and prevent xanthate uptake (Finkelstein and Allison, 1976).

Dextrin is a depressant of sulphide minerals with a blocking action (Liu and Laskowski, 1989a; 1989b; 1989c). Dextrin, which is hydrophilic, is anchored to the mineral system via metal hydroxy species. Liu and Laskowski (1989c) reported that dextrin aided in depressing galena in chalcopyrite flotation; pentlandite (Lukkarinen, 1962) and heazlewoodite (Laskowski and Nyameke, 1994) can also be depressed by dextrin.

The reagent class of interest here as a possible deactivator to counter to Pb activation of sphalerite is polyphosphates. These reagents readily complex with metal ions and could function by either a cleaning or blocking mechanism.

1.1 Objectives

The objectives of this thesis are, therefore:

1) To study the floatability of sphalerite activated by Pb
2) To propose a mechanism for Pb ion activation.
3) To link literature results on Pb production to sphalerite activation.
4) To study polyphosphates as a deactivator and propose a deactivation mechanism.

1.2 Structure of the Thesis

The thesis consists of seven chapters. Some of the chapters are in the style of a manuscript for publication (indicated as appropriate) so inevitably some repetition with earlier chapters occurs.

Chapter one introduces the problems encountered in selective flotation of sulphide minerals related to accidental activation by metal ions particularly lead. The objectives and structure of the thesis are presented.

Chapter two reviews the phosphate family of compounds, their chemistry, applications and potential uses in mineral flotation. This chapter, entitled "Polyphosphates: A review; Their Chemistry and Application with Particular Reference to Mineral Processing", by Fereshteh

Rashchi and James A. Finch has been accepted by *Minerals Engineering*.

Chapter three discusses the experimental techniques used including microflotation, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and conductometric titration.

Chapter four presents the results of investigations aimed at understanding the factors governing activation of sphalerite by Pb and relates flotation response to surface Pb ion concentration. The source of lead, either from solution or contact with galena particles, is considered. A mechanism of lead activation of sphalerite is proposed. By combining with a Pb ion production model proposed in the literature, the possibility of Pb activation of sphalerite for an ore of given Pb grade is discussed. This chapter, entitled "Sphalerite Activation and Surface Pb Ion Concentration", by Fereshteh Rashchi, Caroline Sui, and James A. Finch is to be submitted to *International Journal of Mineral Processing*.

Chapter five demonstrates the effect of different reagents as deactivators in the sphalerite-lead system. The reagents were diethylenetriamine (DETA), sodium bicarbonate ($NaHCO_3$), silica sol (SS), sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) and sodium polyphosphate $(NaPO_3)_n$. The latter was selected for detailed study. The mechanism of polyphosphate (PP) action was investigated by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). This chapter, entitled "Deactivation of Pb-Contaminated Sphalerite by Polyphosphates" by Fereshteh Rashchi, Caroline Sui, and James A. Finch is to be submitted to *Colloids and Surfaces.*

Chapter six presents the polyphosphate (PP) to lead (Pb) ratio in Pb-PP complexes determined from conductometric titration of lead nitrate solution with sodium polyphosphate. This chapter, entitled "Lead-Polyphosphate Complexes" by Fereshteh Rashchi and James A. Finch is to be submitted to *Canadian Metallurgical Quarterly.*

Chapter seven contains overall conclusions and recommendations for future work.

Appendix A discusses the effect of three reagents: DETA, dextrin, and carbonate as deactivators on Pb-contaminated sphalerite and pyrite through zeta potential and xanthate adsorption experiments. This appendix is a pilot study on the deactivation of sphalerite in which floatability is not considered, therefore, it is not included in the main body of the thesis.

Appendix B presents the lead species distribution diagrams at various initial Pb ion concentrations. The data shown in these diagrams are used in chapters 4 and 5.

Appendix C gives detail calculation for the amount of polyphosphate needed to control Pb activation.

Appendix D gives detail calculation for evaluating mean particle size from Gates-Gaudin-Schuhmann particle size distribution.

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CHAPTER 2

POLYPHOSPHATES : A REVIEW

2.1 Abstract

The phosphate family of compounds is reviewed. The IUPAC[1] nomenclature is used with reference to former names summarized as a glossary. Aspects of the chemistry of polyphosphates are introduced which may help identify potential applications of interest to the mineral engineer. General applications are described and current and possible uses in mineral flotation considered. The strong metal ion-polyphosphate complexes that form may find use in controlling metal ions in flotation which cause accidental activation/depression.

2.2 Introduction

The ability of phosphates to form soluble complexes with metal ions has been recognized for more than 160 years. Shortly after the discovery that there were several kinds of phosphates

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[1] International Union of Pure and Applied Chemistry

it was found that some of the chain phosphates had the ability to prevent precipitation or to dissolve precipitates of the alkaline earth metals (Van Wazer and Callis, 1958). Towards the end of the nineteenth century, this phenomenon was attributed to the formation of relatively stable soluble complexes between the metal and the phosphate. The formation of a soluble complex, whether by strong ion association or covalent bonding, had been speculated to interpret various chemical changes found in phosphate solutions. Soluble complex formation remains central to our understanding and exploration of phosphate chemistry.

Polymerization of primary sodium phosphate generates products under various names such as *Graham's salt*, *sodium hexametaphosphate*, *sodium metaphosphate*, and *sodium polyphosphate* (see "Glossary"). Because of their numerous uses, these products have been extensively studied over the last hundred and fifty years, with most advances made during the1940s and 1950s (Lamm, 1944; Samuelson, 1944; Van Wazer, 1950) when their true nature as linear, flexible, and poly disperse polyelectrolytes with average degrees of polymerization ranging up to 200 was recognized.

In this review, the chemistry of polyphosphates is considered including a comparison between chain and ring structures, hydrolysis, and sequestering of metal ions. Applications of polyphosphates are introduced with particular reference to the mineral industry and environmental applications. Literature on the mechanism of the interaction between phosphate modifiers and minerals is limited. As a starting point, it is useful to generalize some aspects of the chemistry of polyphosphates and to review our understanding of the interactions thus far. A glossary of terms with formulae is given at the end to assist the reader with what has become a very convoluted nomenclature. The IUPAC nomenclature for each structure is used with the common former name(s) given in the glossary, and included in the text in parenthesis when judged useful to the reader.

2.3 Classification of Phosphates

Phosphates are defined as compounds which contain P–O Linkages. The P–O bond has a length of 1.62 Å, with bond angles of 130° at the O atoms and 102° at the P atoms (Flory, 1969). The linear chain is illustrated in Figure 2.1. In this review the term "phosphate" will refer to compounds in which the P atoms are surrounded tetrahedrally by four oxygen atoms. Early nineteenth century observations that phosphoric acid and its salts could be transformed into various forms led Graham to his historic classification of phosphates into three types: orthophosphates, pyrophosphates and metaphosphates (Corbridge, 1990).

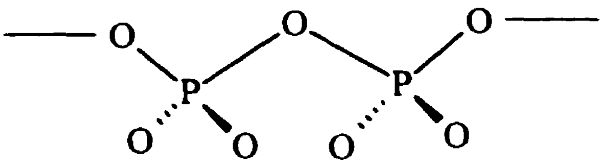


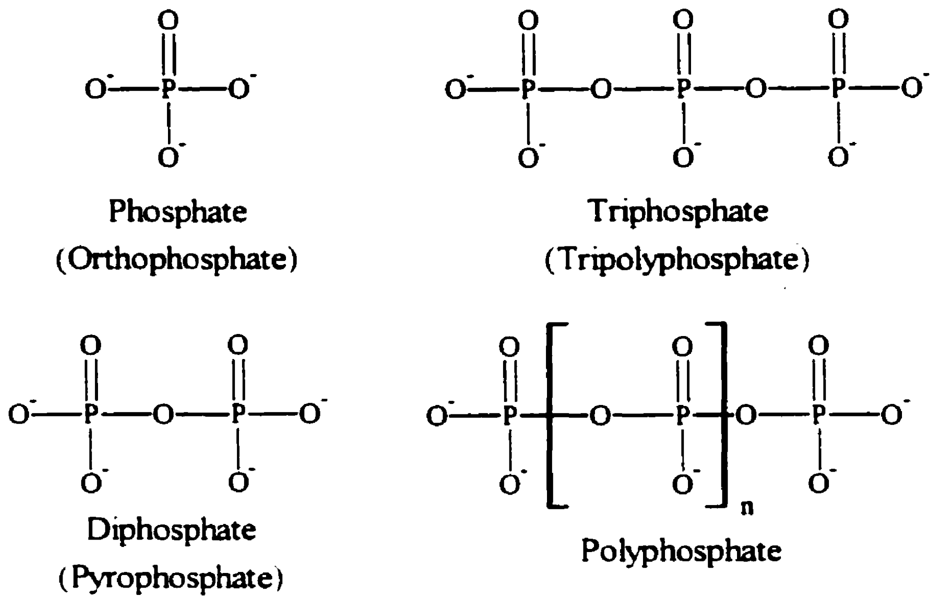
Figure 2.1 A polyphosphate chain.

Orthophosphates are compounds containing discrete PO_4^{3-} ions. The pyrophosphates and metaphosphates are now known as *condensed* phosphates, which are formed by repeated condensation (polymerization) of tetrahedral $[PO_4]$ units. This results in chains of tetrahedra, each sharing the O atom at one or two corners of the $[PO_4]$ tetrahedron. Diphosphate (pyrophosphate), $P_2O_7^{4-}$ is the simplest condensed phosphate anion, formed by condensation of two orthophosphate anions. The term metaphosphate refers to cyclic anions which have the exact composition $(PO_3)_n^{n-}$. In older literature, long chain polyphosphates are frequently referred to as metaphosphates because they have approximately the same composition. This discrepancy will be discussed later.

Due to their wide application, condensed phosphates were the subject of much investigation and controversy for over a century (Corbridge, 1990). These compounds are divided into three major categories: linear polyphosphates, cyclophosphates (metaphosphates), and ultraphosphates (cages, sheets, and 3-D structures). In this review, we will focus on linear polyphosphates and cyclophosphates.

2.3.1 Linear Polyphosphates

These compounds are salts of the linear polyphosphoric acids. Many polyphosphates are now known, although the alkali and alkaline earth salts have been most studied and at present find most application. Figure 2.2 shows some linear polyphosphates. The basic building unit is the orthophosphate ion (PO_4^{3-}). This can be considered the first member of the chain series, with the di- and triphosphate being the second and the third members, respectively.



Phosphate
(Orthophosphate)

Triphosphate
(Tripolyphosphate)

Diphosphate
(Pyrophosphate)

Polyphosphate

Figure 2.2 Linear polyphosphate ions

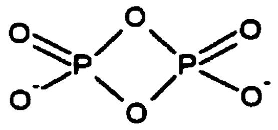
The lower members of the series, $n < 10$, and the most highly polymeric varieties (ca. $n = 50$ and higher) which approximate to the cyclophosphate composition form well-crystallized salts. On the other hand, varieties with intermediate chain lengths ($n = 10 \sim 50$) can usually be obtained only as mixtures in glasses (Corbridge, 1990). The long chain polyphosphates have caused confusion in the past, since they were originally called metaphosphates, a name used for ring compounds. When the number of units in the polymer n becomes very large, the formula of a chain polyphosphate $[(PO_3)_{n-1}\, PO_4]^{(n+2)-}$ becomes indistinguishable from that of a true metaphosphate, that is a ring compound with a formula $(PO_3)_n^{\,n-}$. The long chain compounds are sometimes called linear metaphosphates.

A considerable amount of work on the complexing of metal ions has been carried out with so-called vitreous sodium phosphates. These phosphate glasses consist of chain phosphates with a near-normal size distribution of chain length (Parks and Van Wazer, 1957). The average chain length, as measured by the number of phosphorous atoms per chain, ranges from 4.5 to ca. 18 for the commercial phosphate glasses. Glasses prepared in the laboratory can range from 3 to ca. 3000 phosphorous atoms per average chain.

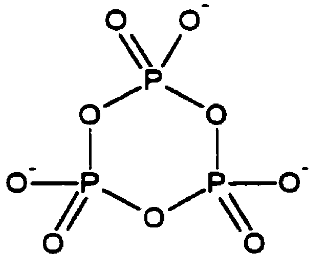
Graham's salt is the best known of the long chain polyphosphates, and is formed by quenching molten $NaPO_3$. It forms a glassy solid instead of crystallizing. In industry it is incorrectly called sodium hexametaphosphate. This is wrong because it does not contain six PO_3 units but is a high molecular weight polymer $(NaPO_3)_n$, which usually has a mean molecular weight of 12000-18000, and up to 200 PO_3 units in the chain. Though mainly composed of long chains, it does contain up to 10% of cyclophosphates (cyclic metaphosphates) and a little cross-linked material. Molecular weight of these long chain polymeric species can be determined by titrating the end groups, and also from osmotic pressure, diffusion, viscosity, electrophoresis, and ultracentrifuge measurements (Lee, 1996). Graham's salt is soluble in water. These solutions give precipitates with metal ions such as Pb^{2+} and Ag^{+}, but not with Ca^{2+} and Mg^{2+}.

2.3.2 Cyclophosphates

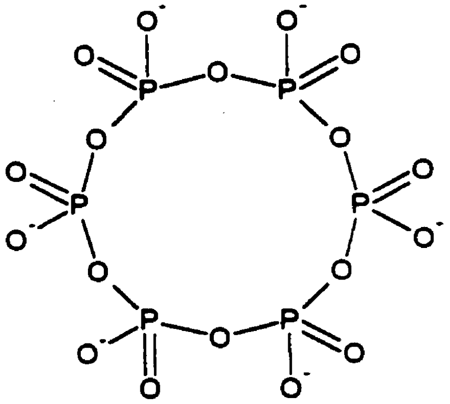
The cyclophosphates form a family of ring compounds. Figure 2.3 shows some of the ring polyphosphates. All simple ring anions have the true polyphosphate composition of $P_nO_{3n}^{n-}$ in which n can, in principle, have any value. The old name of metaphosphates (or sometimes



Cyclodiphosphate
(Dimetaphosphate)



Cyclotriphosphate
(Trimetaphosphate)



Cyclohexaphosphate
(Hexametaphosphate)

Figure 2.3 Cyclophosphate ions

cyclic metaphosphates) is still widely used even though according to IUPAC nomenclature cyclo- should be used to indicate the presence of rings. They can be prepared by heating orthophosphates:

$$nH_3PO_4 \xrightarrow{heat\,316°C} (HPO_3)_n + nH_2O$$

Unlike the long chain linear polyphosphates the cyclophosphates have few applications. There is no evidence for the existence of the first two members of cyclophosphates: monometaphosphate, PO_3^-, or cyclo-diphosphate (di-metaphosphate) ions. The latter would involve the sharing of two corners, that is an edge between two PO_4 tetrahedra, and would impose a considerable strain on the structure. In contrast, cyclo-tri- and cyclo-tetraphosphate (tetra-metaphosphates) are well known.

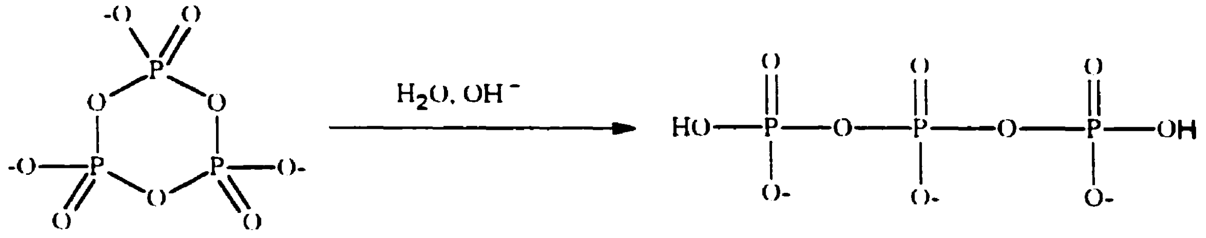
Sodium cyclo-triphosphate (tri-metaphosphate) $Na_3P_3O_9$ is made by heating NaH_2PO_4 to 640°C, and holding the melt at 500°C for some time to allow the condensation to take place and the water to be expelled:

$$3NaH_2PO_4 \xrightarrow{heat} Na_3P_3O_9 + 3H_2O$$

The ring structure has been established by X-ray diffraction analysis. Hydrolysis of the ring compound sodium cyclo-triphosphate by alkali gives the chain compound sodium triphosphate (tripolyphosphate).

$$Na_3P_3O_9 + 2NaOH \rightarrow Na_5P_3O_{10} + H_2O$$

All cyclophosphates undergo cleavage on alkaline hydrolysis to produce, initially, the corresponding linear polyphosphate which then undergoes further splitting until eventually only orthophosphate ions are left in solution.



2.3.3 Separation and Identification of Phosphate Polymers

Chromatographic techniques are widely used for the analysis of condensed phosphates. Paper and thin-layer chromatography were used in the past (Thilo and Feldman, 1959; Van Wazer and Karl-Kroupa, 1956), but high-performance liquid column chromatography is preferred at present. It is useful for the separation, identification and quantification of components of polyphosphate mixtures containing both cyclic and linear condensed phosphates. This method can be used for the characterization of these products to estimate the average chain length. Svoboda and Schmidt (1997) separated mixtures of glassy sodium-potassium condensed phosphates, P_2 to P_{13}, in a single-column chromatographic system.

2.4 Chemistry

2.4.1 Comparing Linear with Ring Structure

In regards to complexing power, it should be noted from the beginning that the chain phosphates are relatively strong, the ring phosphates are less effective, and the orthophosphate is the weakest of all. Indeed for the alkaline earth metals, the orthophosphate ion is a good precipitant with negligible complexing ability (Van Wazer and Callis, 1958).

A long-chain polyphosphate ion is composed of middle PO_3-units and two end PO_3-units. The middle and end units have a formal charge of -1 and -2, respectively. Therefore, the affinity of an end unit for a metal ion is much greater than that of a middle unit. When the chain length of polyphosphate is sufficiently long, the contribution of end units to metal binding is small enough to be neglected. The complexation ability of middle units in a chain polyphosphate is expected to be different from that of middle units in a cyclic phosphate.

Miyajima et al. (1981) evaluated the binding of middle units of long-chain polyphosphate to magnesium ion using a gel chromatographic method. They found the complexation ability of middle PO_3 units to be greater than that of the corresponding cyclic phosphate ion. This was attributed to the flexibility offered by the long chain permitting metal ions to be fitted into the structure. The flexibility of a cyclic phosphate may increase with n (the number of PO_3 units).

They also compared the complexing power of middle PO_3 units of long-chain polyphosphates with those of relatively small polyphosphates. They evaluated the stability constants of the magnesium complexes of diphosphate, triphosphate, tetraphosphate, cyclo-tetraphosphate, and cyclo-hexaphosphate by the gel chromatographic method under the same experimental conditions. By comparing with the stability constants of linear phosphate complexes, it was concluded that the addition of a PO_3 unit does not necessarily contribute to the binding of the first magnesium ion when more than 3 phosphorous atoms are present in the molecule.

The chain phosphates are the only phosphates which show stable complexes with all ions except those of the alkali metals and quaternary ammonium salts. Lithium ion is more strongly bound than sodium ion which in turn, is more strongly bound than potassium ion. For alkali metals, the triphosphate complexes are stronger than the diphosphate complexes (Van Wazer and Callis, 1958). Furthermore, they showed that the pK_D values for the alkali metal complexes of the ring phosphates are close to those of the chain phosphates having the same ionic charge. They attributed this to the electrostatic nature of the complex. They also mentioned that the large difference (four to five orders of magnitude) between the dissociation constants of the alkali metal and alkaline earth metal complexes of the chain phosphates may mean that the ions of the alkaline earth metals are partially covalently bonded in the complexes or at least are held at specific sites. The much smaller difference (one to two orders of magnitude) between the alkali metal and alkaline earth metal complexes of the ring phosphates supported their idea of complexes being held together by simple electrostatic attraction.

2.4.2 Hydrolysis

Hydrolysis of polyphosphates has been studied (Corbridge, 1990; De Jager and Heyns, 1998). The main reason for determining rates of hydrolysis is to check the stability of polyphosphate and to elucidate the mechanism of the reaction in general. Polyphosphates are stable in neutral solutions at room temperature, but hydrolysis occurs under acidic conditions. Soluble varieties of long-chain polyphosphates give solutions which are neutral or very slightly acidic, in contrast to the shorter chain compounds (e.g., $n = 2, 3, 4$) which give an alkaline reaction. Linear polyphosphates are reasonably stable in neutral or alkaline solution at room temperature. Their hydrolysis is strongly acid-catalyzed however, and, like all condensed phosphates, they can be eventually converted to orthophosphates by boiling.

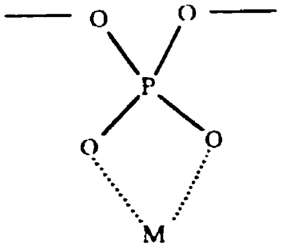
In hydrolysis, a polymer is cut into two strings. The overall reaction can be presented as follows:

$$H-[PO_3H]_n-OH + H_2O \rightarrow H-[PO_3H]_m-OH + H-[PO_3H]_{n-m}-OH$$

where n and m are integers and represent the number of phosphate units; n has a theoretical minimum of two, and m must be smaller than n with a minimum of one.

The principal factors influencing the rate of hydrolysis of a condensed phosphate solution are: (1) the number of corners shared by the PO_4 tetrahedra in the structure, (2) the temperature, (3) pH, (4) concentration (Corbridge, 1990; De Jager and Heyns, 1998). Triply linked polyphosphates hydrolyze faster than those with double linkages. Hydrolysis rates will increase by increasing the temperature or by lowering the pH. The concentration also plays a role. In dilute solutions of sodium polyphosphate, the rate is minimum at ca. pH 9, when complete hydrolysis may take many months at room temperature, although it can be effected in a few hours by boiling (Corbridge, 1990). To a lesser extent, the rate of hydrolysis is also affected by the type of polyphosphate cation (Corbridge, 1990). Polyphosphates containing alkaline earth metals make the polymer more resistant to hydrolysis (Ray, 1978).

The hydrolysis of polyphosphate chains is also catalyzed by heavy metal cations, the effect being most pronounced with cations of high charge and small radius. The effect is believed to be connected with chelation of the cations by the oxygen atoms:



There is a continuous transition in the physical properties of solutions of polyphosphates on passing from low to high molecular weight species. Apart from the initial few members of the series, they all exhibit typical properties of polyelectrolytes. Colloidal behavior is not exhibited by polyphosphates, however, until the average chain lengths are of the order of hundreds (Corbridge, 1990).

De Jager and Heyns (1998) showed that the hydrolysis of a polyphosphate can be followed with Raman spectroscopy by monitoring the P-O-P band of the polyphosphate and the $P(OH)_3$ band of orthophosphoric acid. They concluded that the hydrolysis of a polyphosphate could be regarded as a zero-order reaction. Combining zero-order behavior of hydrolysis as the phosphate production plus their linear relation of concentration with time, they concluded that hydrolysis takes place predominantly at terminal phosphate units.

A polyphosphate solution is thermodynamically unstable with respect to orthophosphoric acid. The enthalpy of the bonding P-O-P is -42 kJ/mol. Since enthalpy is negative, the entropy should be positive. The chain is degraded into its individual units, and therefore the Gibbs free energy (ΔG) must be negative. This means that the reaction is thermodynamically possible.

Triphosphates are less stable towards hydrolysis than diphosphates, and tetraphosphates are less stable than triphosphates, etc. This decrease in stability continues up to 10 phosphate units, after which a progressive increase in stability occurs with increasing number of units (De Jager and Heyns, 1998).

Strauss et al. (1953) have shown that both the viscosity and pH of freshly prepared aqueous solutions of Graham's salts decrease for several hours before becoming constant. They worked on samples with Na/P ratios ranging from 0.968 to 1.055. The phenomenon was observed at Na/P ratios up to 1.01. These effects were ascribed to the hydrolysis of weak P-O bonds at branch points in the polymer chains. They confirmed this by showing that the first-order rate constants of both the decrease in viscosity and the increase in the number of titratable hydrogen ions were equal. This rate constant was found to be $8(\pm 4) \times 10^{-3}$ min.$^{-1}$ at 25°C and was apparently unaffected by the Na/P ratio and the molecular weight of the samples as well as by the pH.

Hydrolysis of linear portions of the chain as a cause for the initial hydrolysis can be excluded because the linear hydrolysis rate constant has been calculated to range from about 8×10^{-6} to 3×10^{-8} min.$^{-1}$ as the pH increases from 3 to 8 which is 3 to 5 orders of magnitude lower than the rate of the initial hydrolysis process. Moreover, unless there were a few especially weak bonds in the linear chain, a degradation involving linear chains would continue. Such weak bonds are difficult to justify unless there are some elements other than phosphorous and oxygen in the polymer chain structure. Thus, the hydrolysis of branch points in the chain is the only remaining possibility.

The number of branch points per 1000 phosphorous atoms is quite small in the composition range where the glasses are commonly known as Graham's salts ($1 \leq Na/P \leq 1.01$), so small in fact that less than one out of every two polymer molecules in the glass can contain a branch. Yet the hydrolysis of this small number of branches accounts for the relatively large initial drop of the viscosity (Strauss and Treitler, 1955).

2.4.3 Sequestering of Metal Ions

The weight of the phosphate needed to prevent the precipitation of alkaline earth salts under practical conditions is known as "sequestering value". Because of the use of the condensed phosphates in water softening, there has been some work on comparing the sequestration of calcium ion with that of magnesium. Generally, the chain phosphates are many times more effective in sequestering magnesium ion than calcium. Also in the case of Mg sequestration, the diphosphate anion is said to be more effective than the triphosphate which, in turn, is more effective than the glassy phosphates, while for calcium ion, the order of effectiveness is reversed. It is usually assumed that about five to ten times the amount of magnesium as compared to calcium will be sequestered by a given phosphate (Van Wazer and Callis, 1958).

There have been several studies of sequestering of iron by the chain phosphates. It appears that chain phosphates are at least several times less effective in holding iron in solution than in holding calcium. In practice, when waters having high iron content are treated with chain phosphates, the resulting fine precipitates are well peptized and hence are usually completely harmless and sequestered. The inability of the chain phosphates to prevent precipitation of ferric hydroxide in basic media is probably due to the low solubility of the ferric hydroxide precipitate rather than to poor stability of the soluble phosphate complex.

The existence of a diphosphate-copper complex has been assumed from the unusually high solubility of the salt $Na_6Cu(P_2O_7)_2.16H_2O$ (Bassett et al.,1936). However, most copper diphosphates (with or without alkali metals) are very light blue and essentially insoluble.

An estimate of the dissociation constant of a soluble complex can be obtained from measurements of the solubility of a salt in a solution of the complexing anion. The concentration of free metal ion is obtained from the solubility product of the salt in pure water, and calculation of the dissociation constant is based on an assumption as to the ratio of metal to anion in the complex ion. Davies and Monk (1949), Jones and Monk (1950), and Monk (1952) estimated the dissociation constants of calcium and strontium complexes of cyclotri- and cyclotetraphosphate.

2.4.4 Titration

Different parameters can be determined by various methods of titration. Relative amounts of metal ion complexed by polyphosphates may be determined from either conductometric, nephelometric, acid/base or polarographic titration. The number of phosphorous atoms and the ratio of Na/P can be obtained by acid-base titration.

2.4.4.1 Acid/base titration

There are two types of hydrogen in polyphosphate, and hence, two important points on the pH titration curves (Van Wazer and Callis, 1958). Titration of phosphoric acids to an endpoint near pH 4.5 corresponds to the strongly ionized hydrogen associated with each phosphorous atom and gives the total number of phosphorus atoms, whether the phosphorus is in a ring or a chain or in the isolated PO_4^{3-} (orthophosphate) ion state. Titration between the endpoint pH 4.5 and 9.5 corresponds to the weakly dissociated hydrogen at each end of chain phosphates. The orthophosphate has a third replaceable hydrogen which is so weak that the corresponding inflection point does not show up in a pH titration curve.

Van Wazer and Campanella (1950) studied titration of a commercial phosphate glass (average chain length 5) with tetramethylammonium hydroxide in the presence of various metal ions. From the pH changes observed, they divided cations into three general groups depending on their ability to form complexes with the chain phosphates: (1) quarternary ammonium ions, which form no complexes, (2) alkali metal and similar single valence cations, which form weak complexes, and (3) alkali earth metals, transition metals, and Pb which form relatively strong complexes.

Rogers and Reynolds (1949) studied the titration of diphosphate with copper, zinc, cadmium, magnesium, nickel, cobalt, aluminum, lead, and iron followed by pH measurements. Similar titrations of diphosphate and triphosphate with calcium, strontium, barium, and magnesium are described by Bobtelsky and Kertes (1954). The observed changes in pH are closely tied to precipitate formation but are not directly interpretable in terms of the formation of soluble complex ions.

Nearly all metallic cations, with the exception of the alkali metal group, react with aqueous diphosphate solutions to form insoluble precipitates. A majority of the precipitates are, however, readily soluble in excess diphosphate.

2.4.4.2 Conductometric titration

Using conductivity data, the existence of a soluble complex with a 1:1 ratio of calcium to triphosphate was found (Van Wazer and Callis, 1958). Rogers and Reynolds (1949) reported conductometric titrations of 4×10^{-4} M solutions of sodium diphosphate with 0.1 M solutions of metal ions such as calcium, cobalt, nickel, magnesium, aluminum, ferric ion, copper, and zinc and found the molar ratios of metal to polyphosphate ranged from 0.93 to 0.97.

Rogers and Reynolds (1949) observed three inflection points with both ferric and aluminum ions corresponding to a mole ratio of diphosphate to metal ion of 2:1, 1:1, and 0.75:1 (there was noticeable precipitation at this point). Bobtelsky and Kertes (1954) also reported conductometric titrations of 0.025 to 0.125 M solutions for diphosphate and triphosphate with calcium, barium, and magnesium ions with no clear result on metal to polyphosphate ratio.

Wall and Doremus (1954) and Schindewolf (1954) determined the degree of dissociation of the sodium salts of chain phosphates from electrolytic conductance measurements. Their results show a decrease in dissociation constant with increasing chain length.

2.4.4.3 Nephelometric titration

Nephelometric titration is based on a photometric analytical technique for measuring the light scattered by finely divided particles of a substance in suspension. The end point corresponds to the formation of a barely discernible precipitate, determined either by visual or electrical means. It has been reported that there are experimental problems in obtaining reproducible nephelometric end points (Van Wazer and Callis, 1958). No matter how a solution containing a metal ion (such as calcium) is added to the anion (such as phosphate), a small amount of precipitate forms because of local excess concentrations. This precipitate dissolves rapidly at the beginning of the experiment but much more slowly as the end point is reached. The intensity of scattered light, following the formation of this small amount of calcium phosphate precipitate, changes slowly and continuously with time.

Extensive nephelometric measurements have been performed to determine the ability of a sodium phosphate to sequester calcium. From the results of such studies coupled with observations on practical systems, operating curves have been developed to show the amount of chain phosphate needed to hold calcium and magnesium in soluble form, even in the presence of commonly used additives, such as sodium carbonate (soda ash), which normally would cause precipitation. Some of the information obtained by nephelometric titration has been put in the form of phase diagrams (Van Wazer and Callis, 1958).

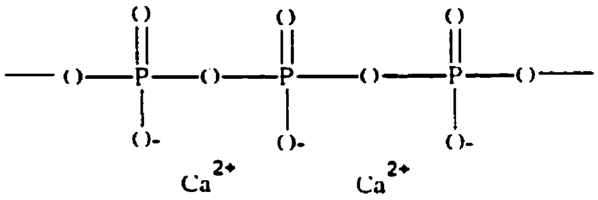
Changgen and Yongxin (1983) determined the ability of phosphates to complex metal ions by nephelometric titration and reported the ratio of the metal ion (Ca^{2+}, Mg^{2+}, and Fe^{3+}) to phosphate (Na_3PO_4, $Na_4P_2O_7$, and $(NaPO_3)_6$) in the complex. The decreasing order of complexing ability of the three phosphates for the metal ions was $(NaPO_3)_6 > Na_4P_2O_7 > Na_3PO_4$. They also found that the decreasing order of the complexing ability of $(NaPO_3)_6$ and $Na_4P_2O_7$ on the different metal ions was $Mg^{2+} > Ca^{2+} \approx Fe^{3+}$, suggesting both types of phosphate could be used for selective separation of magnesium minerals from calcium minerals.

2.5 Applications

2.5.1 General

Many of the glassy sodium polyphosphates (such as Calgon and Graham's salt) are used for water softening, detergency and for descaling boilers and pipes. One of the properties of the phosphates which led to their widespread use in water treatment is their linking capacity or "complexing power" which can prevent the precipitation of calcium by an otherwise effective precipitation agent such as oxalate. They serve as a sort of soluble "ion exchanger".

An important application of soluble chain polyphosphates is in the "threshold" treatment of hard water to prevent blockages of pipes arising from the growth of calcite crystals. About one part per million of soluble sodium polyphosphates, when added to hard water, will inhibit the precipitation of calcite. This is believed to be due to the adsorption of phosphate ions on the surface of the calcite nuclei, which then prevents further crystal growth. The flexibility and dimensions of the polyphosphate chain allow a good "fit" to the array of Ca^{2+} ions on the exposed calcite face:



Polyphosphate chains in concentrations of a few ppm will also protect metal surfaces in hard water by the formation of corrosion-inhibiting films. Corrosion is prevented by anodic polarization which results from the adsorption of the phosphate ion on to the calcite film which deposits on the metal surface. With relatively high concentrations of polyphosphate chains in hard water, sequestration takes place. This involves the formation of readily soluble complexes with Ca^{2+} and Mg^{2+} ions, and consequent water softening by the prevention of insoluble Ca^{2+} or Mg^{2+} soaps being formed (the removal of these cations with orthophosphates, in contrast, involves precipitation).

Sodium polyphosphate, near to cyclophosphate in composition and usually in glassy form, has important applications in detergency and food technology. Their dispersing and de-flocculating action is used in preparing clay and titania slurries for paper coating, for Portland cement slurries, in emulsion paints based on titania, and in treating oil well drilling muds. Generally only small concentrations ~ 0.1% are needed for these applications (Corbridge, 1990).

Polyphosphates are employed in the meat industry to prevent coagulation of blood. Other "calcium complexing" agents (notably sodium citrate) were used previously but polyphosphates have proved more effective with no adverse precipitation of fibrin (an insoluble blood protein). Sodium polyphosphate reacts with albumen and other proteins in weakly acid solutions to give precipitates. The interaction with proteins is used in leather making as a pre-(chrome) tanning agent.

Disodium dihydrogendiphosphate ($Na_2H_2P_2O_7$) mixed with sodium bicarbonate ($NaHCO_3$) is used to leaven bread. They react and evolve CO_2 when heated together. This is an easier way of making bread than using yeast, and is used commercially.

$$Na_2H_2P_2O_7 + 2NaHCO_3 \rightarrow Na_4P_2O_7 + 2CO_2 + 2H_2O$$

Calcium diphospate ($Ca_2P_2O_7$) is used as the abrasive/polishing agent in fluoride toothpaste, and $Na_4P_2O_7$ is mixed with starch and flavoring to make "instant pudding" mixes.

2.5.2 Environmental Applications with Particular Reference to Pb

Considerable research has focused on the environmental use of phosphates to remove Pb from aqueous solution (Takeuchi et al., 1988; Takeuchi and Arai, 1990; Ruby et al., 1994; Ma et al., 1993; Ma et al., 1994 a&b; Xu and Schwartz, 1994). Grimes et al. (1995) studied the exchange reactions in the Pb^{2+}- CO_3^{2-}- PO_4^{3-} system, and established when carbonate films deposit on lead pipework and react with added phosphate. They examined lead pipes exposed to water in the absence of orthophosphate ions, and found that lead carbonates ($PbCO_3$) and lead hydroxy carbonates ($Pb_3(CO_3)_2(OH)_2$), were the predominant surface deposits. In the presence of orthophosphate ions, hydroxypyromorphite (HPY, $Pb_5(PO_4)_3OH$) formed which controlled the lead solubility.

Studying the carbonate deposits prior to addition of orthophosphate provided insight into the types of reaction occurring at the surface (Grimes et al., 1995). A white deposit formed on a cleaned lead surface consisting of hexagonal plates (2-50 μm) of $Pb_3(CO_3)_2(OH)_2$ as the major product, overlaying small acicular (1 μm) $PbCO_3$ and tetragonal PbO (along with small quantities of orthorhombic PbO). Grimes et al. (1995) mentioned that the layer produced initially at the lead surface consisted of PbO and $PbCO_3$, the latter predicted to be the most stable lead carbonate phase under the prevailing conditions. Lead oxide (PbO) must arise as either part of the oxidation process at the surface, or as an existing surface layer which persists even after cleaning and which is not significantly altered by reaction with carbonate, i.e., is not contributing to the over-all solubility.

Grimes et al. (1995) found that the deposits formed in the presence of phosphate and carbonate consisted mainly of tetragonal PbO and $Pb_5(PO_4)_3OH$. The deposit formed in phosphate-containing systems was much thinner than those obtained in the presence of only carbonate. Again, the presence of PbO suggested that this oxide is the most stable under the conditions of surface oxidation in aqueous systems. Apart from calcium, the presence of other ions in the water supply, including chloride, nitrate and sulfate, had no observable effect on the nature of the deposits. In the case of calcium, some of the lead in the hydroxy pyromorphite phase was replaced with Ca^{2-} to give $Pb_{5-x}Ca_x(PO_4)_3OH$.

From studies of lead surfaces exposed to varying concentrations of orthophosphate, Raman spectra confirmed that increasing the phosphorus concentration in solution caused a progressive reduction in the proportion of lead carbonates, accompanied by an increase in the proportion of PbO and $Pb_5(PO_4)_3OH$ or, in the presence of calcium, $Pb_{5-x}Ca_x(PO_4)_3OH$ (Grimes et al., 1995).

Solubility of lead phosphates was studied by Nriagu (1972, 1974). However, his measurements were restricted by the detection limit of atomic absorption spectrometry. Sauve et al. (1998) studied lead contamination of soils and determined the solubility equilibria of two different synthetic lead phosphate minerals (secondary Pb orthophosphate ($PbHPO_4$) and tertiary Pb orthophosphate ($Pb_3(PO_4)_2$)) electrochemically over a wide range of pH and lead and phosphate concentrations. They used a Pb ion selective electrode to measure solubility and correlated the data by regression analysis. From their work, total dissolved lead was high at low pH, decreased until ca. pH 6, and then increased again at higher pH. They attributed this behavior to the strong Pb-complexing capacity of the soil organic matter. The organic matter is solubilized at neutral pH and above.

Farrell-Poe and Etzel (1991) removed heavy metals from wastewater and produced a non-hazardous sludge at near neutral pH using triple superphosphate (TSP) to complex metals. The heavy metals became non-leachable and the resulting sludge non-hazardous. They also examined the use of phosphate as a means to tie up heavy metals in a metal industry sludge. At pH 8.5-9 and phosphate addition of up to 2% by weight of the sludge, they claimed 99.6 to 99.9% removal of copper, lead, nickel, and cadmium. They also proposed that the removal of heavy metal ions from solution appears to be a surface reaction with the ion capable of complexing with the triple superphosphate. The phosphate used was highly insoluble, therefore, the heavy metal ion reacted at the surface of phosphate. When the phosphate was separated from solution, the heavy metal ions were thus separated with the phosphate.

Nriagu (1972, 1973a, 1973b) suggested the application of phosphate as an in-situ method to control hazardous quantities of Pb. The relative solubility of Pb compounds indicated that lead phosphates are more stable under ambient environmental conditions than lead oxides, hydroxides, carbonates, and sulphates (Nriagu, 1984; Ruby et al., 1994). Suzuki et al. (1981, 1982, 1984) have shown that $Ca_5(PO_4)_3OH$, hydroxylapatite (HAP), immobilizes aqueous Pb (Pb_{aq}). Adsorption of Pb on the surface of HAP, followed by cation substitution with Ca was suggested as the mechanism on the basis of macroscopic solution data (Suzuki et al., 1984; Takeuchi et al., 1988; Takeuchi and Arai, 1990). In contrast, Ma et al. (1993, 1994a, 1994b, 1995) and Xu and Schwartz (1994) proposed that the dissolution of HAP provides phosphate for the subsequent precipitation of $Pb_5(PO_4)_3OH$, hydroxypyromorphite (HPY), from solutions containing Pb_{aq} on the basis of macroscopic data with some direct microscopic, spectroscopic, and X-ray diffraction evidence.

Lower et al.(1998) observed that the sorption processes varied with the initial saturation state of the system at various initial [Pb_{aq}]. Their results at high concentrations of Pb_{aq} (≥ 10 mg/L [Pb_{aq}]) supported the hypothesis of Ma et al. (1993) summarized in the following reactions:

$$Ca_5(PO_4)_3OH + 7H^+ \overset{dis}{\rightleftarrows} 5Ca^{2+} + 3H_2PO_4^- + H_2O$$

$$5Pb^{2+} + 3H_2PO_4^- + H_2O \overset{ppt.}{\rightleftarrows} Pb_5(PO_4)_3OH + 7H^+$$

At lower initial [Pb_{aq}] (< 10 mg/L) they were uncertain whether such a two-step process occurred, however a solid Pb phase did precipitate on the surface of HAP.

The solubility of secondary lead orthophosphate ($PbHPO_{4(s)}$) has been measured in dilute phosphoric acid solutions (Nriagu, 1972). By investigating the hydrolysis of secondary and tertiary lead orthophosphates in the pH range 3 to 10, the $\Delta G_f°$ values for the solid phases $Pb_3(PO_4)_2$, $Pb_5(PO_4)_3OH$, and $Pb_4O(PO_4)_2$ were calculated. He observed that tertiary and secondary lead orthophosphates are not normally stable in aqueous systems at ambient temperatures, and that secondary lead orthophosphate does not occur in nature and $Pb_3(PO_4)_2$ occurs only in one mineral, ferrazite, in which lead is partly replaced by barium. The wide stability field of $Pb_4O(PO_4)_2$ is surprising and unexpected.

Phosphate and borate inhibit the dissolution of goethite by H_2S (Stumm and Morgan, 1996). Similarly, the dissolution of lepidocrocite (γ-FeOOH) by EDTA (Y^{4-}) is inhibited by phosphate and arsenate. Both in the reductive dissolution (by H_2S) and the ligand-promoted dissolution (by EDTA) the inhibition effects can be explained by ligand exchange reactions of the type

$$2 \equiv FeS^- + H_2PO_4^- + 3H^+ \rightleftarrows (\equiv Fe)_2HPO_4 + 2H_2S$$

$$2 \equiv FeH_2Y^- + H_2PO_4^- + H^+ \rightleftarrows (\equiv Fe)_2HPO_4 + 2H_3Y^-$$

($\equiv$ represents a surface functional group).

Fytas and Evangelou (1998) suggested using phosphates to control and treat acid mine drainage (AMD). AMD is a serious environmental problem that the mineral industry is aware of its responsibilities with respect to environmental protection. However, some mineral deposit are not economically viable due to a combination of factors, the cost of AMD remediation being one of the contributing factors. AMD is the result of oxidation of sulphide minerals, most notably pyrite, when they are exposed to air and water. This oxidation produces low pH effluents that can mobilize some heavy metals contained in the ore such as iron, zinc, copper and cadmium. Fytas and Evangelou coated pyrite with iron phosphate ($FePO_4$) precipitates to passivate and protect the mineral from oxidation. If the solution is supersaturated with respect to iron phosphate, iron will precipitate in the form of ferric phosphate either as a discrete phase or as a coating on pyrite, depending on the degree of supersaturation.

2.5.3 Mineral Processing

Parsonage et al. (1984) found that sodium triphosphate, $Na_5P_3O_{10}$, has a depressant action on calcite, apatite and dolomite. They claimed that triphosphate was adsorbed at the cation sites on the surface of calcite conferring a high negative zeta potential on the mineral. However, the anticipated presence of any water stabilizing hydrophilic layers with this reagent was not confirmed from their coagulation tests. They also found that the recovery of calcite and dolomite increased at very high sodium triphosphate concentrations (greater than 1 g/L). They could not explain the phenomenon.

Changgen and Yongxin (1983) suggested that cyclohexaphosphate $(NaPO_3)_6$ and diphosphate $(Na_4P_2O_7)$ were not adsorbed by calcite and that their depressant action was through complexing calcium ions in solution, causing more to dissolve and so lowering the number of calcium sites on the mineral. These researchers worked on the selective flotation of scheelite from calcium minerals (calcite and fluorite) with sodium oleate as a collector and phosphates as modifiers. They examined the effects of phosphate on the solubility of calcium minerals in water, on the surface charge of the minerals and on the adsorption of the phosphates and oleate on the mineral surface. They investigated the Auger spectra and the infrared spectra of the minerals treated with these reagents and determined the ability of phosphates to complex metal ions by nephelometric titration.

In summary, Changgen and Yongxin (1983) found that: (1) the phosphates were not extensively adsorbed on the mineral surface; (2) the depression of the calcium minerals by phosphates was closely related to the selective complexation and dissolution of the calcium ion in the minerals; and, (3) the crystal structure of the minerals was a primary factor influencing calcium solubility.

Fuliang and Fenglou (1997) found that flotation of galena improved by removing Ca and Mg with hexametaphosphate. Without Ca, recovery of galena was very high at pH below 9 and dropped significantly at pH 10-11 (Figure 2.4). In the presence of 0.001 M Ca, galena was completely depressed at pH 9 but, in the presence of hexametaphosphate recovery was regained particularly ca. pH 8-10. Same phenomenon was observed for quartz (Iwazaki, 1989)..

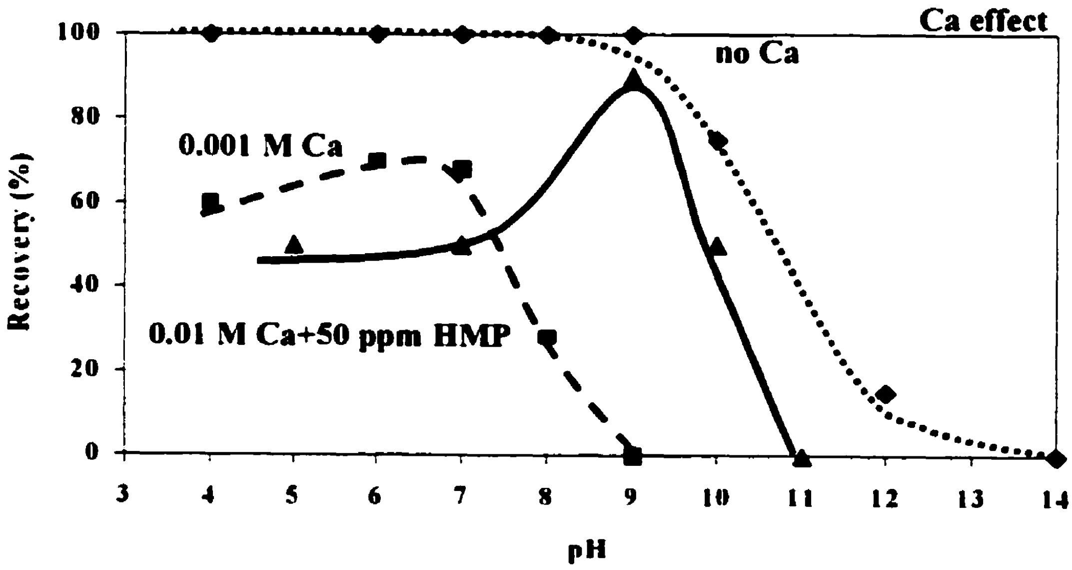


Figure 2.4 Recovery of galena at different conditions (after Fuliang and Fenglou, 1997)

The adsorption of polyphosphates onto the surface of titanium dioxide and silica particles has been studied recently (Michelmore et al., 1999). The polyphosphate samples were designated P_n, where $n = 1, 2, 3$ and 10, referring to the number of repeat PO_3 units in the polymer chain, $Na_{n+2}P_nO_{3n+1}$, and represents the degree of polymerization. Through zeta potential measurements, adsorption isotherms and infrared spectroscopy, they claimed that polyphosphates specifically adsorbed onto the surface of titanium dioxide over a wide range of pH. They found that there was a strong dependence on polymer chain length, with larger species reversing the zeta potential at lower concentrations. In contrast, it was shown that polyphosphates did not interact with the surface of silica. There was a notable pH effect, the maximum amount adsorbed was 5 times greater at pH 4 than at pH 9.1. This was attributed to the surface charge of the titanium dioxide. At pH 4 the charge is positive and the high adsorption was attributed to electrostatic attraction while at pH 9.1, where the electrostatic interaction is repulsive, only chemical interaction between polyphosphate and the surface contributes to adsorption. Their proposed mechanism involved only the terminal PO_3 group chemically bonding to the surface (i.e., the linking PO_2 groups were not involved). The authors did not discuss whether the bonding was through the oxygen or phosphorous.

Feiler et al. (1999) investigated the control of colloidal "slime" particle attachment on oppositely charged surfaces. The model system comprising a titania surface and colloidal silica slimes was studied. It was found that the presence of polyphosphates could prevent adsorption of silica particles onto the titania. The ability of the polyphosphate to modify the adsorption/desorption behavior was related to the molecular weight of the polyphosphate -

larger molecules were more effective. The polyphosphate samples had the same polymer chains $Na_{n+2}P_nO_{3n+1}$, where n = 1, 3 and 10 and represents the degree of polymerization.

In flotation, accidental activation/depression can occur due to contaminant metal ions on the mineral surface. This can result in misplacement of minerals lowering concentrate grades as well as causing a loss in recovery. The complexing power of polyphosphates suggests a possible application in controlling contaminant metal ions. The metal ion-polyphosphate complex might form on the surface, preventing reaction with collector, i.e., a blocking mechanism. The other possibility is the complex solubilizes the metal ion, removing it from the surface, i.e., a cleaning mechanism. A possible role for polyphosphates in controlling accidental activation/depression in mineral flotation is worth exploring. From our knowledge of the chemistry, linear polyphosphates would be best as they form more stable complexes with metal ions than cyclic compounds.

2.6 Conclusions

Polyphosphate chemistry and applications have been reviewed. An attempt was made to clarify the nomenclature which is confusing for someone new to the field. All types of condensed phosphates are formed by repeated condensation of tetrahedral [PO_4] units. The linear polyphosphates are relatively strong complexing agents, the cyclophosphates are less effective, and the orthophosphate is the weakest of all. Linear polyphosphates are stable in neutral or alkaline solutions at room temperature, but hydrolysis occurs in an acidic solutions. These compounds form soluble complexes with metal ions. Many glassy sodium polyphosphates such as Calgon and Graham's salt are used for water softening, detergency and descaling boilers and pipes.

Polyphosphates are used in controlling heavy metal ions in effluents prior to discharge to the environment. Environmental impact of Pb-contaminated wastes is reduced by the ability of hydroxyapatite to rapidly remove Pb^{2+}. A use of phosphates to control and treat acid mine drainage (AMD) is suggested: an iron phosphate coating on pyrite may control the oxidation process.

In mineral processing, phosphates have been used as depressants, dispersing agents for slimes, stabilizers of mineral suspensions, precipitating agents for some metal ions, and as water softening agents. The complexing ability of linear polyphosphates may be of use in mineral flotation to prevent accidental activation of minerals by heavy metal ions.

2.7 Glossary of Terms and Formula

Albumen, commercial term for dried egg white used in the food industry

Apatite, natural calcium phosphate mineral, $Ca_3(PO_4)_2$

Calcite, natural calcium carbonate mineral, $CaCO_3$

Calgon, commercial glassy varieties of sodium polyphosphates, often called sodium hexametaphosphate, which is a misnomer since these glasses are not metaphosphates (no ring structure) but instead are chain phosphates ranging predominantly from tridecapolyphosphate to the octadecapolyphosphate

Condensed phosphates, compounds containing phosphate ions linking together via shared oxygen atoms

Cyclodiphosphate, $P_2O_6^{2-}$, cyclic ion, dimetaphosphate

Cyclohexaphosphate, $(P_6O_{18})^{6-}$, hexametaphosphate

Cyclotetraphosphate, $(P_4O_{12})^{4-}$, cyclic ion

Cyclotriphosphate, $(P_3O_9)^{3-}$, cyclic ion

Cyclophosphate, phosphates with ring structure (metaphosphates)

Dimetaphosphate, see cyclodiphosphate

Diphosphate, pyrophosphate, $(P_2O_7)^{4-}$, straight chain

Disodium dihydrogendiphosphate, $Na_2H_2P_2O_7$

Dolomite, $CaMg(CO_3)_2$

Fluorite, CaF_2

Glass, long-chain polyphosphates or ultraphosphates, depending on Na_2O/P_2O_5 ratio

Graham's salts, a water soluble glass, incorrectly called sodium hexametaphosphate since it does not contain six PO_3 units but is a high molecular weight polymer (mean molecular weight of 12000-18000) with up to 200 PO_3 units. Mainly composed of long chains, with up to 10% of ring metaphosphates and some cross-linked material.

Hexametaphosphate, see cyclohexaphosphate

Hydroxyapatite (HAP), $Ca_5(PO_4)_3OH$

Hydroxypyromorphite (HPY), $Pb_5(PO_4)_3OH$

Lead hydroxy carbonate, $Pb_3(CO_3)_2(OH)_2$

Lead orthophosphate, lead phosphate, $Pb_3(PO_4)_2$

Lepidocrocite, γ-FeOOH

Linear polyphosphate, chain phosphate, see sodium polyphosphate

Linking capacity, moles of metal ions that can complex with one mole of ligand

Meta, less hydrated acid or its salt, to contrast with ortho, a prefix indicating formation of an inorganic acid derived by loss of one molecule of water from 1 molecule of an ortho acid

Metaphosphates, see sodium metaphosphate

Monometaphosphate, PO_3^-

Nephelometric titration. titration based on a photometric analytical technique for measuring the light scattered by finely divided particles of a substance in suspension

Ortho, the most highly hydrated acid or its salt, to contrast with meta

Orthophosphates, see phosphates

Oxalate. $(COO)_2^{2-}$

Peptization, stabilization of hydrophobic colloidal solutions by addition of electrolytes that provide the necessary electrical double layer of ionic charges around each particle. The ions of the electrolyte are strongly adsorbed on the particle surfaces.

Phosphates, PO_4^{3-}

pK_D, negative logarithm of the dissociation constant, -log (K_D)

Polyelectrolyte, a high polymer substance containing ionic constituents, may be either cationic or anionic

Polyphosphates, phosphate polymer, usually referring to a linear structure

Pyro, a prefix indicating formation by heat, specifically, of an inorganic acid derived by loss of one molecule of water from 2 molecules of an ortho acid

Pyrophosphate, see diphosphate

Scheelite, natural calcium tungstate, $CaWO_4$

Secondary lead orthophosphate, $PbHPO_4$

Sequestration, the formation of a coordination complex by certain compounds with metallic ions in solution so that the usual precipitation reactions of the latter are prevented, i.e., the process whereby ions such as Ca^{2+} remain *in solution* and yet act as if they were not (or as if they were there in considerably reduced concentration). The term has been broadened to include the combined complexing and dispersing action of the chain phosphates.

Sodium citrate, $C_6H_5O_7Na_3.2H_2O$

Sodium hexametaphosphate, $(NaPO_3)_6$, incorrect term applied to the class of vitreous phosphates exhibiting average chain lengths of 10 to 25 phosphorous atoms per molecule

Sodium metaphosphate, $(NaPO_3)_n$, commercial name sodium polymetaphosphate, value of n ranges from 3 to 10 (cyclic molecules) or much larger number (polymers). Has also been extended to short chain vitreous compositions, the molecules of which exhibit the polyphosphate formula $Na_{n+2}P_nO_{3n+1}$ with n as low as 4-5. These materials are more correctly called sodium polyphosphates.

Sodium oleate, $C_{17}H_{33}COONa$

Sodium phosphate, any of the following: sodium phosphate, monobasic (NaH_2PO_4, $NaH_2PO_4.H_2O$), sodium phosphate, dibasic (Na_2HPO_4, $Na_2HPO_4.2H_2O$,

$Na_2HPO_4.7H_2O$, $Na_2HPO_4.12H_2O$), sodium phosphate, tribasic ($Na_3PO_4.12H_2O$)

Sodium polyphosphate, $Na_{n+2}P_nO_{3n+1}$, chain phosphate

Tertiary lead orthophosphate, see lead orthophosphate

Tetrametaphosphate, see cyclotetraphosphate

Tetraphosphate, $(P_4O_{13})^{6-}$, straight chain ion, commercial name tetrapolyphosphate

Tetrapolyphosphate, see tetraphosphate

Trimetaphosphate, see cyclotriphosphate

Triphosphate, $(P_3O_{10})^{5-}$, straight chain ion, commercial name tripolyphosphate

Triple superphosphate (TSP), $Ca(H_2PO_4)_2$, a commercial phosphate fertilizer, also used in baking powders and wheat flours, mineral supplement for foods and feeds

Tripolyphosphate, see triphosphate

Ultraphosphates, condensed phosphates in which at least some of the PO_4 tetrahedra share three corner O atoms

Vitreous phosphates, see glass

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CHAPTER 3

EXPERIMENTAL TECHNIQUES

3.1 Introduction

The flotation response of sphalerite under different conditions was determined by a microflotation technique. Scanning electron microscopy (SEM) was employed to provide some visual information regarding the surface condition. Spot analysis (energy dispersive spectroscopy, EDS) and X-ray photoelectron spectroscopy (XPS) were performed to obtain qualitative and quantitative data on the presence of particular elements. Lastly, zeta potential measurements were made as a function of pH in the presence of Pb and various deactivators to study the changes in surface charge and relate it to the action of the deactivators. To study lead/polyphosphate ratio in complexes, conductometric titration was employed.

3.2 Microflotation

Small-scale cells for basic research on 1-2 g samples were first designed by Hallimond (1944) with modifications in procedure and cell construction suggested by Fuerstenau, Metzger and

Seele (1957). Since then there have been several variations, including one by Partridge and Smith (1971), the design used here.

3.2.1 Apparatus

Figure 3.1 illustrates the experimental set-up. The cell was made of glass to facilitate cleaning and was closed at the bottom by a glass frit of nominal pore size < 5 µm. The cell diameter was 1.8 cm with a height of 16 cm and a launder diameter of 6 cm. The particles were maintained in suspension by a gently rotating magnetic stirrer. The capacity was about 75 mL and sample size was 1.5 g. Feed was added to the cell column using a funnel. A controlled flow of nitrogen was passed through the frit as flotation gas at 12 mL/min. at 25 psig corresponding to a volumetric flow rate of 19.7 mL/min. at atmospheric pressure or a superficial gas velocity of 1.5 mm/s. The flotation time was one minute and the float and non-float products were collected and dried to determine recovery.

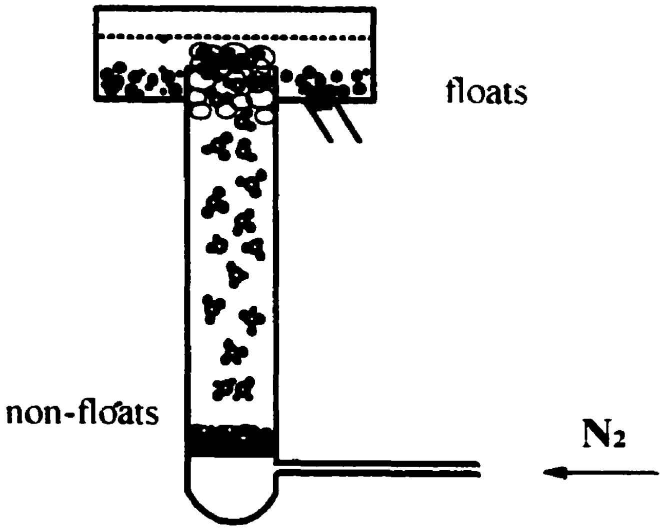

Figure 3.1 Microflotation cell.

3.3 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is widely used to examine surfaces with a resolution down to a few thousand nanometers, depending on the nature of the sample. Scanning electron microscope images formed from secondary electrons reveal topography through variations in shades of gray and characteristically have a wide range of contrast. The images have great depth of focus; they are sharp at both low and high points of the surface. The result is that even quite rough surfaces show in revealing clarity with an impression of depth. Images formed using backscattered electrons give less topographical detail but give some compositional information as the intensity of backscattering depends on the average atomic number of the material.

The SEM is frequently equipped with a spectrometer capable of detecting X-rays emitted by the specimen during electron-beam excitation. In this method (energy dispersive spectroscopy, EDS) the X-rays characteristic of the elemental composition of the specimen are detected. The ability of SEM to combine surface morphology with X-ray microanalysis is unique.

3.3.1 Basic Theory

3.3.1.1 Scanning Electron Microscopy (SEM)

The SEM uses a beam of electrons focussed 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 emitted. 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 to yield several signals that are gathered by various detectors in the specimen chamber.

The two signals emitted by the electron beam-sample interactions used in this study to provide images are secondary electrons and backscattered electrons. Secondary electrons (SE) are electrons ejected from the sample atoms. They are low energy and consequently 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. As a result, the secondary electron signal carries topographic information about the sample.

Backscattered electrons (BSE) are primary electrons (electrons from the source beam) which strike the nucleus of a sample atom and rebound, i.e., are backscattered. Backscattered electrons have more energy than secondary electrons and can escape from deeper within the sample. Because phases with high average atomic number scatter more electrons than materials with low atomic number, the backscattered signal provides compositional as well as topographic information. The phases are distinguished by different shades of grey.

Images (or more correctly micrographs) from secondary electrons and backscattered electrons were used in this work. The magnification was 600 times unless otherwise stated.

3.3.1.2 Energy Dispersive Spectroscopy (EDS)

Beam electrons can excite atoms by ejecting inner shell electrons. As the atom returns to ground state X-rays characteristic of the elements present are emitted. The technique is generally limited to atoms with atomic number greater than sodium.

3.3.2 Instrumentation

The instrument is the JSM-840 (Figure 3.2). The main components are:

(1) The illuminating/imaging system to produce the electron beam and direct it onto the sample;

(2) The information system including the sample which releases a variety of data signals during electron bombardment and detectors for analysing the information signals. The

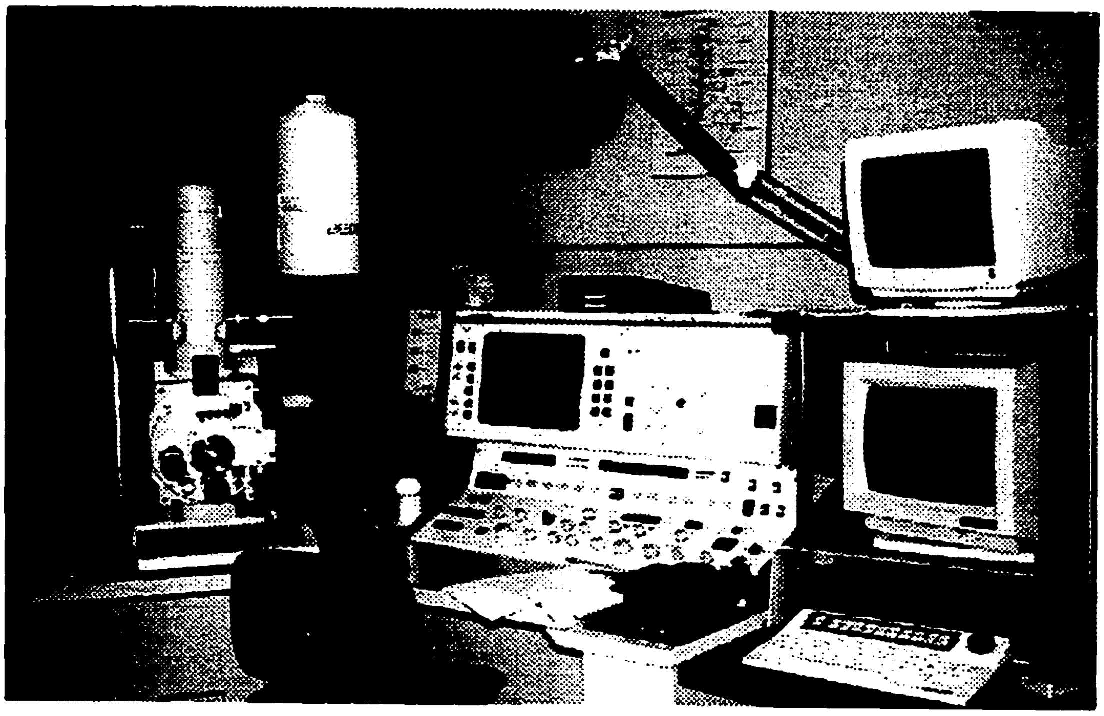

Figure 3.2 The JSM-840 scanning electron microscope

sample is mounted on a conductive substrate, usually from aluminum or carbon;

(3) The display consol consisting of one or two cathode-ray tubes for observing and photographing the surface of interest;

(4) The vacuum system for removing gases from the microscope column - which would otherwise interfere with the electron beam, reducing the image resolution (Gabriel, 1985).

3.4 X-Ray Photoelectron Spectroscopy (XPS)

The technique of X-ray photoelectron spectroscopy is relatively new to the field of surface analysis. It is capable of revealing the elemental and valence state composition of the surface and near surface atoms up to a maximum depth of about 5-10 nm. The initial information is a qualitative indication of the atoms present. The second level of information is of the structure and oxidation state of the element.

3.4.1 Basic Theory

The basis of the XPS technique is shown schematically in Figure 3.3. It involves irradiation of a specimen under ultra high vacuum, usually with a non-monochromatic X-ray source (e.g., Al/Mg) of low energy. 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 which is ejected from the atom. This process is termed photoelectric absorption, and the ejected electron is a photoelectron (Figure 3.4).

These ejected electrons have energies characteristic of the elements present in the 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. The technique is known as electron spectroscopy for chemical analysis (ESCA) or X-ray photoelectron spectroscopy (XPS). The XPS spectrum is a plot of electron counts or intensity versus binding energy.

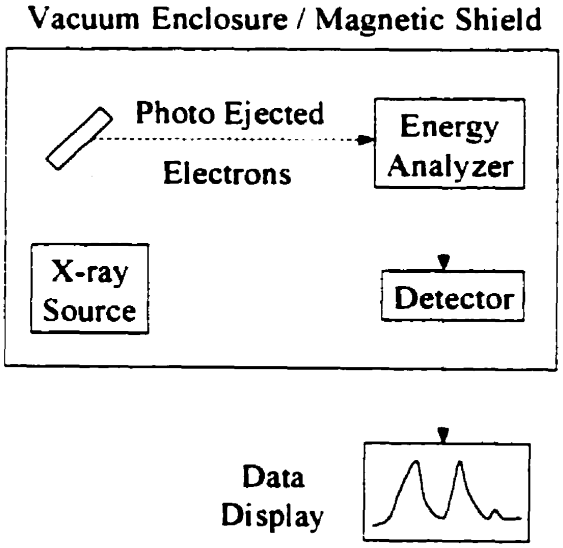

Figure 3.3 Schematic representation of XPS experiment (after Riggs and Parker, 1975).

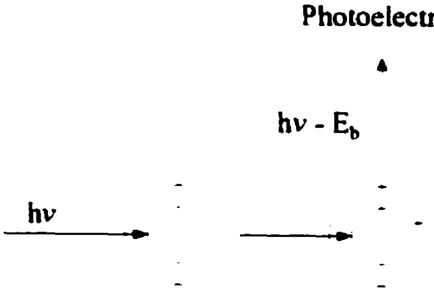

Figure 3.4 Schematic representation of photoelectron generation in XPS

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

$$E_{x\text{-}ray} = h\nu = E_k + E_b + \phi \qquad \textbf{(3-1)}$$

where $E_{x\text{-}ray}$ is the energy of the incident photon, $h\nu$ the energy of the exciting radiation (h is Plank's constant, and ν the frequency of the photon), E_k the kinetic energy of the ejected photoelectron, E_b the binding energy of the electron in the solid, and ϕ the energy required to remove an electron from the specimen surface. All energies are in electron volts. Since ϕ is only a few electron volts, the above equation is usually simplified to

$$E_k = E_{x\text{-}ray} - E_b \qquad \textbf{(3-2)}$$

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 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 a shift gives information on the chemical bonds of the elements, (e.g., the oxidation state and molecular environment).

In this study, the Wagner empirical sensitivity factor method (Briggs and Seah, 1990) was used to perform quantitative XPS. The quantification process involves first the identification of all elements present on the surface. Then it is necessary to measure the peak area or peak height intensity is measured of the most intense core-level peak for each element in the spectrum. The peak areas were obtained using XPSPEAK 95 v. 3.1, an XPS peak fitting program (Kwok, 1997). Finally each peak is divided by its sensitivity factor corrected for the photoelectron escape depth with energy:

$$NPA = \frac{PA}{SF \, . \, KE^{0.6}} \quad \textbf{(3-3)}$$

where, *NPA* is the normalized peak area, *PA* is the peak area, *SF* is the empirical sensitivity factor and *KE* is the kinetic energy of the core-level, given by

$$KE = 1486.6\,eV\,(\text{for Al X-ray}) - BE\,(\text{centre of peak}) \quad \textbf{(3-4)}$$

where, *BE* is the binding energy.

The concentration in atomic % is then calculated as follows:

$$C_x = \frac{NPA_x}{NPA_x + NPA_y + NPA_z} \times 100 \quad \textbf{(3-5)}$$

where C_x is the concentration of element x in % in a matrix of elements x, y, and z (in this example). A possible source of error arises from the method of background subtraction used for calculation of peak area intensity. There is also uncertainty in the sensitivity factors. Non-homogeneous surface distribution of a particular element or elements within the analysis area may be a source of error.

3.4.2 Instrumentation

Figure 3.5 shows the XPS-ESCALAB 220i-XL used. The main component parts are the X-ray source, preparation chamber with a pressure of 1×10^{-3} torr, the analysis chamber with a pressure less than 1×10^{-9} torr, the transferring system which brings a specimen on a support from the preparation chamber to the analysis chamber, the vacuum system, multichannel detector, a monitor to see the sample is transferred correctly, and a computer with appropriate (in this case Eclipse) software.

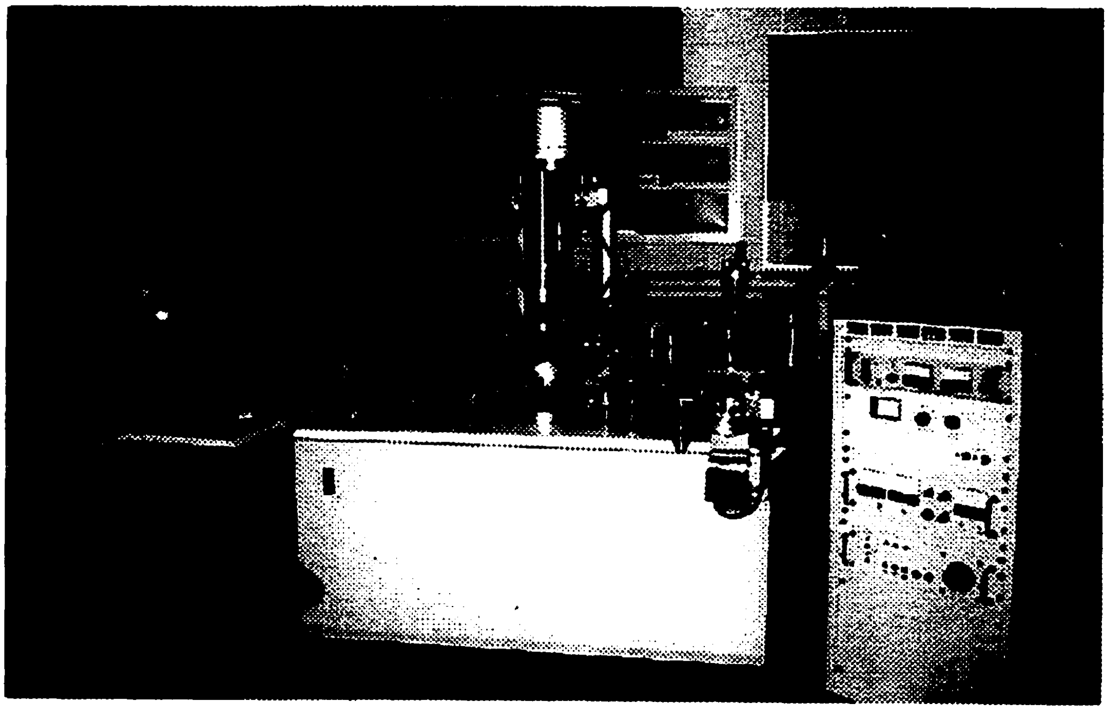

Figure 3.5 The XPS-ESCALAB 220i-XL

3.5 Zeta Potential Measurements

3.5.1 Basic Theory

When a solid particle is in a polar medium like water, a charge develops on the surface. This is due to ionization of surface groups or adsorption of ions from solution. To counteract this charge, ions of opposite charge (counter-ions) are attracted towards the surface while ions of like charge are repelled from the surface (Figure 3.6). This interfacial region is commonly known as electrical double layer because it consists of two separate and oppositely charged regions. The inner region which is bounded by the surface is the Stern plane, a region about one atomic radius in width. The outer region which starts from the Stern layer and extends beyond until the potential is zero, is known as the diffuse layer.

As the particles move with respect to water, there is a surface of shear on the water-side of the interface (Figure 3.6). 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.

On applying an electric field across a suspension, small particles will tend to move toward either the anode or the cathode depending whether the solid surface carries a positive or negative charge. The migration speed of the particles (electrophoretic velocity) is directly proportional to the magnitude of the zeta potential, and to the applied field strength. An equation proposed by Smoluchowski relates mobility to the zeta potential, ζ

$$U = \zeta \epsilon / \eta \qquad \textbf{(3-6)}$$

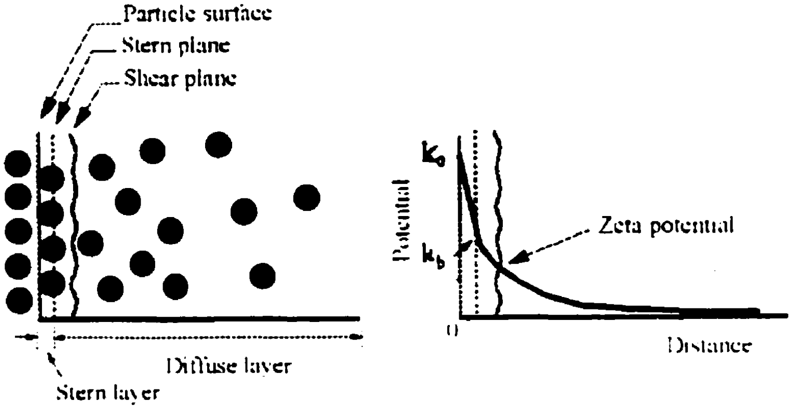

Figure 3.6 Diagramatic interpretation of the electric nature of the water-solid interface.

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

The zeta potential does change with ionic strength since an increase in electrolyte concentration decreases the thickness of the double layer. 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 prefered since the radius of the K^- and Cl^- ions is similar, therefore, they move in solution with a simillar speed. The background electrolyte (type and concentration) is chosen according to the type of 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. The pH of zero zeta potential is known as the isoelectric point (iep). In many cases, the iep and pzc are equal.

3.5.2 Instrumentation

A LASER ZEE meter (Model 501, Penkem, Inc., Figure 3.7) was used to measure the zeta-potential of particles suspended in an electrolyte. The suspension is inserted into the cell (Figure 3.8).

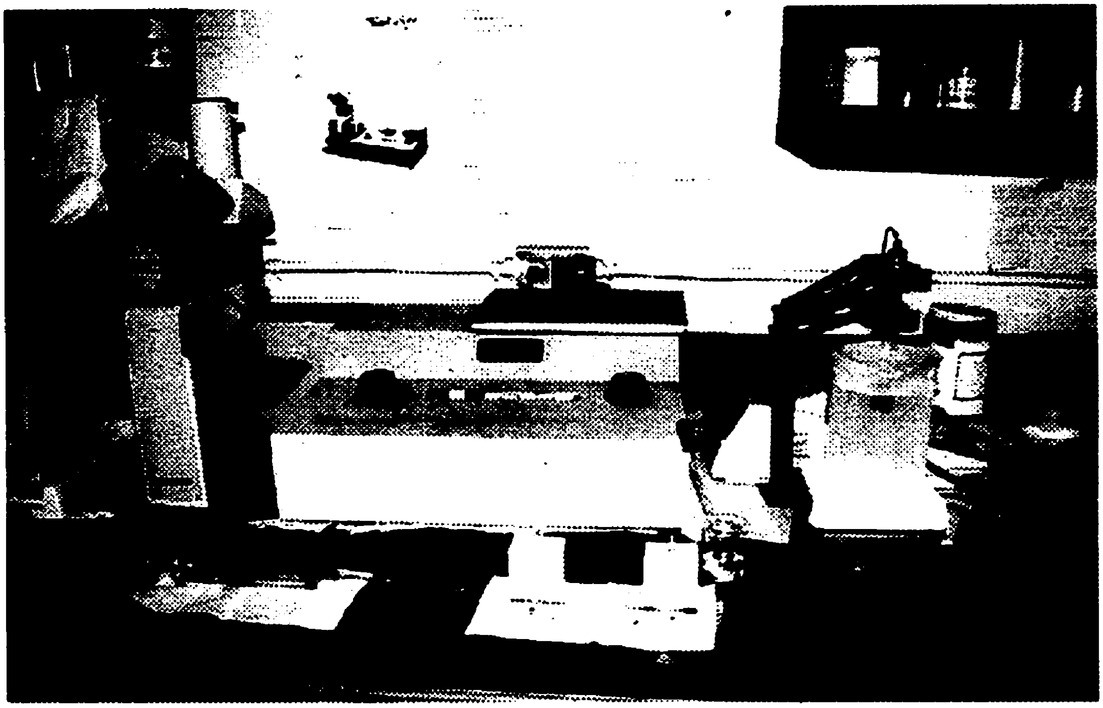

Figure 3.7 Penkem Laser Zee Meter, Model 501.

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

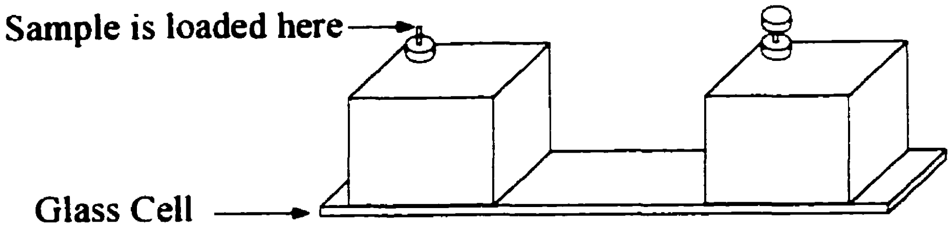

Figure 3.8 Detail of the cell used for electrophoretic mobility (zeta potential) measurements.

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.

Values of zeta potential are generally between ±100mV. Typically measurement takes about one minute. The claimed accuracy is ±5% or ±1 mV (Penkem, 1995).

3.6 Conductometry

Conduction of electricity through an electrolyte solution involves migration of positively charged species toward the cathode and negatively charged ones toward the anode. The conductance depends directly upon the number of charged particles in the solution. All ions contribute to the conduction process, but the fraction of current carried by any given species is determined by its relative concentration and its inherent mobility in the medium.

Conductometric titrations, in which conductance measurements are used for end-point detection, can be applied to the determination of numerous substances (Skoog and West, 1998). The principle advantage to the conductometric end point is its applicability to the titration of very dilute solutions and to systems in which the reaction between the titrant and analyte is relatively incomplete. Conductometric titrations become less accurate with increasing total electrolyte concentration.

Conductometric measurements provide a convenient means for locating end-points in titrations. Conductance increases linearly with electrolyte concentration (in the absence of reactions) and the slope of the conductivity vs volume of titrant is proportional to the mobility of ions in the solution A steep slope in the conductometric titration curve indicates a highly mobile ion while a gentle slope is caused by less mobile ions. Thus, a change in the slope indicates a change in the ions in solution. The two linear portions are then extrapolated, the point of intersection being taken as the equivalence point. At least three to four data points before and after the equivalence point are needed to define the titration curve (Skoog and West, 1998).

Because reactions fail to proceed to absolute completion, conductometric titration curves invariably show departures from strict linearity in the region of the equivalence point. Curved regions become more pronounced as the reaction becomes less favorable and as the solution becomes more dilute. The linear portions of the curve are best defined by measurements sufficiently far from the equivalence point so that the common ion effect forces the reaction more nearly to completion. It is in this respect that the conductometric technique appears to best advantage, in contrast to potentiometric or indicator methods.

3.6.1 Conductometric Titration Set-Up

Conductometric titration experiments to determine PP/Pb ratio were performed at room temperature using a burette to add polyphosphate solution to a beaker containing lead nitrate solution. The samples were agitated using an overhead stirrer. A digital conductivity meter (VWR Scientific Products, model 2052) was used.

3.7 References

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CHAPTER 4

SPHALERITE ACTIVATION AND SURFACE Pb ION CONCENTRATION

4.1 Abstract

Activation of sphalerite by lead in the presence of ethyl xanthate was investigated by microflotation, EDTA extraction, and X-ray photoelectron spectroscopy. Flotation response as a function of surface concentration of Pb, $[Pb]_{surf}$ (mg/cm^2), showed a unique response regardless of source of lead (from solution or contact with galena). Interactions in the sphalerite/lead/xanthate system to account for the flotation are proposed. An estimate of the critical $[Pb]_{surf}$ causing activation is linked with a model of Pb ion production to estimate the Pb ore grade which could pose potential accidental activation problems.

4.2 Introduction

Sphalerite can be activated to flotation with short chain xanthates by heavy metal ions such as Cu(II), Pb(II), Ag(I), Au(I), Cd(II), and Fe(II) (Finkelstein, 1997,1999). These metal ions may be deliberately added, notably Cu, or be present unintentionally, deriving from the process water, being released from one mineral and transferred to sphalerite, or coming from impurities in the sphalerite lattice itself (Finkelstein and Allison, 1977; Mielczarski, 1986). In flotation of polymetallic sulphide ores, Cu and Pb derived from Cu-minerals and galena, are frequently suspected of inadvertent activation of sphalerite causing misplacement to Pb/Cu concentrates.

Lead ions are the focus here. They are readily produced from oxidation of fine galena enhanced by galvanic interaction with noble metal sulphides, particularly pyrite (Sui et al., 1995; 1999a). For example, at particle size $< 10\mu m$ more than 10% of Pb relative to the bulk Pb in galena became EDTA extractable (a measure of lead ion production) in a study by Sui et al. (1999a). This experience mirrors that in the plant: high Pb extraction by EDTA have been reported in surveys of Cu circuits (Kant et al., 1994), Pb circuits (Greet et al., 1994) and Zn circuits (Sui et al., 1999a).

Activation of sphalerite by Pb ions has been studied periodically for many years. Rey and Formaneck (1960) in tests on both natural and synthetic ores found that oxidized lead minerals tended to activate sphalerite. Houot et al. (1992) showed that Pb ions added to a flotation pulp increased the recovery of sphalerite. They proposed formation of surface PbS by Pb-Zn exchange. Trahar et al. (1997) through systematic batch flotation tests on sphalerite-quartz mixtures, found that sphalerite was activated by lead at pH between 4 and 9.

Activation of sphalerite with both Cu and Pb has been studied recently (Laskowski et al., 1997; Sui et al., 1999c). Laskowski et al. found hydrophilic Cu-Pb-OH species formed at pH 10.5 - 11.5 and decreased sphalerite recovery. Sui et al. demonstrated that the amount of Pb adsorbed was greater than that of Cu when sphalerite was treated with the metal ions individually. In the presence of both, Cu adsorption was enhanced and Pb adsorption was suppressed.

Mechanisms of Pb activation of sphalerite have been proposed. Fuerstenau and Metzger (1960) reported that adsorption of Pb was quite slow and the mechanism more complex compared to Cu adsorption. In contrast, Ralston and Healy (1980a - b; 1981) and Sui et al. (1999c) found that adsorption of Pb was characterized by three stages: a rapid initial stage (0 - 1 min.), a second one constant with time (1-5 min.), and lastly a slow increase stage (>5 min.). Ralston et al. suggested that in alkaline media hydroxide $Pb(OH)_2$ reacted on the surface to yield (Zn, Pb) S, $Zn^{2+}_{(aq)}$ and OH^-. However, Trahar et al. (1997) presented indirect but convincing evidence that under alkaline conditions $Pb(OH)_2$ does not transform to PbS. In acidic media, Ralston et al. suggested adsorbed metal ions exchanged with $Zn^{2+}_{lattice}$ and then formed PbS on the ZnS surface. This possibility is supported by recent electrochemical work which shows that the reaction of Pb (and Cd) with sphalerite is not influenced by the potential applied during activation (Finkelstein, 1997). Finkelstein also notes that the possibility of such exchange is limited to the first layer.

Pattrick et al. (1998), employing X-ray absorption spectroscopy (XAS) to determine the nature of lead on the surface of synthetic ZnS, reported a lead sulphide species. They suggested that the activation in mildly acid solutions takes place via the development of a "disordered Pb-O" species and that Pb will not easily migrate into the bulk lattice of ZnS or bond to S on the surface, explaining why the Pb is bound to the surface via oxygen. Their proposed mechanism involved interaction of the Zn with a negatively charged hydrated Pb species to form Zn-O-Pb linkages. Once xanthate is added the xanthate S reacts with the Pb on the surface to form Pb-S bonds. Their calculation of lattice energy showed that the Zn-Pb exchange is unfavourable.

Popov et al. (1989), from infrared (IR) analysis, detected lead ethyl xanthate in various proportions on the sphalerite surface, depending on the experimental conditions. The maximum xanthate adsorption was achieved in 15 minutes of conditioning time. A conditioning time of 30 minutes had an adverse effect, i.e., the IR peak intensity reduced. They did not detect dixanthogen. Also using infrared spectroscopy, Basilio et al. (1996) did detect dixanthogen (as well as Pb-amyl xanthate in their case): they may have found dixanthogen because of the high xanthate concentration used, 10^{-4} M.

The studies rarely consider the Fe-content in the sphalerite although it is known that natural sphalerite exceeds 10% Fe (the high Fe member is known as marmatite). Recently Zielinski et al. (2000) found in a survey at three concentrators that low Fe sphalerite was more likely to misreport to the Pb concentrate than high Fe sphalerite. They suggested low Fe sphalerite was less oxidized and had fewer hydrophilic oxidation product sites and thus was more susceptible to activation by metal ions such as Pb. The implication of this observation invites a similar survey at other plants.

Lead contamination could occur at any stage in the process sequence, from mining through to flotation. Copper/lead flotation, in which sphalerite can misreport, is typically conducted at alkaline pH (8 - 11), but the "contamination pH" may be different. Both the contamination (or conditioning) pH and flotation pH have been considered in this study. The source of Pb ions was also considered, from solution (the convenient way to perform the tests) and from galena. By determining floatability as a function of surface concentration of Pb the effect of the two sources of Pb ion can be compared. A mechanism of Pb activation is proposed. Lastly, an attempt is made to link literature results on Pb ion production to predict the likelihood of accidental sphalerite activation.

4.3 Experimental

4.3.1 Material Preparation

4.3.1.1 Minerals

Sphalerite and galena samples were obtained from Ward's Natural Science Establishment. The samples were crushed in a jaw crusher and hand picked specimens were ground in a pulveriser and dry-screened to obtain selected size fractions. Sphalerite was collected as the 38 - 74 μm size fraction and wet screened to remove fines. The sample was washed by dilute hydrochloric acid (pH 2) to remove products of oxidation, then by distilled water until the pH of solution approached the natural pH of the mineral distilled water system. They were stored under acetone until required. The surface area of sphalerite, measured by BET, was 0.0973 m^2/g and the chemical analysis is shown in Table 4.1.

Table 4.1 Chemical composition of sphalerite and galena used in experiments

Mineral	% Wt. of element				Purity*
	Zn	Fe	Pb	Cu	%
Sphalerite	64.95	0.31	0**	0.12	96.81
Galena	0**	0**	85.5	0**	98.74

* Compared to stoichiometric ZnS and PbS
** Detection limit (ppm) for Zn: 0.04, Fe: 0.005, Pb: 0.02, Cu: 0.002.

For galena -38 μm and -8 μm samples were prepared. The -38 μm fraction was prepared as described for sphalerite. A portion of that was exposed to air and is referred to as "oxidized". For the -8 μm sample, in one case a sample was isolated from the -38 μm material by wet screening and drying on filter paper. This is referred to as "oxidized"-8 μm as no attempt to exclude air was made. A 0.3 g sample was used for conditioning with sphalerite.

To screen the -8 μm sample, a small scale screen was made by cutting a hole in the lid of a plastic specimen container from which the bottom was cut off. An 8 μm nylon mesh (SPECTRUM Laboratory Products) was held by the lid and the sample screened through the opening in an ultrasonic bath.

In a second procedure, -8 μm galena was freshly prepared immediately prior to use by grinding 2 g of the -38 μm sample in 5 mL distilled water in a ceramic mortar and pestle for 10 minutes. The sample was directly screened through the 8 μm screen into the conditioning beaker. By this procedure, about 0.3 g, referred to as "unoxidized" -8 μm galena, was produced.

4.3.1.2 Reagents and solutions

Table 4.2 shows the reagents used in this study. Buffer solutions were needed to eliminate pH variation in the sphalerite-galena tests and for lead nitrate concentrations below 50 ppm Pb (2.4×10^{-4} M). For concentrations > 50 ppm Pb pH did not vary and there was no need for buffering. The buffer solution was prepared using sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) + HCl for pH 7.5.

Potassium ethyl xanthate (KEX) was purified by dissolving in acetone and reprecipitating by petroleum ether following a standard technique (Rao, 1971). Fresh 5×10^{-3} M xanthate stock solution was prepared daily at ca. pH 9, and then diluted to 5×10^{-5} M with distilled water at ca. pH 9.

Table 4.2 Reagents

Chemical	Grade	Supplier	Usage
HCl	ACS reagent	Fisher Scientific Co.	Wash minerals
NaOH	Analytical reagent	ACP Chemicals INC.	pH regulator
$Pb(NO_3)_2$	ACS reagent, 99.9%	Fisher Scientific Co.	Lead pretreatment
KEX	Purified	Cytec Industries Ltd.	Collector
Acetone	ACS reagent	BDH Chemicals	Dry mineral storage
Petroleum ether	Analytical reagent	BDH Chemicals	Purification and storage of KEX
Sodium tetraborate decahydrate	ACS reagent	Aldrich Chemical Company, Inc.	Buffer, pH 7.5
Disodium ethylene- diamine tetraacetate	Reagent grade	Fisher Scientific Co.	Complexant

Lead nitrate stock solution of 1000 ppm Pb (4.8×10^{-3} M) was prepared by dissolving $Pb(NO_3)_2$ powder in distilled water at natural pH, and diluting to the desired concentration. Lead concentrations of 50 ppm (2.4×10^{-4} M), 100 ppm (4.8×10^{-4} M), 200 ppm (9.6×10^{-4} M) and 400 ppm (1.9×10^{-3} M) were generally used.

4.3.2 Microflotation Set-Up

The microflotation cell was the version devised by Partridge and Smith (1971). The liquid volume was 75 mL and sample size was 1.5 g. The cell was made of glass to facilitate cleaning and was closed at the bottom by a glass frit of nominal pore size < 5 μm. The particles were maintained in suspension by a gently rotating magnetic stirrer. A controlled flow of nitrogen was used as flotation gas with a gas supply of 12 mL/min. at 25 psig corresponding to a volumetric flow rate through the cell of 19.7 mL/min. at atmospheric pressure or a superficial gas velocity of 1.5 mm/s.

4.3.3 Test Procedure

4.3.3.1 Lead contamination pH

A set of microflotation tests was carried out as a function of contamination pH. It was established that sphalerite contacted with lead solution at pH 7.5 gave a strong activation effect. This was the Pb conditioning pH for most experiments

4.3.3.2 Sphalerite conditioning

The sphalerite was exposed to Pb ions in two ways, via solution and from contact with galena. For the solution case, a 1.5g sample was conditioned on an orbital shaker at 250 rpm for 15 minutes in 100 mL of a given concentration of lead ([Pb]) at pH 7.5. The suspension was filtered and the solids transferred to the flotation cell.

For the contact with galena tests, 1.5 g sphalerite was conditioned with 0.3 g galena for 15 minutes in 100 mL buffer solution at pH 7.5. The galena particle size was -38 µm or -8 µm (oxidized or unoxidized).

4.3.3.3 Flotation

The solids were conditioned in the cell with 5×10^{-5} M xanthate at the set pH (9 or 10.5). Flotation time was one minute. At the end of each test, the float and non-float products were collected, dried, weighed and the recovery calculated. In the case of the mixed sphalerite-galena tests, the products were screened at 8 µm to separate the minerals. Repeat tests showed an absolute standard deviation of ca. 2% at recoveries above 90%, 5% at recoveries ca. 50%, and ca. 8% at recoveries below 20%.

4.3.4 Surface Analysis

4.3.4.1 EDTA extraction - Determining surface Pb concentration

After selected microflotation tests, the floated sphalerite was washed with 25 mL distilled water and treated with EDTA. This involved contacting 37.5 mL of 0.05 M EDTA (25 mL/g sphalerite) solution with the mineral for half an hour (Grimmelt, 1998). The suspension was filtered, and the extract analysed (by atomic absorption spectroscopy) to measure the amount of Pb extracted. This is taken as a measure of Pb ions present on the surface and knowing the surface area of sphalerite gives surface concentration, $[Pb]_{surf}$, with the units selected as mg/cm^2. For the contact with galena tests, the products were separated by screening (as described) followed by the same EDTA extraction procedure. Repeat tests showed a relative standard deviation of ca. 8% on $[Pb]_{surf}$.

4.3.4.2 X-ray photoelectron spectroscopy (XPS)

The XPS spectra were recorded using a VG Escalab 220i-XL spectrometer with an Al K-alpha X-ray source (hv = 1486.6 eV) at a normal take off angle and a band-pass energy of 50 eV corresponding to an energy resolution of 1.2 eV. The vacuum pressure in the chamber was about 10^{-9} to 10^{-10} Torr. The X-rays were non-monochromated and the instrument was calibrated against the $Ag_{3d5/2}$ Fermi edge. The charge compensation was adjusted on each sample to obtain the maximum signal possible for $Zn_{2p3/2}$ at Ek = 464 eV.

As a blank test to characterize the surface of the untreated sphalerite, a 1.5 g sample was conditioned in 100 mL distilled water (pH 7.5) for 15 min., filtered and rinsed once. To study the effect of lead, the sphalerite sample was treated in 100 ppm lead solution at pH 7.5 for 15 min. The suspension was then filtered, rinsed and the samples dried in air.

An initial survey of the surface was made to determine the elements present then the predetermined regions of interest were scanned to measure atomic concentrations. The atomic concentrations were determined from XPS peak areas knowing the respective sensitivity factors and are reported as a percentage of all elements observed. The peak areas were obtained using XPSPEAK 95 v. 3.1, an XPS peak fitting program (Kwok, 1997). The XPS spectra were charge shifted according to the C_{1s} peak at 284.8 eV (Briggs and Seah, 1990) before peak fitting was performed.

4.4 Results

4.4.1 Microflotation

4.4.1.1 Effect of contamination pH

Figure 4.1 shows the recovery at flotation pH 9 as a function of contamination pH. In the absence of collector, sphalerite did not float appreciably over the pH range 4 to 9 with or without Pb. In the presence of xanthate, with no Pb sphalerite recovery was slightly elevated at pH below 6, consistent with the findings of others (Girczys and Laskowski, 1972; Guy and Trahar, 1985; Trahar et al., 1997), an effect generally attributed to interaction with lattice impurities (Girczys and Laskowski, 1972; Marouf et al., 1986; Mielczarski, 1986; Leroux et al., 1987). With 200 ppm Pb, sphalerite recovery was about 95% up to pH 7.5 and dropped

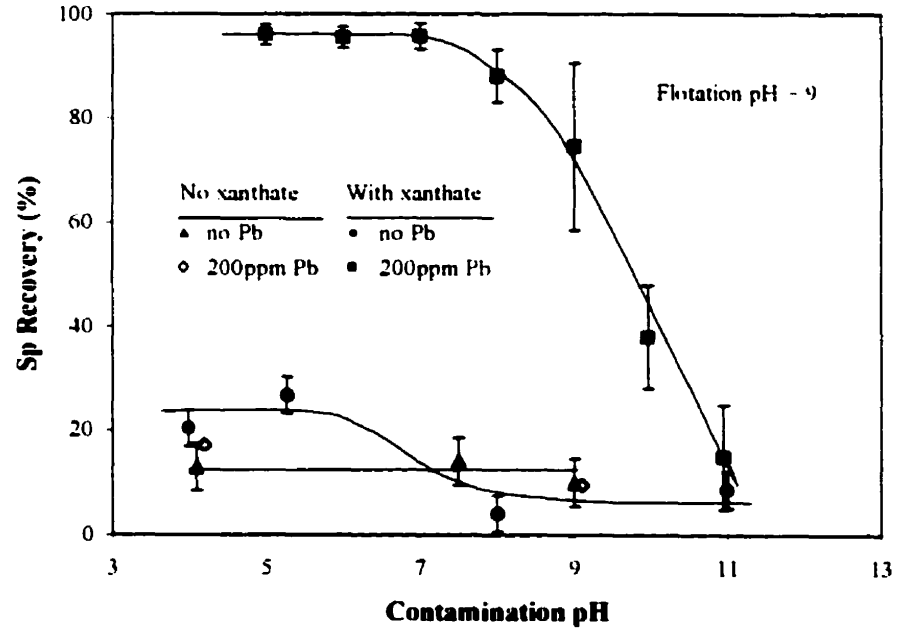

Figure 4.1 Effect of contamination pH, presence of xanthate and Pb ions on floatability of sphalerite (Sp).

substantially above pH 9. At pH 11, sphalerite recovery was the same as in the absence of xanthate. The upper pH bound to flotation is similar to that found by Trahar et al. (1997).

Figure 4.2 shows the effect of Pb concentration on flotation at pH 9 and 10.5 as a function of contamination pH. At flotation pH 9 (Figure 4.2a), sphalerite recovery increased sharply with Pb concentration at contamination pH 5 and 7.5 levelling out at [Pb] ≥ 100 ppm. At contamination pH 11, recovery was low, especially at [Pb] > 100 ppm. Similar trends were observed for flotation pH 10.5 (Figure 4.2b), but with lower recovery. The reduced flotation at high pH, whether the contamination pH (Figure 4.1) or flotation pH (Figure 4.2b), is attributed to the formation of hydrophilic lead hydroxide precipitates. This, and the statistically significant activation effect at 50 ppm in Figure 4.2a, is discussed later.

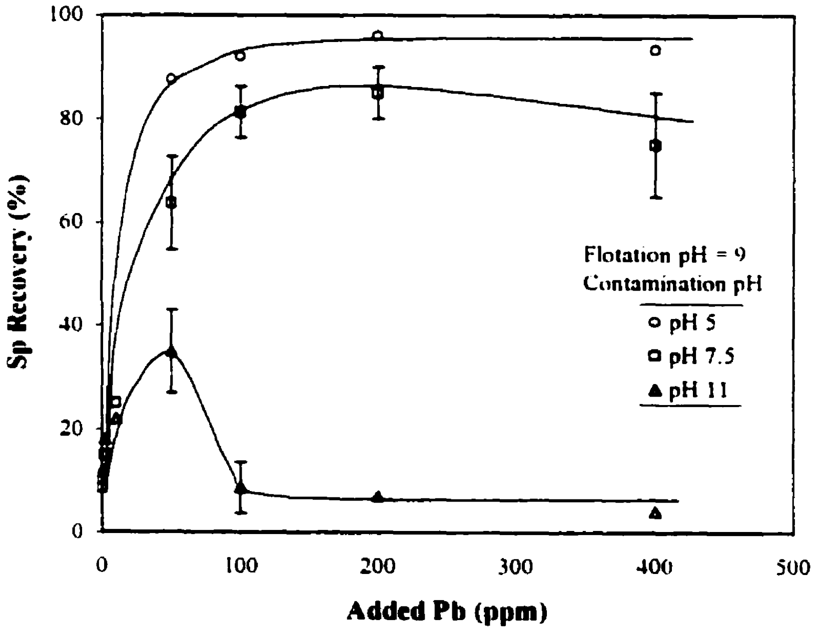

Figure 4.2a Effect of Pb concentration and contamination pH on floatability of sphalerite at flotation pH 9.

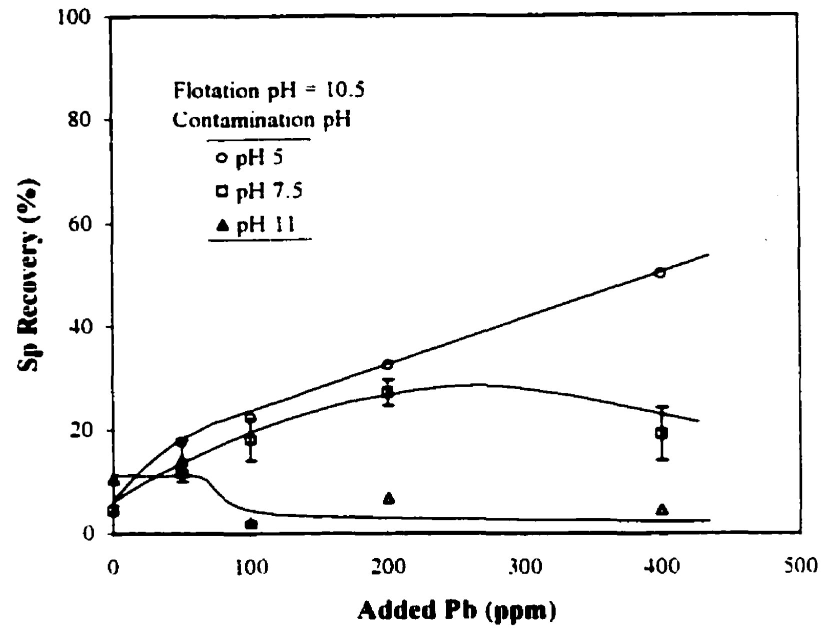

Figure 4.2b Effect of Pb concentration and contamination pH on floatability of sphalerite at flotation pH 10.5.

From Figure 4.2, the effect of Pb is revealed more at flotation pH 9 than 10.5, therefore pH 9 was selected for flotation. Figure 4.2a shows the most sensitive contamination pH is 5. However, it is judged that such a low pH is not commonly encountered in practice and as a compromise between sensitivity and pragmatism a contamination pH 7.5 was selected for further work.

4.4.1.2 Effect of galena particles

Figure 4.3 shows that the recovery of sphalerite increased in the presence of galena particles, especially when galena was fine (compare oxidized -8 μm and -38 μm galena) and oxidized (compare -8 μm oxidized and unoxidized). At this stage, the higher recovery of sphalerite

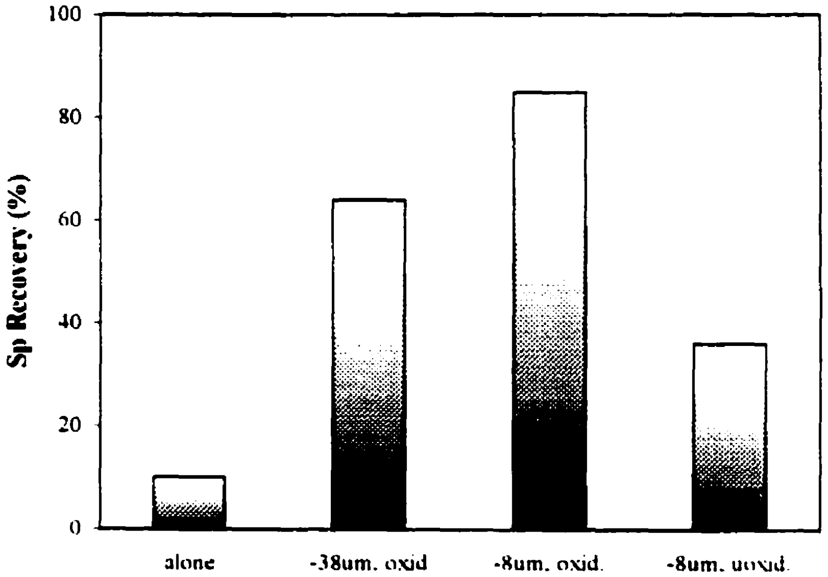

Figure 4.3 Floatability of sphalerite in the presence of galena particles.

in the presence of galena could be due to Pb ions derived from the galena.

4.4.2 EDTA Extraction - Correlation between Recovery and Surface Pb

Figure 4.4 shows sphalerite recovery as a function of surface concentration of Pb ($[Pb]_{surf}$) for contamination pH 7.5 and flotation pH 9 using both the solution and contact with galena test results. As evident, recovery increased with $[Pb]_{surf}$ yielding recovery > 80% at $[Pb]_{surf} \geq 2 \times 10^{-4}$ mg/cm^2. By cross-reference with the curve of recovery vs initial [Pb], $[Pb]_{surf} = 2 \times 10^{-4}$ mg/cm^2 corresponds to [Pb] ≈ 100 ppm. This was the reason 100 ppm Pb was used in the XPS tests.

Also evident in Figure 4.4 is that the results of the solution tests and the contact with galena

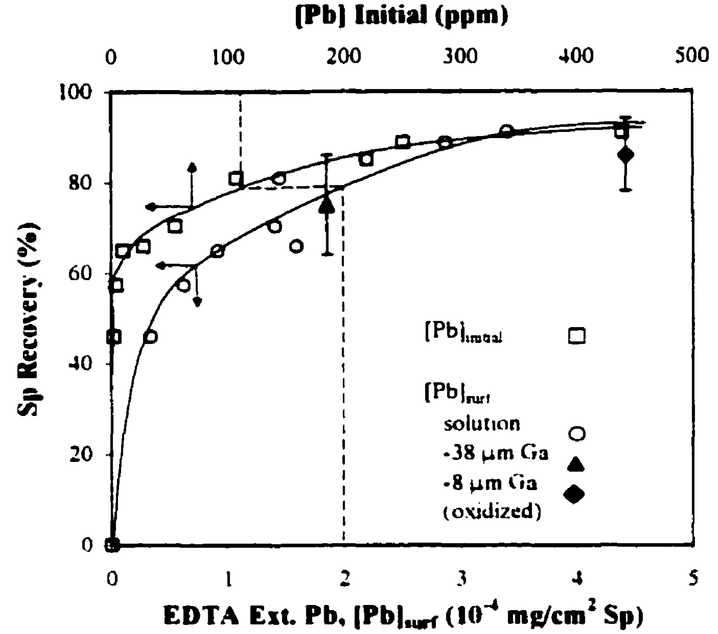

Figure 4.4 Sphalerite recovery as a function of initial and surface Pb concentration $[Pb]_{surf}$ deduced from EDTA extraction.

tests lie on the same trend line. This implies that Pb ions derived from galena are activating the sphalerite rather than some other mechanism causing flotation. Taking a recovery of 50% as a measure of an undesirable level of accidental activation, a critical level of contamination can be defined: $[Pb]_{surf}^{crit}$ appears to be about 0.5×10^{-4} mg/cm^2. It should be remembered that the conditions in Figure 4.4 are a sensitive test of activation by Pb ions (contamination pH 7.5, flotation pH 9), i.e., they represent close to a worst case scenario.

4.4.3 X-ray Photoelectron Spectroscopy (XPS)

The Pb_{4d5} spectral region is presented in Figure 4.5. The results confirm the presence of Pb on the surface of sphalerite, the Pb_{4d5} peak being in the expected position (~413 eV, Briggs and Seah, 1990) for spectrum (b). There is a possible Pb peak in the untreated sphalerite ca.

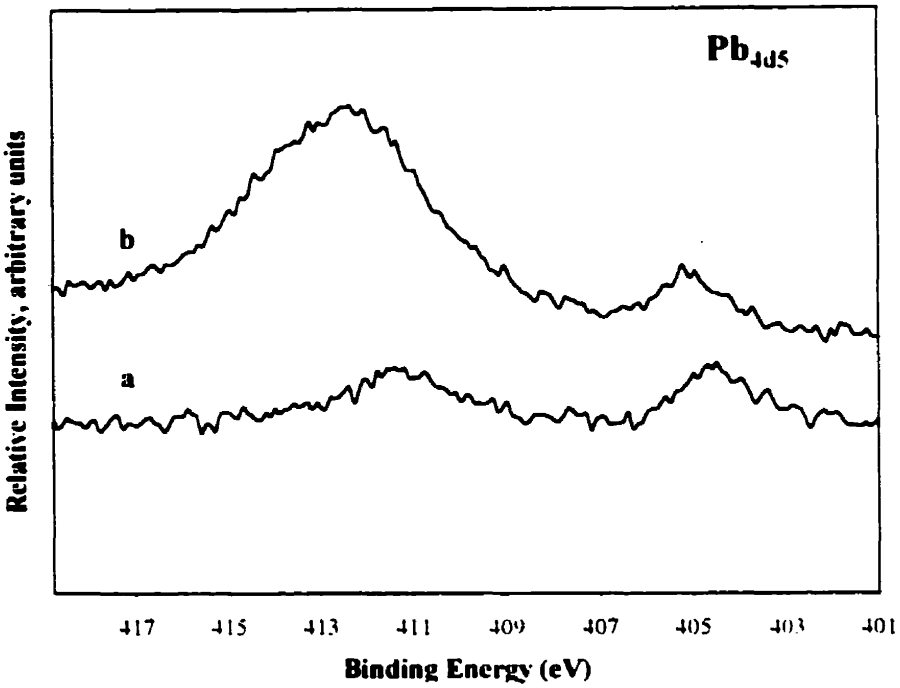

Figure 4.5 Pb_{4d5} photoelectron spectra from sphalerite surface: (a) sphalerite alone; (b) treated with 100 ppm Pb.

411 eV which could reflect a minor amount of Pb in the lattice, although no Pb was detected by bulk analysis. The persistent peak at ~ 405 eV is due to impurities such as cadmium (Briggs and Seah, 1990). The corresponding surface atomic concentration of Pb, along with the other elements detected, is given in Table 4.3.

Table 4.3 Elemental surface concentrations of sphalerite determined by XPS

Conditions	Atomic Concentrations (%)				
	Zn	S	C	O	Pb
(a) 15 min. in distilled water (pH 7.5)	18	37	32.6	11.8	0.6
(b) 15 min. in 100 ppm Pb (II) (pH 7.5)	19.8	39.9	25.3	10.7	4.3

4.5 Discussion

4.5.1 Proposed Mechanisms for Pb/Xanthate Interaction with Sphalerite

The Pb activation effect is clearly pH dependent, reflecting the different species present. Species distribution for the following, Pb^{2+}, $PbOH^{+}$, $Pb(OH)_{2(aq)}$, $Pb(OH)_3^-$, $Pb(OH)_4^{2-}$, Pb_2OH^{3+}, $Pb_3(OH)_4^{2+}$, and $Pb(OH)_{2(S)}$ was calculated by "EQUILCOM" (Sui and Huang, 1998). Figure 4.6 shows the result as a function of pH for initial Pb concentration of 100 ppm, and Figure 4.7 shows the result for pH 11 as a function of Pb concentration. By comparing with the pH range giving strongest activation, pH ≤ 7.5, then Pb^{2+} and $PbOH^{+}$ appear to be the species responsible. At pH 11 as the Pb concentration increases the concentration of $Pb(OH)_{2(s)}$ increases while that for $Pb(OH)_{2(aq)}$ and $Pb(OH)_3^-$ decreases.

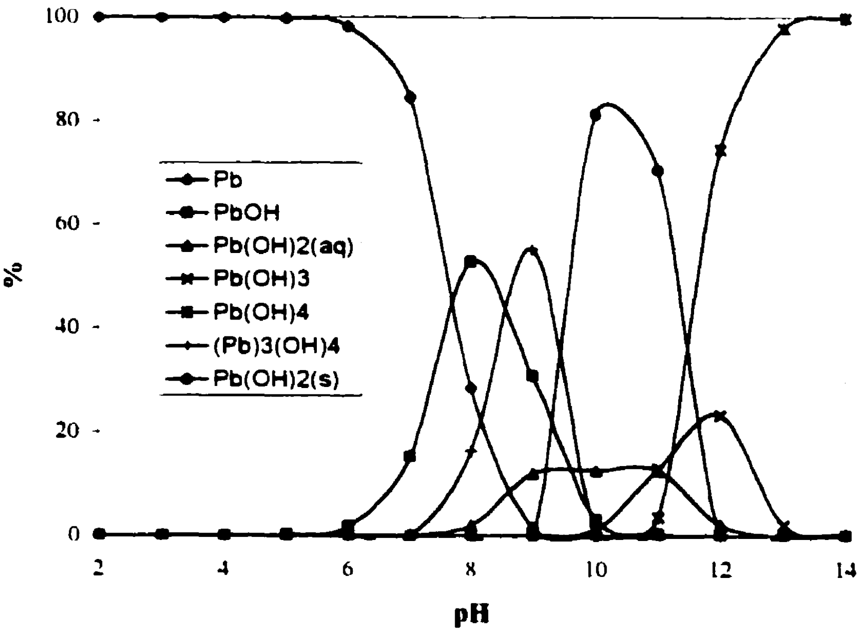

Figure 4.6 Species distribution diagram for [Pb] = 100 ppm as a function of pH.

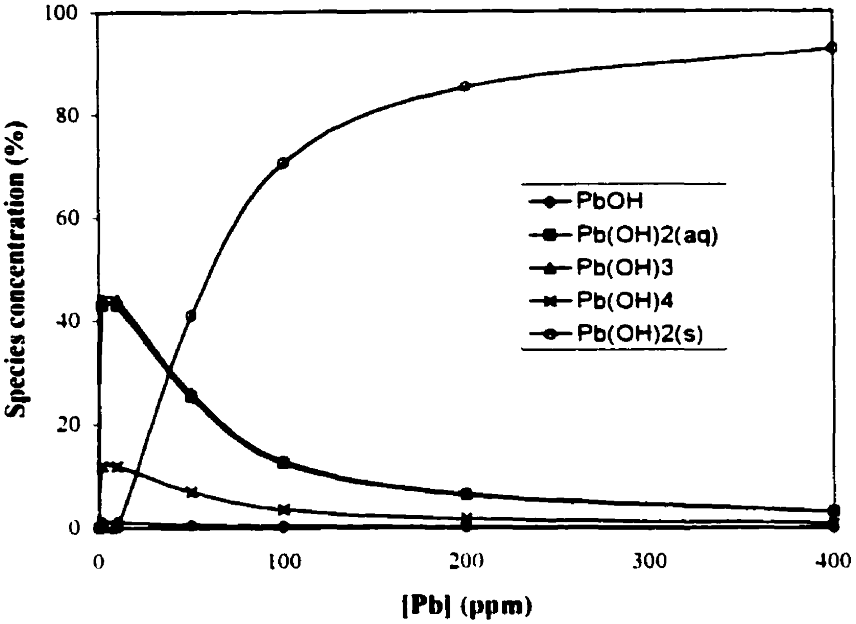

Figure 4.7 Pb species distribution as a function of initial Pb concentration at pH 11.

Consequently $Pb(OH)_{2(s)}$ precipitates, which are hydrophilic and do not react with xanthate, are dominant at high Pb concentration (> 100 ppm). However, at low concentration (< 100 ppm) Pb is present more as Pb-hydroxy species which can react with xanthate. This may explain the mild activation seen in Figure 4.2a at pH 11 at [Pb] < 100 ppm.

From the Pb species distribution combined with the observed flotation response, Figure 4.8 has been constructed to suggest the possible reactions in the sphalerite/Pb/xanthate system. At pH < 7.5, Pb^{2+} and $PbOH^{+}$ react to form PbX_2 and Pb(OH)X, respectively, which make sphalerite floatable, whereas at pH > 9 $Pb(OH)_{2(s)}$ renders the surface hydrophilic. The competition among PbX_2, Pb(OH)X and $Pb(OH)_2$ determines the flotation response of sphalerite in the presence of Pb ions.

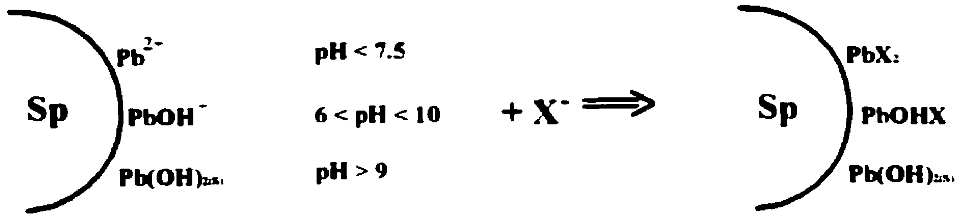

Figure 4.8 Proposed interactions of sphalerite with Pb species and xanthate.

The interactions in Figure 4.8 do not specify whether this is the contamination or flotation pH. To a large extent this does not appear to matter. From Figures 4.1 and 4.2a contamination at pH 11 did not yield flotation at pH 9 implying that the reaction forming $Pb(OH)_{2(s)}$ is not readily reversed. Figure 4.2b shows that contamination at pH 5, which has a strong flotation effect at pH 9, has only a limited activation effect at pH 10.5. Nevertheless, it does persist at high Pb concentrations, suggesting the absolute amount of Pb^{2+} and $PbOH^{+}$ available provides sufficient reaction sites for xanthate uptake.

Figure 4.1 shows a high scatter ca. pH 9 that appears to be related to the onset of $Pb(OH)_{2(s)}$ precipitation. Slight changes in pH around 9 have a marked effect on the amount of precipitate, which could account for the variation in flotation response.

4.5.2 Link between Pb Ion Production and Activation

Sui et al. (1999a) presented a model of Pb ion production (measured as % EDTA extractable Pb) for an ore as a function of particle size:

$$\%\ \text{EDTA extracted Pb} = \frac{0.01}{d} \tag{4-1}$$

where d is the particle size (cm). Knowing (or calculating) the surface area of particles and assuming that all the Pb ions produced are adsorbed and evenly distributed, the resulting surface concentration of Pb can be predicted and compared to a critical level for activation. Hence, the likelihood of accidental sphalerite activation can be assessed. By taking the following steps $[\mathrm{Pb}]_{surf}$ can be predicted:

1. From Eq. (4-1), Pb produced in terms of mg/g is

$$= \frac{0.1\,g}{d} \tag{4-2}$$

where g is fractional Pb content in the ore.

2. Converting to a surface area basis, the surface area per unit mass, cm^2/g, assuming spherical particles, is

$$= \frac{6}{\rho d} \tag{4-3}$$

where ρ is ore density (g/cm^3).

3. Combining Eqs. (4-2) and (4-3) gives $[\mathrm{Pb}]_{surf}$, mg/cm^2, as

$$= \frac{0.1g}{d} \cdot \frac{\rho d}{6} \qquad (4\text{-}4)$$

$$= 0.0167 \,.\, g \,.\, \rho$$

Eq. (4-4) shows $[Pb]_{surf}$ depends on ore grade and density but is independent of particle size, a consequence of the Pb production model, Eq. (4-1).

The value of $[Pb]_{surf}$ is plotted in Figure 4.9 as a function of Pb grade for ore densities ranging from 2.8 to 4.5 g/cm^3 (i.e., low to high sulphide mineral content). The predicted $[Pb]_{surf}$ can be compared with the $[Pb]_{surf}^{crit}$ needed for activation. From Figure 4.4 taking 50% recovery, $[Pb]_{surf}^{crit}$ was ca. 0.5×10^{-4} mg/cm^2. As Figure 4.9 shows an ore containing as little as 0.1% Pb generates $[Pb]_{surf}$ of this order, i.e., such ores appear to have the potential for activation

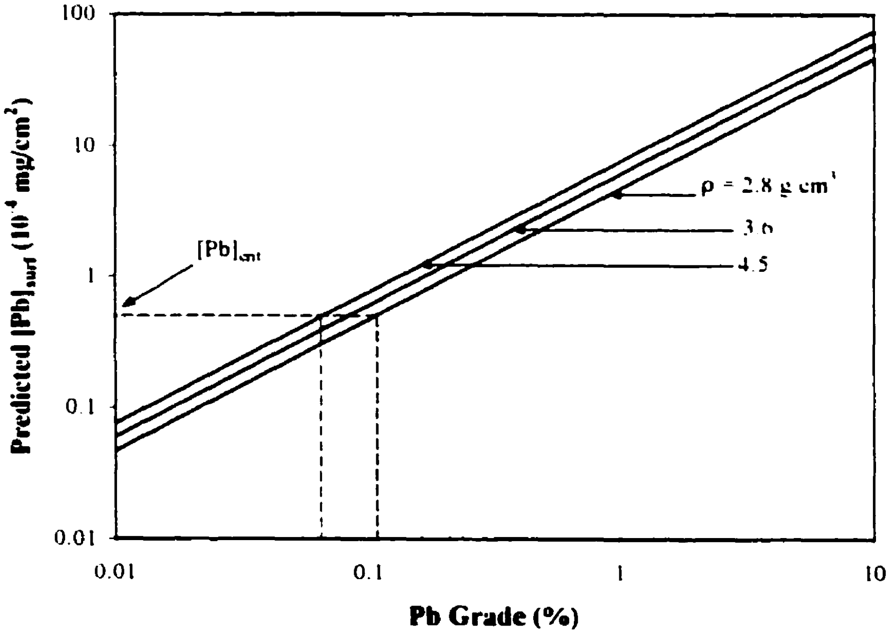

Figure 4.9 Predicted surface concentration of Pb as a function of Pb ore grade.

of sphalerite. Sui et al. (1999b) observed that there are grounds for suspecting activation with ores containing these low levels of Pb.

The calculation of $[Pb]_{surf}$ and estimation of a critical $[Pb]_{surf}$ for activation necessarily involves assumptions. These will be considered, starting with prediction of $[Pb]_{surf}$.

First, it was assumed that all Pb ions produced are absorbed. This is justified by the observation that pulp liquor analyses rarely reveal heavy metal ions in solution, compared to the amount on the surface revealed by EDTA extraction. Second, it was assumed that Pb ions are evenly adsorbed on all particles. Without evidence to the contrary this is judged reasonable; certainly it would not be reasonable to assume all Pb ions adsorb only on the sphalerite portion of the ore.

A consequence of the Pb ion production model is that $[Pb]_{surf}$ is independent of particle size. This does not mean that flotation response to Pb activation is independent of particle size. Indeed, accepting Trahar's (Trahar, 1981) floatability/hydrophobicity/particle size interaction relationship, a higher $[Pb]_{surf}$ is probably required to cause equal floatability of coarse particles compared to fine.

The concept of a critical surface concentration for activation is a useful aid to thought but estimation will remain somewhat arbitrary. The experience here based on recovery of a single size class, needs to be broadened to other sizes and rather than recovery the effect on flotation rate may provide a more general approach to estimating $[\mathrm{Pb}]_{\mathrm{surf}}^{\mathrm{crit}}$.

4.6 Conclusions

1. Sphalerite activation by lead under acid to mildly alkaline pH is attributed to adsorption of Pb^{2+} and $PbOH^{+}$ and reaction with xanthate (X) to form PbX_2 and PbOHX, respectively.
2. At > pH 10, $Pb(OH)_{2(s)}$ forms which is hydrophilic and depresses flotation.
3. Contamination at low pH gives a strong activation effect which is countered but not completely eliminated by floating at high pH.
4. Flotation was uniquely related to surface concentration of Pb, $[\mathrm{Pb}]_{\mathrm{surf}}$ mg/cm^2, regardless whether contamination was with Pb solutions or contact with galena; thus the activation effect of galena is due to release of Pb ions.
5. A critical $[\mathrm{Pb}]_{\mathrm{surf}}$ causing activation was derived. From a model to predict $[\mathrm{Pb}]_{\mathrm{surf}}$ an ore grade of ~ 0.1% Pb was judged sufficient to cause accidental activation.

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CHAPTER 5

DEACTIVATION OF Pb-CONTAMINATED SPHALERITE BY POLYPHOSPHATE

5.1 Abstract

Different reagents as deactivators in the sphalerite-lead system were compared using microflotation. The reagents were diethylenetriamine (DETA), sodium bicarbonate ($NaHCO_3$), silica sol (SS), sodium phosphate ($Na_3PO_4 \cdot 12H_2O$) and sodium polyphosphate (PP). The latter showed the strongest effect and was selected for a detailed study. The mechanism of polyphosphate action was investigated by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). It is concluded that polyphosphate acted to remove Pb (i.e., a "cleaning" mechanism) from sphalerite by forming a soluble complex. The presence of excess calcium ion did not markedly reduce the cleaning action. The polyphosphate consumption is estimated to be in line with typical modifier consumption in the processing of complex sulphide ores.

5.2 Introduction

Unintentional activation of minerals by contaminant metal ions is widely suspected as a source of mineral misplacement in separation by flotation. Such activation of sphalerite is an important case in point. There are typically four sources of contaminant metal ions in flotation systems: the water, especially if recycle is practised; soluble / semi-soluble minerals; oxidation of sulphide minerals; and corrosion of grinding steel (releasing Fe ions).

Release of metal ions by mineral oxidation is arguably the most important source being common to the processing of all sulphide ores. With certain sulphide mineral combinations, oxidation is enhanced by galvanic interactions (Nakazawa and Iwazaki, 1986; Rao and Finch, 1988; Yelloji Rao and Natarajan, 1989). For example in the presence of pyrite, oxidation of galena is enhanced resulting in release of additional Pb ions (Sui et al., 1995). The metal ions undergo pH controlled hydrolysis and mono-hydroxy species ($M(OH)^+$) form that appear to be the principal species interacting with minerals, both sulphide and non-sulphide (James and Healy, 1972; Jain and Fuerstenau, 1985).

The processing of polymetallic Cu/Pb/Zn ores generally involves first the flotation of Cu and Pb concentrates (sequentially or as a bulk). A widespread concern is possible accidental activation of sphalerite by metal ions causing misplacement of sphalerite to these concentrates resulting in lower grades as well as a loss of Zn. In the case of sphalerite, the important activating ions are probably Pb and Cu (Finkelstein, 1999).

The concentration of Pb and Cu ions in water is usually low because they are adsorbed on surfaces either as ions such as M^{2+}, $M(OH)^{+}$ or as insoluble compounds (hydroxide, carbonate, sulphate etc.). The evidence is that all these compounds are surface active (Predali et al., 1979) and therefore, are present mostly on surfaces rather than in solution.

One way to counter accidental activation is to add a reagent that either removes the metal ions (a "cleaning" mechanism) or forms a surface product that prevents reaction with collector (a "blocking" mechanism). In this role these reagents could be termed deactivators.

Complexing agents are a class of reagents that appear promising as deactivators. An organic complexing agent used in this way commercially is diethylenetriamine (DETA). It is used to depress pyrrhotite in the flotation of pentlandite (Marticorena et al., 1995; Yoon et al., 1995; Xu et al., 1997) and functions, in part, by solubilizing Cu and Ni ions which otherwise activate pyrrhotite. An inorganic complexing agent is polyphosphate, used to control metal ions in water treatment which hints at a possible role in deactivation. There are occasional references to its use in flotation.

Polyphosphates are long chain phosphates, $(P_nO_{3n+1})^{(n+2)-}$. The shortest member, orthophosphate[1] (PO_4^{3-}), is used to control lead solubility in lead pipes (Grimes et al., 1995) and has been suggested to immobilize aqueous Pb (Suzuki et al., 1981; 1982; 1984). The orthophosphate functions by forming a precipitate. The longer chain members form soluble

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[1] Referred to subsequently as phosphate.

complexes.

In flotation systems, Changgen and Yongxin (1983) studied selective flotation of scheelite from calcite and fluorite with sodium oleate as a collector and polyphosphates (cyclohexaphosphate $(NaPO_3)_6$ and diphosphate ($Na_4P_2O_7$)) as modifiers. They found selective depression of calcite and fluorite which was related to the ability of polyphosphate to remove Ca ions from the surface of these minerals as soluble complexes but not from scheelite because the Ca-O bond in scheelite is shorter and therefore stronger than is the case with the two other minerals. This is a form of cleaning action.

Parsonage et al. (1984) found that triphosphate ($Na_5P_3O_{10}$) had a depressant action on calcite, apatite and dolomite. They suggested that rather than solubilizing a cation, triphosphate was adsorbed at the cation sites conferring a high negative zeta potential on the mineral and reducing the adsorption of collector (i.e., a blocking action). They also found that the recovery of calcite and dolomite increased in excess triphosphate concentrations (greater than 1 g/L) which they could not explain.

In the flotation of quartz with dodecylammonium acetate calcium ions are depressants. Iwasaki (1989) testing sodium tripolyphosphate and sodium hexametaphosphate to control Ca ions found at low concentration depressant action increased. He attributed this to formation of Ca-PP precipitates that, through heterocoagulation, coated the quartz (i.e., a blocking mechanism). At high concentrations, however, flotation was restored. This was attributed to formation of soluble Ca-PP complexes and cleaning of the surface.

Fuliang and Fenglou (1997) found that flotation of galena improved by removing Ca and Mg with hexametaphosphate. In the presence of these cations, galena was depressed but after hexametaphosphate addition recovery was regained particularly around pH 8-10.

Polyphosphate as a deactivator for Pb-contaminated sphalerite is the focus here. To establish its potential a comparison with other possible deactivators is performed first. These reagents are diethylenetriamine, sodium bi-carbonate, and silica sol, the latter being suggested by its use in water treatment (Black, 1953; Gibson, 1993). The mechanism of polyphosphate action was explored by X-ray photoelectron spectroscopy and scanning electron microscopy studies.

5.3 Experimental

5.3.1 Minerals and Reagents

Sphalerite specimens were obtained from Ward's Natural Science Establishment. The sample was crushed in a jaw crusher, and hand picked specimens were ground in a pulverizer, then dry-screened to obtain 38-74 μm size fraction. The sample was wet screened to remove fines. It was washed by dilute hydrochloric acid (pH 2) to remove products of oxidation, then by distilled water until the pH of solution approached the natural pH of the mineral distilled water system. The sample was stored under acetone until required. The surface area, measured by BET, was 0.0973 m^2/g. Table 5.1 shows the chemical analysis.

Table 5.1 Chemical composition of sphalerite used in experiments

Mineral	% Wt. of element			
	Zn	Fe	Pb	Cu
Sphalerite	64.95	0.31	0*	0.12

*Detection limit for Pb: 0.02 ppm

Table 5.2 shows the reagents used in this study. The sodium polyphosphate employed is a linear polyphosphate with 16-19 PO_3 groups (average 17), and calculated molecular weight 1773.3 g/mol (Chapter 6).

5.3.2 Methodology

5.3.2.1 Solutions

Potassium ethyl xanthate (KEX) was purified by dissolving in acetone and reprecipitated by petroleum ether following a standard technique (Rao, 1971). A fresh 5×10^{-3} M xanthate stock solution was prepared daily at ca. pH 9, and then diluted to 5×10^{-5} M with distilled water at ca. pH 9.

Lead nitrate stock solution of 1000 ppm (4.8×10^{-3} M) was prepared by dissolving $Pb(NO_3)_2$ powder in distilled water at natural pH, and then diluting to the desired concentration. A lead concentration of 100 ppm (4.8×10^{-4} M) was generally used.

Table 5.2 Reagents

Chemical	Grade	Supplier	Usage
Hydrochloric acid	ACS reagent	Fisher Scientific Co.	pH regulator
Sodium hydroxide	Analytical reagent	ACP Chemicals Inc.	pH regulator
Lead nitrate	ACS reagent, 99.9%	Fisher Scientific Co.	Lead pretreatment
Potassium ethyl xanthate	Purified	Cytec Industries Ltd.	Collector
Acetone	ACS reagent	BDH Chemicals	Dry mineral storage
Petroleum ether	Analytical reagent	BDH Chemicals	Purification and storage of KEX
Diethlenetriamine	Reagent grade	Fisher Scientific Co.	Deactivator
Sodium bicarbonate	Laboratory grade	Fisher Scientific Co.	Deactivator
Sodium phosphate	98%, ACS reagent	Aldrich Chemical Co.	Deactivator
Sodium polyphosphate	96%	Aldrich Chemical Co.	Deactivator
Sodium silicate solution	37 - 38%, Technical grade	Fisher Scientific Co.	Deactivator
Calcium sulphate hemihydrate	98%	Aldrich Chemical Co.	Source of Ca
Sodium tetraborate decahydrate	ACS reagent	Aldrich Chemical Company, Inc.	buffer, pH 7.5
Nitric acid	69.0 - 71.0%	Fisher Scientific Co.	pH regulator

An aqueous solution of 1% DETA was prepared with distilled water. The pH of this stock solution was about 11. Before each experiment, the DETA solution was diluted to 100 ppm (9.7×10^{-4} M) with natural pH ca. 8.

Carbonate stock solution 10^{-2} M (6000 ppm CO_3^{2-}) was prepared by dissolving sodium bicarbonate powder in distilled water. Before each experiment, the carbonate solution was diluted to 10^{-3} to 5×10^{-3} M with a natural pH ca. 8.2.

Silica sol (SS) was prepared from sodium silcate solution following the procedure of El-Ammouri et al. (1997). Natural pH was ~ 8.3.

Sodium phosphate ($Na_3(PO_4)_3$) stock solutions of 1000 ppm or 3000 ppm (as salt) were prepared by dissolving sodium phosphate decahydrate crystals in distilled water. Natural pH of the stock solutions was ~11.5. Solutions 4 - 200 ppm salt were prepared by dilution with distilled water with pH over this concentration range varying from ~ 7-10.3.

Sodium polyphosphate stock solution of 1000 ppm (as salt) was prepared by dissolving sodium polyphosphate crystals in distilled water. Solutions down to 1 ppm (pH 7-7.8) were prepared by dilution with distilled water.

5.3.2.2 *Microflotation*

A previous study (Rashchi et al., 2000)[2] established that flotation at pH 9 after conditioning with 100 ppm Pb at pH 7.5 gave a sensitive response to Pb activation. The same procedure was used here.

A 1.5 g sample of sphalerite was conditioned with 100 mL lead nitrate solution at 100 ppm (5×10^{-4} M) and pH 7.5. The suspension was conditioned on an orbital shaker at 250 rpm for 15 minutes, then was decanted and 100 mL of deactivator added at a given concentration and natural pH and conditioned for a further 15 minutes. The solution was decanted and the particles were transferred to a Partridge-Smith microflotation cell (Partridge and Smith, 1971). The particles were conditioned with potassium ethyl xanthate solution at 5×10^{-5} M, pH 9. Flotation time was one minute and the float and non-float products were collected, dried, and weighed to calculate recovery. Repeat tests showed an average absolute standard deviation of 5%.

Tests with polyphosphate included the effect of concentration, order of addition with xanthate and presence of calcium ions (which are nearly always present in plant waters). In the order of addition test, after Pb conditioning the sample was treated next with xanthate (5×10^{-5} M, pH 9) for 5 min., then decanted, conditioned with polyphosphate and floated in xanthate solution (5×10^{-5} M, pH 9). In the case of calcium, after the Pb conditioning step the sample was decanted and 500 ppm Ca (as calcium sulphate) was added with 100 mL of the

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[2] Chapter 4

polyphosphate. The pH of the mixture was ~ 7.3. The presence of calcium made the solution cloudy.

5.3.2.3 Scanning Electron Microscopy (SEM)

A JEOL 840A Scanning Electron Microscope was used. EDS analysis were done with a Noran I2 system. After conditioning, the solution was filtered and the particles on the filter paper were washed using distilled water and dried in air. Secondary and backscattered images were taken. Spot analysis (energy dispersive spectroscopy, EDS) was performed to help identify surface species.

5.3.2.4 X-Ray Photoelectron Spectroscopy (XPS)

The XPS spectra were recorded using a VG (Vacuum Generators) ESCALAB 220i-XL spectrometer with an Al K-alpha X-ray source (hν = 1486.6 eV) at a normal take off angle and a band-pass energy of 50 eV corresponding to an energy resolution of 1.2 eV. The vacuum pressure in the chamber was about 10^{-9} to 10^{-10} Torr. The X-rays were non - monochromated and the instrument was calibrated against the $Ag_{3d5/2}$ Fermi edge. The charge compensation was adjusted on each sample to obtain the maximum signal possible for $Zn_{2p3/2}$ at Ek = 464 eV.

As a blank test to characterize the surface of the untreated mineral, 1.5 gram of sphalerite was conditioned in 100 mL distilled water (pH 7.5) for 15 min., filtered and rinsed once. To study the effect of lead, the sphalerite sample was treated in 100 ppm lead solution (pH 7.5) for 15 min., the suspension was either filtered, rinsed (and dried in air) or decanted and the solids conditioned in 10 ppm sodium polyphosphate solution at natural pH of 7.5 (then filtered, rinsed and dried in air). In one test, 500 ppm Ca was added with the polyphosphate.

An initial survey of the surface was made to determine the elements present then the predetermined regions of interest were scanned to measure atomic concentrations. The atomic concentrations were determined from XPS peak areas knowing the respective sensitivity factors and are reported as a percentage of all elements observed. The peak areas were obtained using XPSPEAK 95 v. 3.1, an XPS peak fitting program (Kwok, 1997). The XPS spectra were charge shifted according to the C_{1s} peak at 284.8 eV (Briggs and Seah, 1990) before peak fitting was performed.

5.4 Results and Discussion

5.4.1 Microflotation

5.4.1.1 Comparison of deactivators

Figure 5.1 shows the recovery of sphalerite in the presence of sodium bicarbonate, DETA, silica sol (SS), sodium phosphate, and sodium polyphosphate (PP). The polyphosphate clearly had the strongest effect, reducing recovery to < 5% with only 1 ppm. Indeed the concentration of the other reagents was selected to try to match the polyphosphate effect. From these findings polyphosphate was chosen for further detailed study.

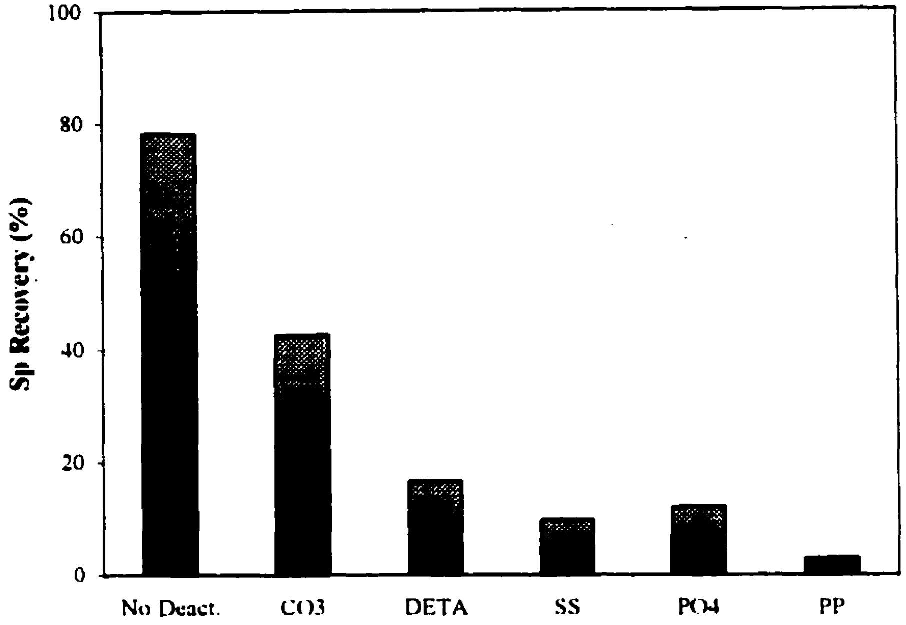

Figure 5.1 Recovery of Pb-activated sphalerite in the presence of deactivators: $[CO_3^{2-}]$ = 600 ppm; [DETA] = 100 ppm; [SS] = 100 ppm; $[PO_4^{3-}]$ = 1000 ppm; [PP] = 1 ppm.

5.4.1.2 *Effect of polyphosphate concentration*

A set of flotation tests was performed to select an effective polyphosphate concentration (Figure 5.2). From these results 0.07 mg polyphosphate/g sphalerite was selected, equivalent to 1 ppm polyphosphate in solution. The presence of 500 ppm Ca moderated the deactivation effect presumably because some polyphosphate is complexed (i.e., consumed) by calcium. However, at 0.07 mg/g significant deactivation was still achieved. Figure 5.2 also gives further results for sodium bicarbonate and sodium phosphate. Both are less effective than the polyphosphate, the phosphate approaching the same level of deactivation at high concentration.

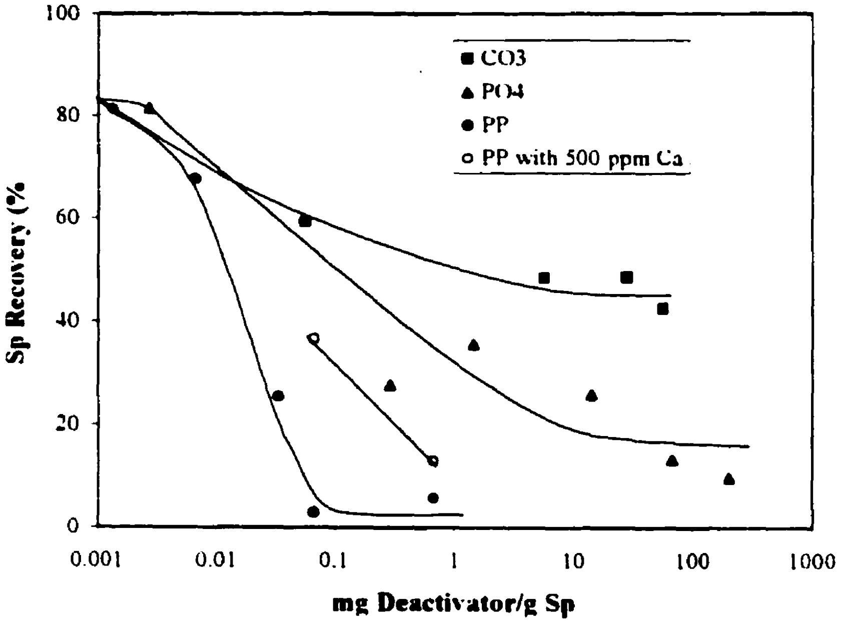

Figure 5.2 Recovery of Pb-activated sphalerite as a function of deactivator concentration

Figure 5.3 shows the order of addition test. When xanthate (X) is added prior to PP the deactivation effect is reduced suggesting that polyphosphate does not remove Pb as easily once reaction with xanthate has occurred. Increasing the polyphosphate concentration to 10 ppm did not change the result significantly.

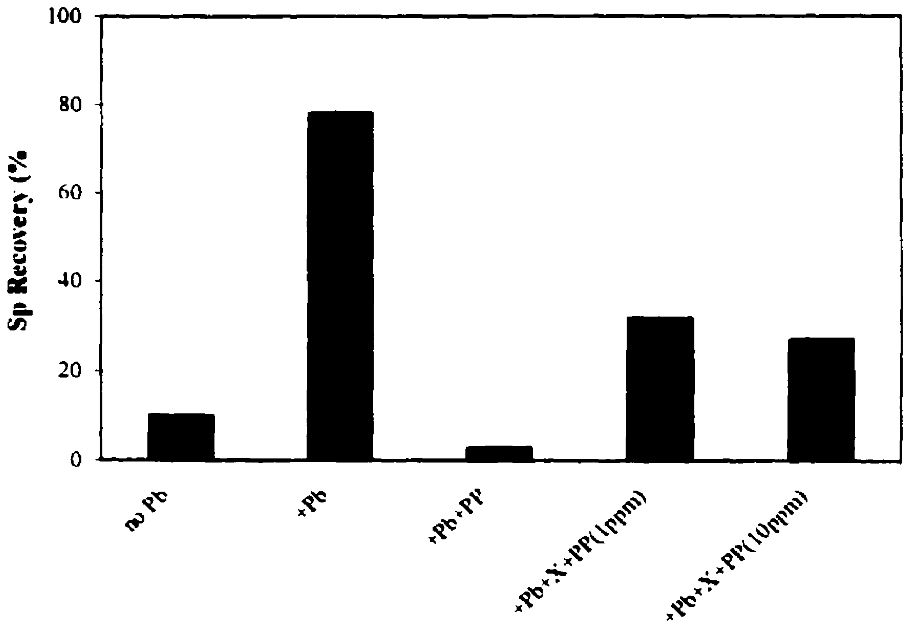

Figure 5.3 Recovery of sphalerite: alone; activated with 100 ppm Pb; with polyphosphate (1 ppm); with xanthate (11 ppm), then polyphosphate (1 ppm); and with xanthate (11 ppm), then polyphosphate (10 ppm).

5.4.2 X-Ray Photoelectron Spectroscopy (XPS)

The Pb_{4d5}, S_{2p}, C_{1s}, Ca_{2p}, and P_{2s} spectral regions are presented in Figures 5.4 - 5.7, respectively. All the spectra have been charge-shift corrected. The four conditions, a - d, shown in these figures are defined in Table 5.3 which also gives the corresponding surface atomic concentrations.

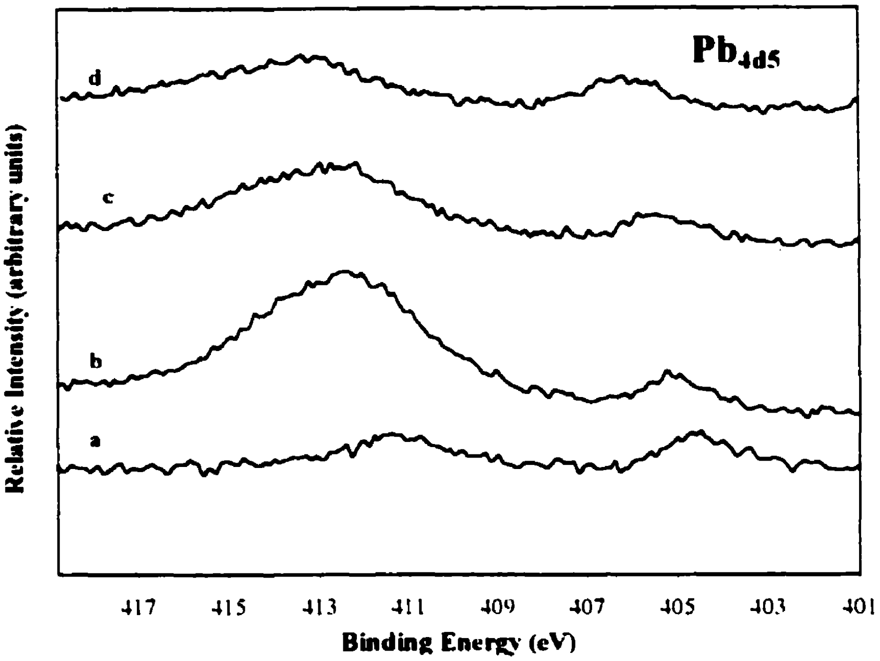

Figure 5.4 Pb_{4d5} photoelectron spectra from sphalerite surface. Conditions (a)-(d) are given in Table 5.3.

Table 5.3 Elemental surface concentrations determined by XPS for conditions a-d.

Conditions	Atomic Concentration (%)						
	Zn	S	C	O	Ca	Pb	P
(a) 15 min., distilled water (pH 7.5)	18	37	32.6	11.8	-	0.6	-
(b) 15 min., 100 ppm Pb (II) (pH 7.5)	19.8	39.9	25.3	10.7	-	4.3	-
(c) condition (b) decanted, 10 ppm PP at pH 7.5	17.2	37.2	31.3	11.9	-	2.3	-
(d) condition (b) decanted, 500 ppm Ca + 10 ppm PP at pH 7.5	19.2	38.2	26.2	13	1.6	1.8	-

The Pb_{4d5} peak shown in Figure 5.4 was in the same position (~ 413 eV) for conditions (b), (c) and (d). (There is also a small peak in the untreated sphalerite at ca. 411 eV which may reflect a minor amount of Pb in the lattice although chemical assay of the sample did not show any Pb. The persistent peak at ~ 405 eV is probably due to impurities such as cadmium (Briggs and Seah, 1990).) The peak intensity is lowered by about 50% in the presence of polyphosphate whether Ca is present (d) or not (c), as reflected in the atomic concentration data in Table 5.3. Given the excess Ca present, Pb complexation with polyphosphate appears preferential over that with Ca.

The sulfur region in the XPS spectrum (Figure 5.5) demonstrates a distinct peak assignable to the S_{2p} band at a binding energy ~ 163 eV (Mielczarski, 1986). This peak is asymmetric

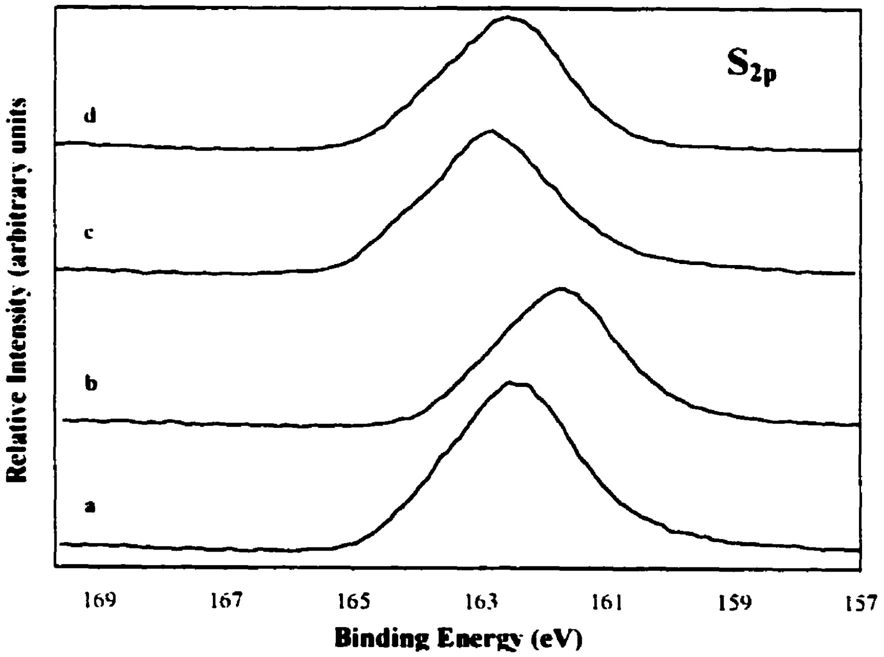

Figure 5.5 S_{2p} photoelectron spectra from sphalerite surface. Conditions (a)-(d) are given in Table 5.3.

due to the presence of an additional spin orbit ($S_{2p1/2}$) at a binding energy 1.18 eV above the main peak; this energy difference is just below the resolution of the instrument. The band is assigned to sulfur as sulfide ion in the sphalerite lattice by comparison with the XPS spectra of untreated sphalerite (a). There is essentially no impact on sulphur, the change in atomic concentration over the different conditions being less than 7%.

The Ca_{2p} signals (Figure 5.6, Table 5.3) clearly show the presence of calcium on the surface (d), indicating that the polyphosphate concentration was not sufficient to complex both lead and calcium. Figure 5.7 shows the region where the P_{2s} signal is expected (191 eV). It is clear that no phosphorous is adsorbed on the surface under the conditions studied. The XPS data indicate polyphosphate removes Pb and does not adsorb, i.e., it functions by a cleaning

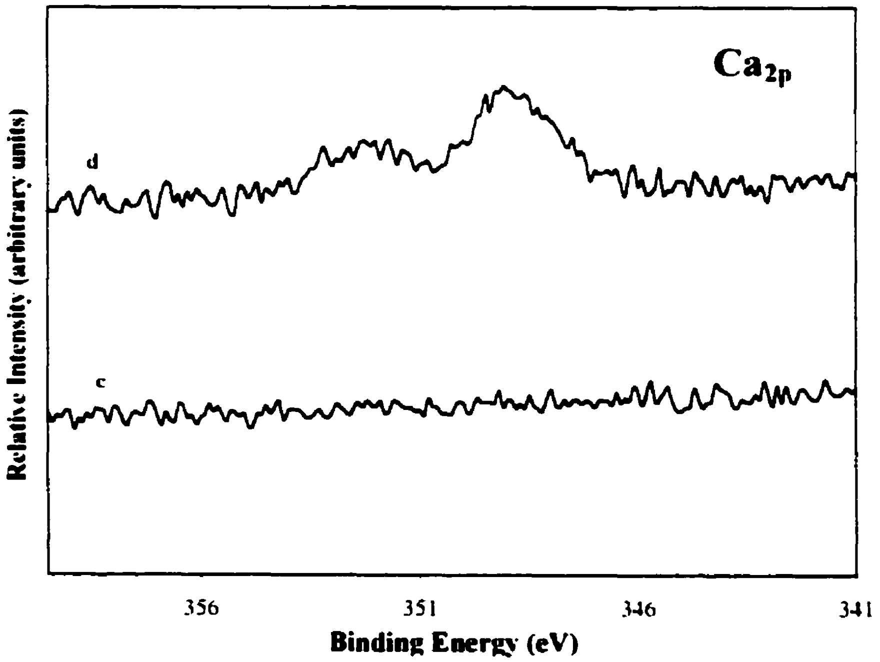

Figure 5.6 Ca_{2p} photoelectron spectra from sphalerite surface. Conditions (c) and (d) are given in Table 5.3.

action.

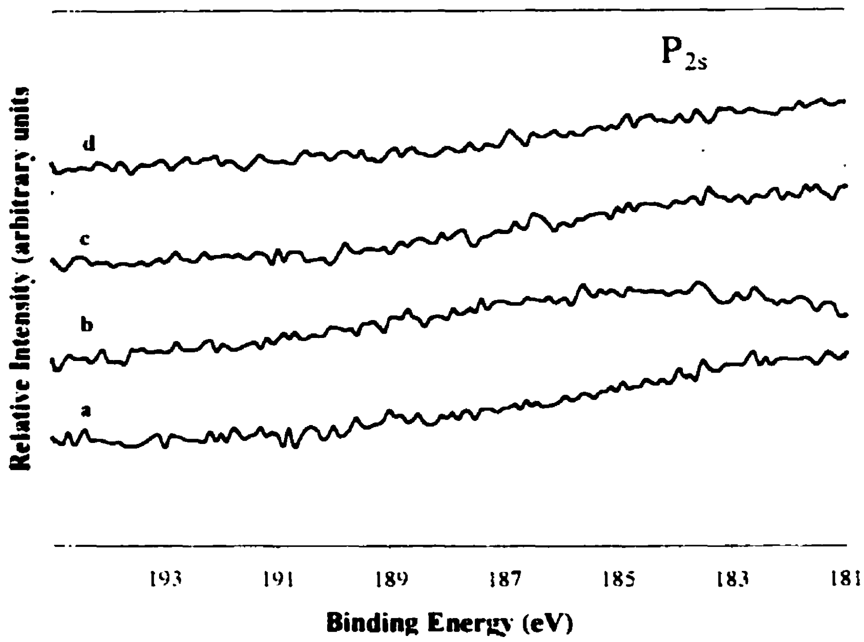

Figure 5.7 P_{2s} photoelectron spectra from sphalerite surface. Conditions (a)-(d) are given in Table 5.3.

5.4.3 Scanning Electron Microscopy (SEM)

Conditioning was performed at 500 ppm Pb and pH 10 to render the Pb species visible as the hydroxide. Figure 5.8a shows a backscattered (BS) image of the sphalerite prior to polyphosphate addition. Electron dispersive spectroscopy (EDS) performed on the bright spots revealed Pb. Figure 5.8b shows the same sample after treatment with 10 ppm polyphosphate. It is evident that while Pb precipitates remained on the surface the density is greatly reduced. Increasing the polyphosphate concentration to 100 ppm produced a clean surface (Figure 5.8c). EDS did not show lead or phosphorous on the surface, reinforcing polyphosphate has a cleaning action.

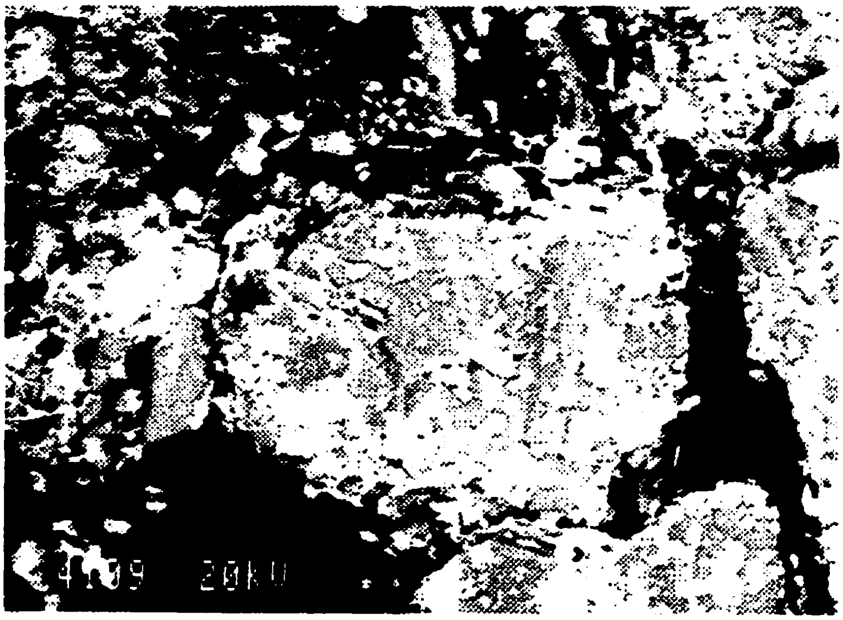

Figure 5.8a SEM (BS) micrograph of sphalerite at pH 10 in the presence of 500 ppm Pb.

Figure 5.8b SEM (BS) micrograph of sphalerite at pH 10 in the presence of 500 ppm Pb and 10 ppm PP.

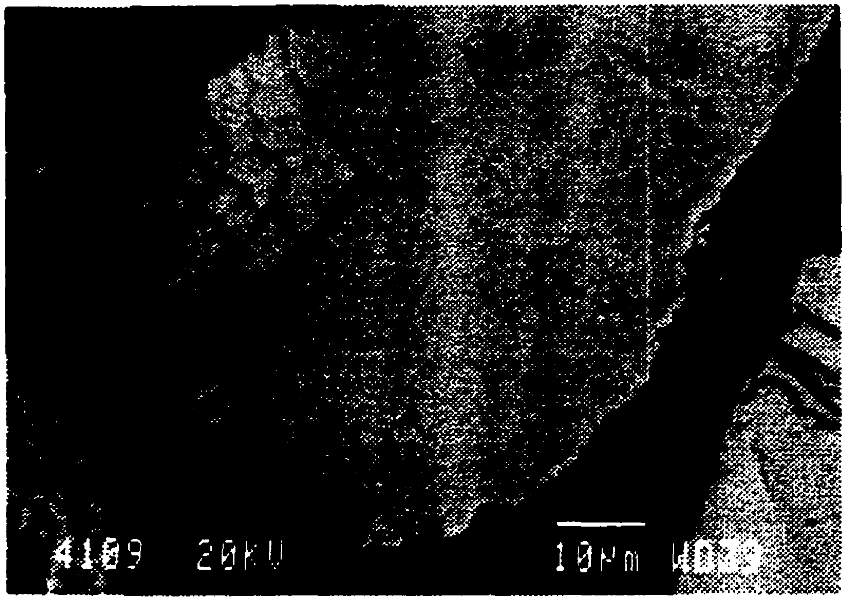

Figure 5.8c SEM (BS) micrograph of sphalerite at pH 10 in the presence of 500 ppm Pb and 100 ppm PP.

In summary, the XPS and SEM data show that polyphosphate removes Pb from the sphalerite surface, presumably as a soluble complex, and does not adsorb. As a deactivator, therefore polyphosphate functions by a cleaning action.

5.5 Potential Significance to Flotation

Of the reagents tested, microflotation showed that polyphosphate was the most effective in countering Pb activation of sphalerite. A concentration of 0.07 mg/g of sphalerite reduced recovery from 80% to less than 5%. The XPS and SEM studies identified a cleaning action, the polyphosphate removing the Pb, probably to form a soluble Pb-PP complex. The presence of excess Ca was not a major factor but the order of addition test showed that polyphosphate removes Pb more easily before reaction with xanthate. This suggests that polyphosphate should be added, if feasible, ahead of xanthate.

The economics of phosphate application will depend on the amount of Pb that needs to be complexed and the nature of the complex formed (e.g., PP/Pb ratio). Complementary studies on the amount of Pb that constitutes an accidental activation problem (Sui et al., 1999; Rashchi et al., 2000) and on the chemistry of the complex (Rashchi and Finch, 2000)[3] may permit the amount of polyphosphate to be predicted. The calculation steps are given below (see Appendix C for details of calculations):

1. The predicted concentration of Pb on a surface area basis ($[Pb]_{surf}$, mg/cm^2) given by Sui et al. (1999) is:

$$= 0.0167 \cdot g \cdot \rho \qquad \textbf{(5-1)}$$

where g is fractional Pb content in the ore and ρ is the density of the ore, g/cm^3.

2. Converting to a mass of ore basis, mg Pb/g ore, assuming spherical particles gives:

$$= \frac{0.1\,g}{\bar{d}} \qquad \textbf{(5-2)}$$

where $\bar{d}$ is the mean size of the ore, cm.

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[3] Chapter 6

3. Knowing that the minimum ratio of PP/Pb to complex Pb is 1/2 (Rashchi and Finch, 2000), the minimum amount of polyphosphate required, mol PP/kg ore, to remove Pb from the surface is:

$$= \frac{2.41 \times 10^{-4}\, g}{\bar{d}} \qquad \textbf{(5-3)}$$

4. For the polyphosphate used in this study with molecular weight of 1773.3 g/mol, the minimum amount of polyphosphate required, g PP/kg ore, is

$$= \frac{0.428\, g}{\bar{d}} \qquad \textbf{(5-4)}$$

Mineral processors rarely consider the mean size of a distribution. To convert to a more meaningful measure, it is assumed the distribution follows a Gates - Gaudin - Schuhmann distribution (Schuhmann, 1940):

$$Y = \left(\frac{d}{k}\right)^{\alpha} \qquad \textbf{(5-5)}$$

where Y is the cumulative weight fraction of particles finer than size d, α is termed the distribution modulus (dimensionless), and k is termed the size modulus (with dimension of size). Taking $\alpha = 0.8$ (Charles, 1957) the mean size was computed as a function of the 50% passing, d_{50} (see Appendix D for details of calculations). The result is illustrated in Figure 5.9 where polyphosphate consumption in mol/kg ore (Eq. 5.3) and in g/kg ore (Eq. 5.4, right hand scale), is plotted against the mean particle size, $\bar{d}$ and d_{50} (upper scale) for Pb grades of 0.01, 0.1 and 1%.

The d_{50} ranging from 2 to 50 μm is representative of that encountered in flotation feeds for polymetallic ores. According to Sui et al. (1999) and Rashchi et al. (2000) the 0.1% Pb grade is sufficient to reach a critical surface concentration of Pb to cause sphalerite activation, indicated by critical ore grade the figure.

Considering the 0.1% Pb case, with decreasing size case the consumption ranges from 0.1 to 1 g PP/kg ore (100 - 1,000 g/tonne). This is in line with the consumption of some modifiers used in processing complex sulphide ores (Table 5.4), for example, sulphur dioxide and copper sulphate. In that sense the consumption is technically reasonable. The present laboratory results gave deactivation at ca. 0.07 mg/g, i.e., 70 g/tonne, also in the range predicted.

For Pb grades higher than 0.1% polyphosphate consumption will rise; at 1% it ranges up to 1 g/kg (1 Kg/tonne) which is probably too high to be of immediate practical interest. One caveat is that the Pb activation study on which the critical $[\mathrm{Pb}]^{\mathrm{crit}}_{\mathrm{surf}}$ was based represented a worst case scenario (Rashchi et al., 2000); by a judicious combination with pH regulation deactivation may be achieved at lower polyphosphate consumption. A second caveat is that since the intended application is to prevent misplacement of sphalerite to Cu/Pb concentrates, polyphosphate must be added early in the process (preferably before xanthate) in which case the impact downstream, notably on Zn flotation, must be considered.

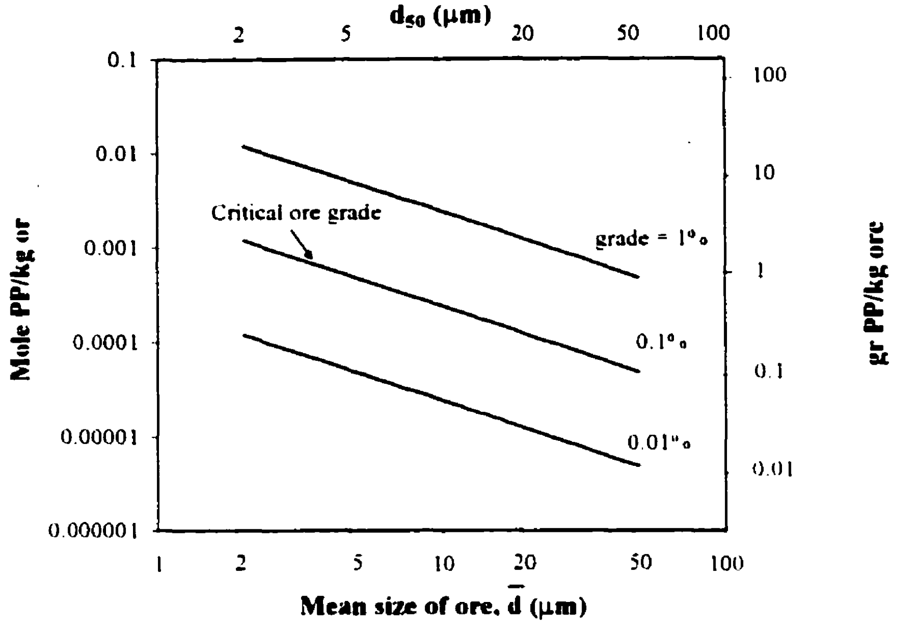

Figure 5.9 Minimum amount of polyphosphate required to remove Pb from the surface of ore particles as a function of mean particle size and 50% passing size (see text). Note, the "0.1%" line corresponds to critical surface concentration of Pb causing activation (corresponding to 1 min. flotation time) derived by Rashchi et al. (2000), chapter 4.

Table 5.4 Some reagents consumption in complex sulphide ore flotation (after Schnarr, 1978)

Reagent	Use	Consumption g/tonne ore
Lime	pH, pyrite depressant	3400
Sodium carbonate	pH	1800
Sulphur dioxide	Zn, pyrite depressant	1000
Copper sulphate	Zn activation	750
Dextrin	Pb depressant	50

5.6 Conclusions

1. Microflotation showed polyphosphate had a strong deactivation effect on Pb-contaminated sphalerite. One ppm polyphosphate in solution - equivalent to 0.07 mg polyphosphate/g sphalerite - was found to be effective under the conditions studied.
2. From XPS and SEM studies polyphosphate was shown to function by a cleaning mechanism, removing the Pb as a soluble complex.
3. Polyphosphate is more effective when added prior to xanthate. The presence of up to 500 ppm calcium had little effect on the Pb-cleaning action of polyphosphate.
4. The polyphosphate consumption is estimated to be in line with typical modifier consumption in the processing of complex sulphide ores.

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CHAPTER 6

LEAD-POLYPHOSPHATE COMPLEXES

6.1 Abstract

Polyphosphate (PP) has been suggested as a mean of controlling accidental flotation of sphalerite by lead (Pb) ion activation through formation of soluble Pb-PP complexes. The polyphosphate to lead ratio in the complexes was determined from conductometric titration of polyphosphate against lead nitrate solution. Initially a precipitate forms with PP/Pb of 1/3. The precipitate dissolves in excess polyphosphate, resulting in a variety of Pb-PP complexes with PP/Pb of 1/2, 1/1, 3/2, 2/1, and 3/1.

6.2 Introduction

The ability of phosphates to form soluble complexes with metal ions has been recognized for more than 160 years. Shortly after the discovery that there were several kinds of phosphates it was found that some of the linear phosphates had the ability to prevent precipitation or to dissolve precipitates of the alkaline earth metals (Van Wazer and Callis, 1958). Towards the end of the nineteenth century, this phenomenon was attributed to the formation of relatively stable soluble complexes between the metal and the phosphate. The formation of a soluble complex, whether by strong ion association or covalent bonding, has been proposed to interpret the various chemical changes found in phosphate solutions. Soluble complex formation remains central to our understanding and exploitation of phosphate chemistry.

Some chemical properties of polyphosphates can be determined by appropriate titration methods. The amount of metal ion complexed by polyphosphates can be determined from conductometric, nephelometric, acid/base or polarographic titration.

Van Wazer and Campanella (1950) titrated a commercial phosphate glass with tetramethylammonium hydroxide in the presence of various metal ions. From the pH changes, they divided cations into three general groups depending on their ability to form complexes with the linear polyphosphates: (1) quarternary ammonium ions, which form no complexes, (2) alkali metal and similar single valence cations, which form weak complexes, and (3) alkali earth metals, transition metals, and Pb which form relatively strong complexes.

Using a conductometric technique, the existence of a soluble complex with a 1/1 ratio of calcium to triphosphate was found by Gray and Lemmerman (1954). Rogers and Reynolds (1949) reported conductometric titration of sodium diphosphate with solutions of metal ions such as calcium, nickel, iron, and zinc and found the molar ratio of metal to polyphosphate ranged from 0.93 to 0.97.

Rogers and Reynolds (1949) observed three inflection points in a conductometric titration with both ferric and aluminum ions corresponding to a mole ratio of diphosphate to metal ion of 2/1, 1/1, and 0.75/1 (there was precipitation at this point). Bobtelsky and Kertes (1954) also reported conductometric titration of 0.025 to 0.125 M solutions of diphosphate and triphosphate with calcium, barium, and magnesium ions with no clear result on metal to polyphosphate ratio.

In the present work, conductometric titration is carried out to determine the PP/Pb ratio in lead-polyphosphate complexes. The work was undertaken as linear polyphosphates have been suggested as reagents in mineral flotation to control accidental activation of sphalerite by Pb ions through formation of soluble Pb-PP complexes (Rashchi et al., 2000)[1]. The quantity of PP required will depend on the amount of Pb and the PP/Pb ratio in the complexes.

6.3 Experimental

6.3.1 Reagents and Set-Up

6.3.1.1 Reagents

Lead nitrate solutions of 0.05, 0.1, and 0.2 M were prepared by dissolving $Pb(NO_3)_2$ (Fisher Scientific Co., ACS reagent, 99.9%) in distilled water at natural pH. Sodium polyphosphate

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[1] Chapter 5

(Aldrich Chemical Co., 96% pure) used in this study is a linear polyphosphate with 16-19 PO_3 groups (average 17). The pH of polyphosphate solution was about 7 - 7.8. This suggests the middle PO_3 groups are completely neutralized - otherwise the pH would be ≤ 4.5 (Van Wazer and Callis, 1958) - and the end groups are partially neutralized - otherwise pH would be ≥ 9.5 (Van Wazer and Callis, 1958). Uncertainty in the Na/H ratio of the end groups generates only a small uncertainty in molecular weight (1751.4 g/mol (no Na) to 1795.3 g/mol (all Na)). Taking a ratio Na/H = 1 the formula is $Na_{18}HP_{17}O_{52}$ and molecular weight is 1773.3 which is used throughout. Solutions of 88.7 g/L, 177.3 g/L, and 354.7 g/L (0.05, 0.1, and 0.2 M, respectively) were prepared by dissolving sodium polyphosphate powder in distilled water.

6.3.1.2 Titration set-up

Conductometric titration experiments to determine the PP/Pb ratio were performed at room temperature using a buret to add polyphosphate solution to a beaker containing 10 mL lead nitrate solution. The samples were agitated using an overhead stirrer. A digital conductivity meter (VWR Scientific Products, model 2052) was used.

6.3.2 Titration

Conductivity vs volume of titrant is linear and the slope is proportional to the mobility of ions in the solution, a steep slope indicating a highly mobile ion while a gentle slope reflects less mobile ions. Thus, a change in the slope indicates a change in the ions in solution. When the two linear portions are extrapolated, the point of intersection is the equivalence point. At least three to four data points before and after the equivalence point are needed to define the titration curve (Skoog and West, 1998). In the present case, each slope corresponds to a particular complex of given PP/Pb ratio and every change of slope is related to formation of a new complex.

Ten mL Pb solutions of 0.05, 0.1, and 0.2 M were titrated with polyphosphate solutions of 0.05, 0.1, and 0.2 M, respectively. The molar concentration of both were selected the same to have volumetric ratios equal to mole ratios. The conductivity electrode was immersed in the solution and read after each addition of polyphosphate. As soon as the polyphosphate was added to the lead solution, a precipitate formed (the solution became cloudy) which later dissolved in excess polyphosphate.

6.4 Results and Discussion

6.4.1 The PP/Pb Ratio in the Complexes

Examples of the conductometric titration curves are shown in Figure 6.1. Due to the scale, the figure does not reveal the equivalent points. In order to do so and to determine the PP/Pb ratio at the end points directly, conductivity is plotted against the PP/Pb mole ratio. Figures 6.2 a-f show there were six changes in slope, i.e., there are six complexes formed. Essentially the same PP/Pb ratio was found for each concentration used, the range being given in the figure caption. Taking the nearest simple ratio, the PP/Pb ratios in the order a - f are ca. 1/3, 1/2, 1/1, 3/2, 2/1, and 3/1. Only in the case of e there is some doubt; the data better fit a ratio 7/4 but 2/1 is felt to be more likely. The ratios could reflect mixed complexes but the data

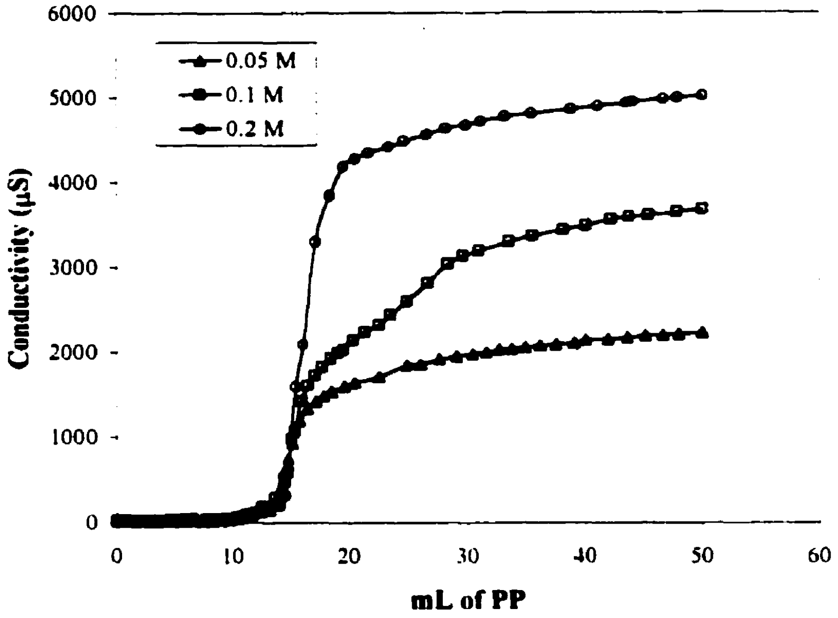


Figure 6.1 Conductometric titration of lead nitrate solutions with polyphosphate solutions of the same concentration.

are insufficient to unravel that possibility. In each case, the initial addition of polyphosphate to the lead solution resulted in formation of a precipitate, i.e., the first change in slope (Figure 6.2a) corresponds to this precipitate. It dissolved at a PP/Pb ~ 1/3 suggesting a formula of Pb_3PP for the precipitate. Therefore, the PP/Pb ratios shown in Figures 6.2a-f correspond to Pb_3PP precipitate and Pb_2PP, PbPP, $Pb_2(PP)_3$, $Pb(PP)_2$, and $Pb(PP)_3$ soluble complexes. From the practical flotation point of view, knowing that Pb has to be solubilized to avoid activation the minimum amount of PP to add corresponds to a PP/Pb ratio of 1/2. Knowing the amount of Pb that needs to be complexed, therefore the minimum polyphosphate concentration required could be predicted. If a higher polyphosphate concentration is used the other Pb-complexes are formed.

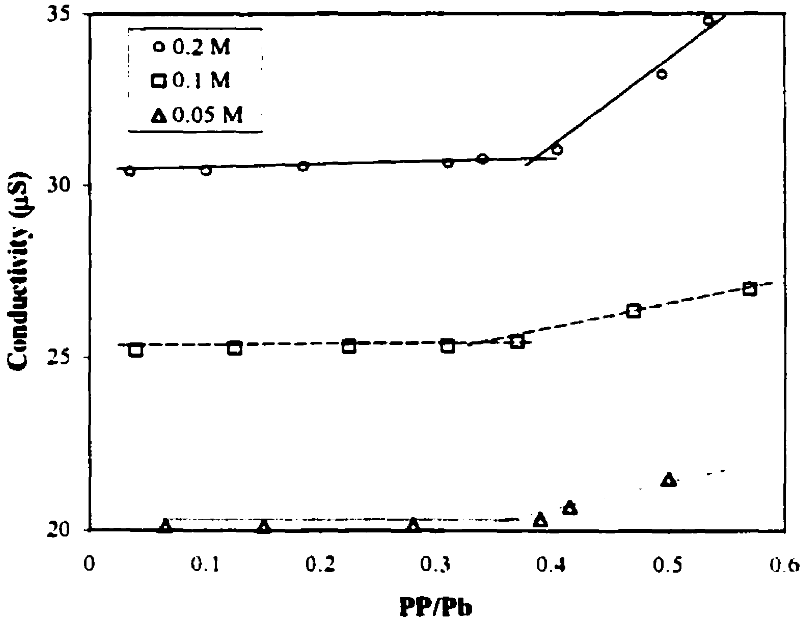


Figure 6.2a Evaluating polyphosphate to lead ratio from conductometric titration curve: PP/Pb = 0.33 - 0.38.

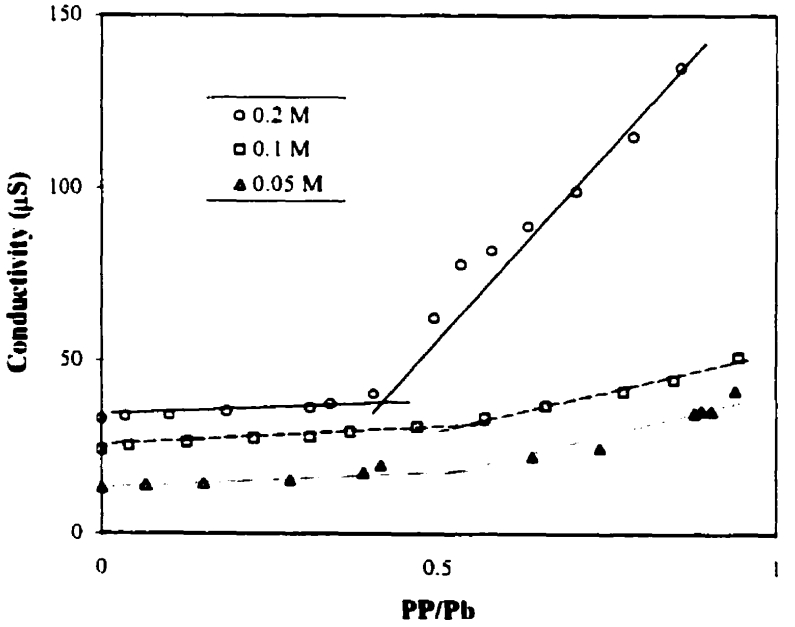


Figure 6.2b Evaluating polyphosphate to lead ratio from conductometric titration curve: PP/Pb = 0.42 - 0.52.

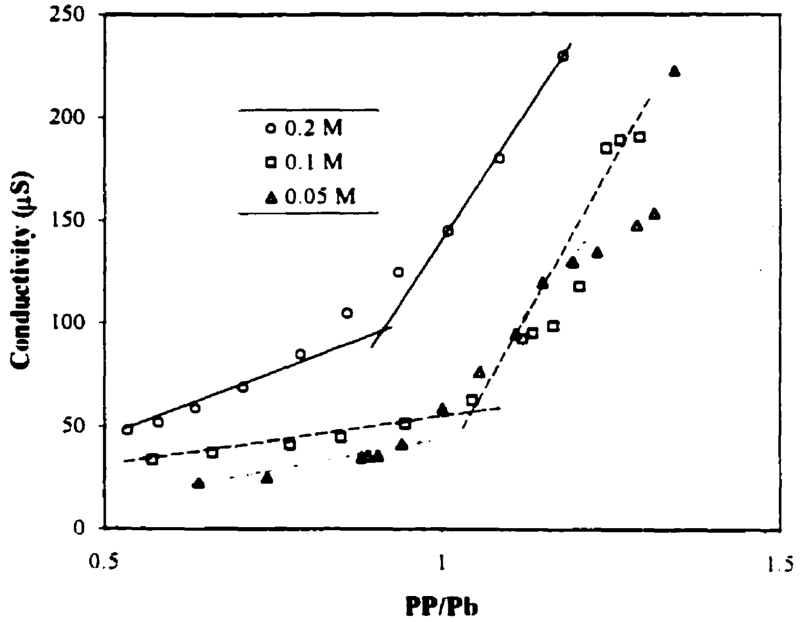


Figure 6.2c Evaluating polyphosphate to lead ratio from conductometric titration curve: PP/Pb = 0.92 - 1.05.

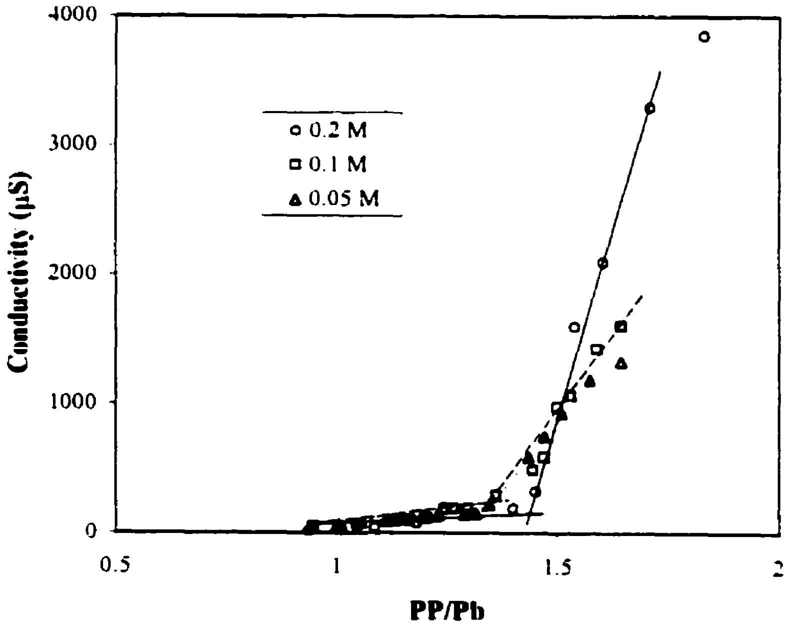


Figure 6.2d Evaluating polyphosphate to lead ratio from conductometric titration curve: PP/Pb = 1.35 - 1.45.

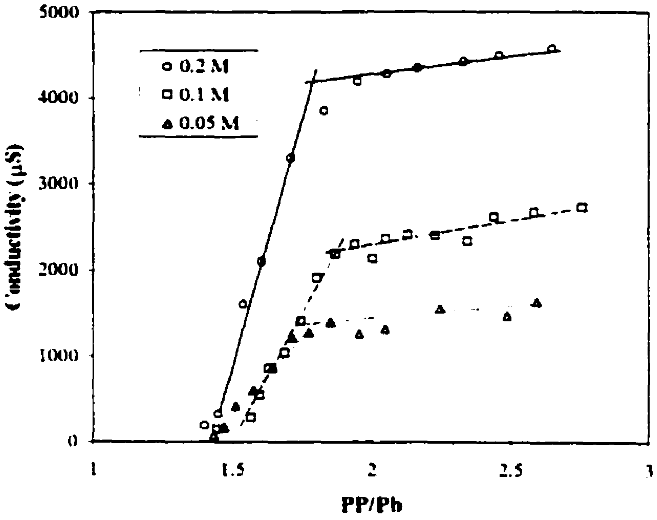


Figure 6.2e Evaluating polyphosphate to lead ratio from conductometric titration curve: PP/Pb = 1.65 - 1.85.

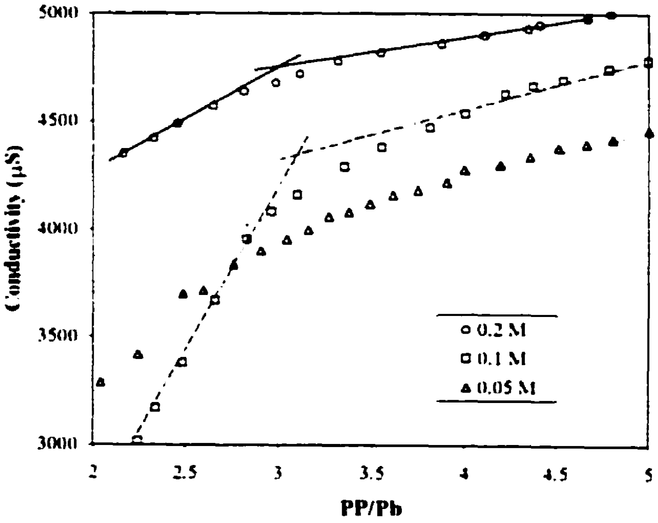
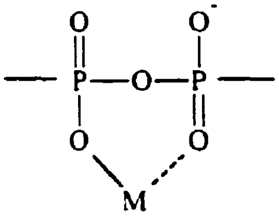
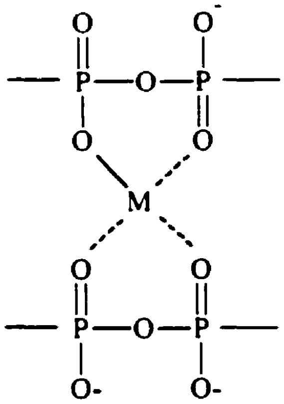


Figure 6.2f Evaluating polyphosphate to lead ratio from conductometric titration curve: PP/Pb = 2.85 - 3.1. The y-scale of 0.1 M and 0.05 M has been multiplied by 1.3 and 2, respectively, to show all curves on the same graph.

6.4.2 Chemical Structure of Pb-Polyphosphate Complexes

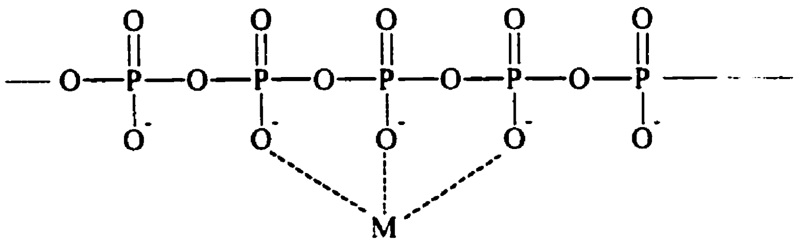
Langmuir and Schaefer (1937) assumed only the sodium atoms at the ends of the chain become ionized and suggested the complex with calcium has the form of a ring made by each end of a linear polyphosphate attaching to the calcium. The type of chelate structure suggested by Van Wazer and Campanella (1950) was different. They advanced the idea that the strong complexing ability of the linear polyphosphates is due to the formation of chelate rings. They gave the following structures:





They also suggested that since the weak acid hydrogen comes from the terminal PO_4 groups of polyphosphate molecules, complex formation involves the terminal groups. Because of resonance, the formation of such a chelate ring at the end of a polyphosphate chain would cause the weak acid hydrogen atom to become strongly dissociated.

Other authors (Melchior, 1954; Watters et al., 1957) proposed the following structure for binding in metal complexes with linear polyphosphates:



They observed that the geometry of the linear polyphosphate is such that an oxygen atom from each of three neighbouring PO_4 groups making up the chain can be brought into close proximity with a metal ion. This structure explains why the linear polyphosphates form more stable complexes with the multiple charged cations than do the ring polyphosphates: the ring polyphosphates are sterically hindered from assuming all possible configurations, while the linear polyphosphates are flexible in assuming different positions.

Bivalent lead forms a seven coordination complex with a lone electron pair which can polymerize (Mumme and Winter, 1971; Drew, 1977). Drew describes the complex as a pentagonal bipyramid. There are six potential coordination sites around the lead ion that might be occupied by the oxygens from polyphosphate molecule. The five positions in the equatorial plane surrounding the metal atom are at a shorter bond distance from the central metallic atom than the two axial locations (Figure 6.3).

Combining the above ideas the proposed structure of the complexes, with PP/Pb equal to 1/2 and 1/1 as examples, are shown in Figure 6.4. According to the available coordination sites of Pb (Figure 6.3) the Pb atoms in the complexes suggested in Figure 6.4 still have coordinate sites that could be occupied by oxygens from other polyphosphate molecules. This is how the other complexes 3/2, 2/1, and 3/1, can be formed.

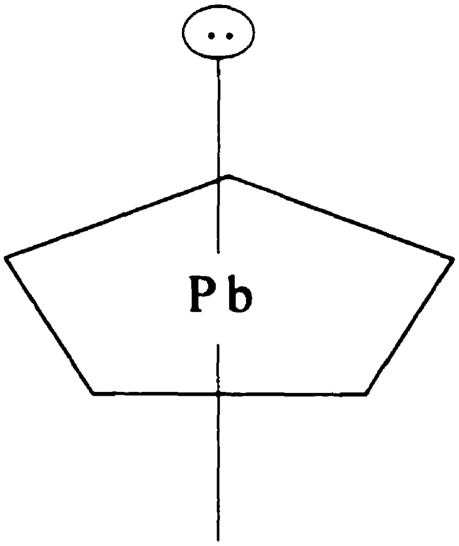
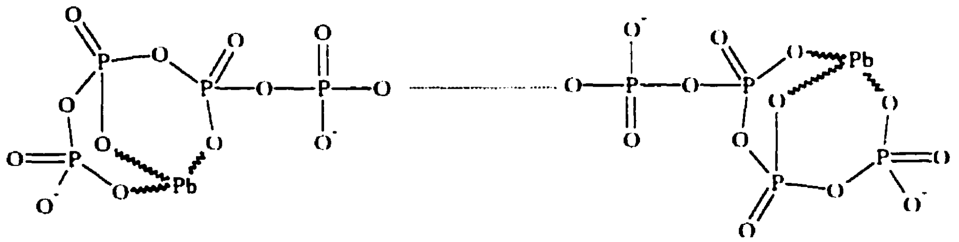


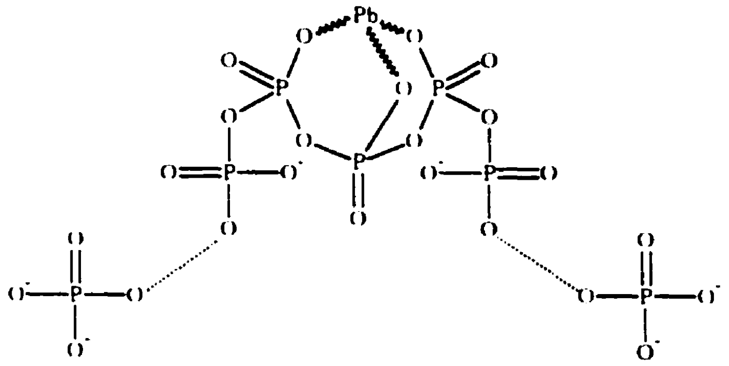
Figure 6.3 Pentagonal bipyramid.

6.5 Conclusions

Conductometric titration showed that polyphosphate precipitates with lead at PP/Pb ratio of 1/3. The precipitate dissolves in excess polyphosphate solution, resulting in a variety of Pb-PP complexes with PP/Pb of 1/2, 1/1, 3/2, 2/1, and 3/1. The minimum PP/Pb to keep lead in solution, therefore, is 1/2.



(a) PP/Pb = 1/2.



(b) PP/Pb = 1/1

Figure 6.4 Proposed structure of some Pb-PP complexes

6.6 References

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CHAPTER 7

CONCLUSIONS, CLAIMS TO ORIGINAL KNOWLEDGE AND SUGGESTIONS FOR FUTURE WORK

7.1 Conclusions

7.1.1 Sphalerite Activation and Surface Pb Ion Concentration

a) Flotation response of sphalerite as a function of pH and surface concentration of Pb ($[Pb]_{surf}$) was determined. Conditioning ("contaminating") with Pb at pH 7.5 and flotation at pH 9, selected as a practical condition for study, gave a sensitive response to Pb activation. Sphalerite recovery increased with $[Pb]_{surf}$ yielding recovery > 80% at $[Pb]_{surf} \sim 2 \times 10^{-4}$ mg /cm^2 corresponding to $[Pb] \approx 100$ ppm. At more alkaline pH the response reduces even with high surface concentrations of Pb.

b) The activation effect of contact with galena is attributable, in this case at least, entirely to Pb ions transferred to sphalerite.

c) Sphalerite activation is caused by Pb^{2+} in the weakly acidic region, and Pb^{2+} and $PbOH^{+}$ in the neutral to mildly alkaline regions. Hydrophilic $Pb(OH)_{2(s)}$ precipitates depress sphalerite at high pH.

d) A critical surface concentration of Pb causing accidental activation of sphalerite was estimated as $[Pb]^{crit}_{surf} = 0.5 \times 10^{-4}$ mg /cm^2. By combining with a Pb ion production model, the possibility of accidental Pb activation for an ore of given Pb grade is explored. Ores with as little as 0.1% Pb pose a potential activation problem.

7.1.2 Deactivation of Pb-Contaminated Sphalerite by Polyphosphate

a) Microflotation showed several deactivators appear promising with polyphosphate giving the greatest effect. One ppm polyphosphate in solution - equivalent to 0.07 mg polyphosphate /g sphalerite - was found to be effective under the conditions studied. The effect was moderated only slightly by the presence of excess calcium.

b) XPS and SEM showed that phosphorous was not present on the surface suggesting it did not adsorb but rather functioned by a cleaning action, removing Pb as a soluble complex.

c) Polyphosphate is more effective when added prior to xanthate.

7.1.3 Lead Polyphosphate Complexes

a) Conductometric titration showed polyphosphate precipitates with lead at PP/Pb ratio of 1/3. The precipitate dissolves in excess polyphosphate, resulting in Pb-PP complexes with PP/Pb ratio of 1/2, 1/1, 3/2, 2/1, and 3/1. The minimum ratio of PP/Pb to keep lead in solution, therefore, is 1/2.

b) By knowing the lead concentration in a given system, the minimum concentration of polyphosphate required to solubilize the lead was estimated.

7.2 Contributions to Original Knowledge

a) Flotation response of sphalerite as a function of surface concentration of Pb on an area basis ($[Pb]_{surf}$, mg/cm^2) was determined. This demonstrated a unique response regardless of source of lead - from solution or contact with galena.

b) Polyphosphate was introduced and studied as a deactivator for Pb-contaminated sphalerite. The mechanism of deactivation was determined to be a cleaning action.

c) A conductometric titration technique was adapted to determine the PP/Pb ratio in the lead-polyphosphate complexes, and structures for the complexes were proposed.

d) A means of calculating the amount of polyphosphate needed to control lead ions for a given ore was introduced.

7.3 Suggestions for Future Work

a) Study the microflotation of mixed minerals with a larger cell to investigate if the flotation of mixtures follows the predictions made on the basis of single mineral studies. The minerals should include chalcopyrite, galena, and sphalerite, to explore the effect of Pb derived from galena on selectivity and its control by polyphosphate.

b) Other size classes should be considered to generalize the estimation of the critical $[Pb]_{surf}$ for activation. Perhaps the impact on the flotation rate constant should be the determining factor rather than on recovery.

c) Study the effect of Pb on sphalerite samples with different iron contents to investigate the hypothesis of Zielinski et al. (2000) that iron content is important in the misplacement of sphalerite.

d) Batch flotation tests on ore samples to explore the potential of polyphosphate.

e) Determine the formation constants of the Pb-polyphosphate complexes and the solubility product of the Pb-polyphosphate precipitate.

f) Study the effect of number of phosphorous atoms in the polyphosphate chain on complexing ability and on mineral selectivity.

7.4 Reference

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APPENDIX A

DEACTIVATION OF Pb-CONTAMINATED SPHALERITE AND PYRITE

A.1 Executive Summary

The effect of three reagents, diethylenetriamine (DETA), dextrin, and carbonate, as depressants for Pb-contaminated minerals, sphalerite, pyrite and galena, was investigated by measuring zeta potential and xanthate adsorption.

The zeta potential of sphalerite was significantly increased in the presence of Pb ions, indicating adsorption of cationic Pb species (mainly $PbOH^+$) on the negatively charged surface. These species create potential sites for adsorption of xanthate.

The addition of DETA increased the zeta potential of both clean and Pb-contaminated sphalerite. This may result from adsorption of DETA (which is positively charged) including formation of a Pb-DETA complex. This adsorption competes with xanthate adsorption. The mechanism of depression by DETA appears similar to that reported for Pb/pyrite and different from that of Ni/pyrrhotite where removal of Ni activating species as soluble Ni-DETA complexes is suggested.

Dextrin, similar to DETA, increased the zeta potential of both clean and Pb-contaminated sphalerite. The action is similar to that for other sulphide minerals: Adsorption of dextrin competes with xanthate adsorption resulting in formation of a hydrophilic sites. The presence of metal ions on the surface creates more adsorption sites for dextrin.

Addition of carbonate did not significantly vary the value of the zeta potential of clean and Pb-contaminated sphalerite except at ca. pH 9.5-10.5. The action of carbonate as a depressant may result from formation of $PbCO_3$ or $Pb_2(OH)_2CO_3$ which may suppress xanthate uptake.

All reagents and the combination of DETA plus dextrin suppressed xanthate adsorption on the three Pb-contaminated minerals. The order of "depression strength" is:

1) for sphalerite: DETA+dextrin > dextrin > soda ash > DETA;

2) for pyrite: DETA > DETA+dextrin = dextrin > soda ash;

3) for galena: Dextrin > DETA > DETA+dextrin > soda ash.

The results suggest that, among the reagents tested, the best selective depression of sphalerite and pyrite against galena is given by DETA+dextrin.

A.2 Introduction

A variety of depressants, organic (e.g., DETA, dextrin) and inorganic (e.g., lime, cyanide) is known to affect selective sulphide flotation. The main depression mechanisms may be classified as follows:

1) Formation of hydrophilic species, e.g., complexes of metal/H_2O/OH^-, Fe-ferrocyanide, $PbSO_3$, and metal-dextrin;
2) Removal of activating heavy metal ions, e.g., using metal chelants such as EDTA and DETA, or dispersing reagents such as carbonate and silicate;
3) Prevention of collector adsorption based on the mixed potential model, e.g., adding a reducing reagent to inhibit anodic adsorption of xanthate or oxidation to dixanthogen;
4) Removal of hydrophobic species, e.g., adsorbed collector.

In this study dextrin, DETA, their combination, and sodium bicarbonate (equivalent to soda ash) were chosen as depressant reagents for Pb-contaminated minerals.

Dextrin

Dextrin is derived from starch by partial thermal degradation under acidic conditions. During this process, the starch chain is broken into smaller units, which then recombine to form dextrin. As a result, the dextrin molecule has the same chemical composition as starch (i.e., $(C_6H_{10}O_5)_n$) and molecular weight (800 to 70,000), but the molecular chain is highly branched (Pigmann and Goepp, 1948; Caesar, 1968).

Dextrin has been used to depress hydrophobic minerals such as molybdenite in Cu-Mo sulphide separation (Wie and Fuerstenau, 1974) and to depress coal in the flotation of pyrite (Miller and Baker, 1972). Dextrin adsorption on hydrophobic minerals has been explained by hydrophobic bonding between the dextrin and the surface of hydrophobic minerals (Wie and Fuerstenau, 1974; Huang et al., 1978; Miller et al., 1983).

Dextrin is used to depress sulphide minerals. Liu and Laskowski (1989c) reported that dextrin aided in the selectivity of galena from chalcopyrite when the flotation process was carried out in an alkaline environment. Pentlandite (Lukkarinen, 1962) and heazlewoodite (Laskowski and Nyamekye, 1994) can also be depressed by dextrin, with both minerals displaying similar behaviour towards dextrin and giving best depression around pH 11.5. Liu and Laskowski (1989a; 1989b; 1989c) proposed a mechanism of depression based on dextrin interaction with metal hydroxy species on the mineral surface. The type of metal hydroxide need not necessarily derive from the host mineral; oxidation of neighbouring minerals releasing and transferring metal ions can be the source. In a study on pyrite Bogusz et al.

(1997) showed that dextrin adsorbed in the presence of both Pb and Fe the former being more effective. The adsorption of dextrin inhibited dixanthogen formation on the pyrite.

DETA

Diethylenetriamine (DETA, NH_2-CH_2-CH_2-NH-CH_2-CH_2-NH_2) is a polyamine with molecular weight 103.1, specific density 0.9586, and is soluble in water and alcohol (CRC Handbook, p C-245). Polyamines are well known chelating agents. Their use in flotation is quite recent relative to their use in hydrometallurgy. Forward et al. (1960) reported that DETA (and other polyamines) were highly effective leaching agents for lead sulphate generated from acid pressure oxidation of galena. Later, Watson et al. (1972) and Eresen and Kammel (1981) used polyamines to extract copper, chromium, cobalt, and nickel from their oxide ores. Recently, DETA has been reported to selectively extract base metals from waste hydroxide sludge (Rao et al., 1995).

The most significant application in flotation is pyrrhotite depression. Use of DETA greatly improved pyrrhotite rejection at INCO's Sudbury operations (Marticorena et al., 1994, 1995) and in laboratory/pilot scale tests at Falconbridge (Kelebek et al., 1995). Unsuccessful attempts have been made to extend the application to depression of pyrite (Sui et al., 1997a).

The action of DETA is linked to its selective chelation of base metal ions. Examination of flotation concentrates by LIMS[1] and XPS[2] showed that there was a significant amount of nickel and copper on the surface of pyrrhotite upon exposure to plant water which could act as activation ions. The amount of base metal ions decreased considerably when contacted with DETA. Yoon et al. (1995) showed after DETA treatment that xanthate adsorption on pyrrhotite was significantly decreased, with a corresponding reduced floatability. The suspicion that Ni and Cu ions caused accidental activation and that they could be removed by DETA is substantiated by these observations. Infrared spectra of pyrrhotite contacted with DETA showed no trace of this reagent on the surface, suggesting that the role of DETA was solely as a solubilizing (complexing) or "cleaning" agent for nickel and copper ions.

DETA is an excellent complexing agent for Cu^{2+}, Ni^{2+}, and Fe^{2+}, but not for Fe^{3+}, Ca^{2+}, and Mg^{2+}. Therefore the potential activating ions, copper and nickel, are removed from pyrrhotite, leaving a surface dominated by iron species (oxy-hydroxides) which are hydrophilic. This selective retention of iron oxy-hydroxides may contribute to the depression of pyrrhotite (Yoon et al., 1995; Xu et al., 1997). Additionally, the formation of hydrophilic DETA-metal ion-sulphoxy precipitates may also add to the depression of pyrrhotite. The complexing strength of DETA is sufficient to desorb copper and nickel species from pyrrhotite regardless of whether they are present as hydroxide or xanthate (Xu et al., 1997). Recent work has shown DETA works best in conjunction with sulphur dioxide and that triethylenetetramine (TETA) may be more powerful than DETA (Kelebek and Tukel, 2000).

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[1] Laser Ionization Mass Spectroscopy

[2] X-ray Photoelectron Spectroscopy

Combination of DETA and dextrin

The combined use of DETA and dextrin as a depressant is based on trying to take advantage of possible complementary actions: DETA tends to selectively remove potential activating ions such as Cu^{2+} and Ni^{2+} while leaving behind other ions such as Fe^{3+}, Ca^{2+}, and Mg^{2+} which could act as adsorption sites for dextrin. The combination DETA + dextrin might, therefore give a "double depression effect" which may be more effective than the use of only one reagent.

Soda ash

A study on the effect of carbonate on Pb-contaminated quartz showed that with sufficient carbonate concentration the surface of quartz was cleaned probably because $PbCO_3$ or $Pb_3(OH)_2CO_3$ precipitates formed and dispersed from the surface into suspension (Rashchi et al., 1997). A study on Pb-contaminated pyrite showed that xanthate adsorption was suppressed when soda ash was used as the pH modifier instead of lime. This may also be attributed to the properties of $PbCO_3$ and $Pb_3(OH)_2CO_3$ precipitates, which either "disperse" the Pb or effectively "block" the Pb-activation sites (Sui et al., 1997b).

The aim of the present work is to compare different depressants by determining their effect on xanthate adsorption on Pb-contaminated sphalerite, pyrite and galena.

A.3 Experimental

A.3.1 Minerals

The mineral studied were sphalerite, pyrite, and galena. The minerals (200-400 mesh) were washed with acidic solution (pH = 2, HCl), followed by distilled water, and stored under acetone. As required, samples were retrieved from the acetone, dried in air, and washed with distilled water to remove the residual acetone before being used.

A.3.2 Reagents

Lead nitrite solution was prepared by dissolving $Pb(NO_3)_2$ powder (Fisher Scientific Co., ACS reagent, 99.9% pure) in distilled water at natural pH, and then diluting to the desired concentrations: 10^{-4} M (20 ppm Pb) and 2.5×10^{-5} M (5 ppm Pb) for zeta potential measurement and for xanthate adsorption tests, respectively (natural ca. pH 6).

Reagent grade diethylenetriamine (100%) from Aldrich Chemical Co. was used. An aqueous solution of 1% DETA was prepared with distilled water. The pH of this stock solution was about 11. Before each experiment, the DETA solution was diluted to 20 - 40 ppm with natural ca. pH 8.

The dextrin was obtained from ACROS Organics. Dextrin stock solution (1000 ppm) was prepared daily due to rapid deterioration. From the stock solution, the desired concentration of 100 ppm was made at natural ca. pH 7. The procedure used to make the stock solution was as follows: A few mL of distilled water was added to 1 gram of dextrin to produce a thick paste. A part of a 0.01 M NaCl solution was added to the paste and mixed thoroughly. The solution was then added to a 1 L volumetric flask and brought to mark with the rest of the NaCl solution. The NaCl was used to maintain the ionic strength of the dextrin solution (Liu and Laskowski, 1989a-c).

Laboratory grade sodium bicarbonate ($NaHCO_3$) from Fisher Scientific Co. was used. Carbonate solutions (10^{-2} to 10^{-1} M, 600 - 6000 ppm CO_3) were prepared by dissolving sodium bicarbonate powder in 100 mL distilled water ca. (pH 8 -8.5).

Potassium ethyl xanthate (KEX) from Cytec Industries Ltd. was purified twice by dissolving in acetone and reprecipitated by petroleum ether following a standard technique (Rao, 1971). Fresh 5×10^{-3} M xanthate stock solution was prepared daily at ca. pH 9, and then diluted to 5×10^{-5} M with distilled water at ca. pH 9.

A.3.3 Methodology

A.3.3.1 Mineral conditioning

Reagents following the order Pb, depressant, xanthate were added to the mineral. After being conditioned on an orbital shaker at 250 rpm with one reagent, the slurry was filtered, the solids were washed once with distilled water and the next reagent was introduced.

1) Treatment with Pb

Mineral particles were conditioned in 5 or 20 ppm Pb solution at natural pH (ca. 6) for 15 minutes.

2) Treatment with DETA, dextrin, and sodium bicarbonate

The Pb-treated minerals were introduced to the solution containing a depressant and conditioned for 15 minutes. The pH of the solution was about 8 for DETA, 7 for dextrin, 7.5 for DETA+dextrin, and 8.3 for sodium bicarbonate.

3) Interaction with xanthate

After being conditioned with Pb/depressant as above mineral particles were reacted with xanthate (100 mL) for 15 minutes at pH 9.5.

A.3.3.2 Zeta potential measurement

A Laser-Zee meter (model 501, Penkem Inc., USA) was used. In the experiments, 0.5 g sphalerite (38-74 μm) was ground with a ceramic mortar and pestle and transferred to a 500 mL beaker containing 0.01 M KNO_3 electrolyte solution. The solution pH was adjusted by HNO_3 and KOH over a range of 1.5-12. After the pH was set, the suspension was conditioned for 2 minutes, then the zeta potential was measured at that pH.

A.3.3.3 Determination of xanthate concentration

After being conditioned with xanthate the suspension was filtered, and the filtrate analyzed by ultra-violet (UV) spectroscopy for residual xanthate. The amount of xanthate adsorption on the mineral was calculated from the difference between initial and residual xanthate concentrations and reported as mole xanthate adsorbed per gram mineral (mol/g).

A.4 Results

A.4.1 Zeta potential of Sphalerite

A.4.1.1 With and without Pb

As shown in Figure A.1, the zeta potential of sphalerite decreased as pH increased, giving an iep ca. pH 2. The small peak at ca. pH 7.5 was attributed to adsorption of Zn or Fe ions released from sphalerite (Zhang et al., 1995).

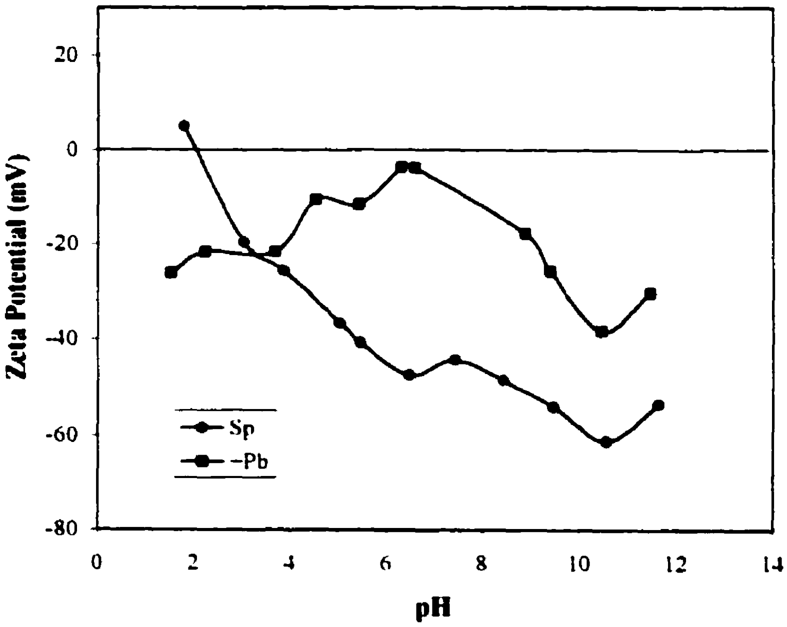

Figure A.1 Zeta potential of sphalerite in the absence and presence of Pb

Upon adding 10^{-4} M (20 ppm) Pb, the zeta potential increased (became less negative), indicating adsorption of a positively charged species. The adsorption reached a maximum at ca. pH 6.5. According to the known species distribution, around pH 6.5 the main Pb species is $PbOH^+$. The $PbOH^+$ could act as adsorption sites for depressants or xanthate.

A.4.1.2 With DETA

In the presence of 20 ppm DETA, the zeta potential of sphalerite was less negative compared to sphalerite alone, suggesting adsorption of DETA (Figure A.2). This is consistent with the case of pyrite (Sui et al., 1998) but not with the pyrrhotite (Xu et al., 1997).

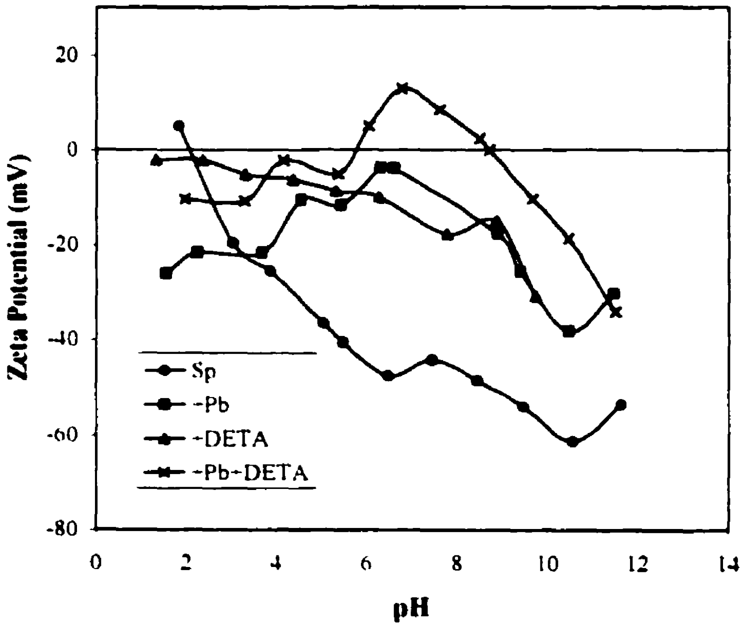

Figure A.2 Zeta potential of sphalerite in the presence of Pb and/or DETA

The zeta potential was also increased after addition of 20 ppm DETA to Pb-contaminated sphalerite (Figure A.2), and continued to increase with DETA concentration (Figure A.3).

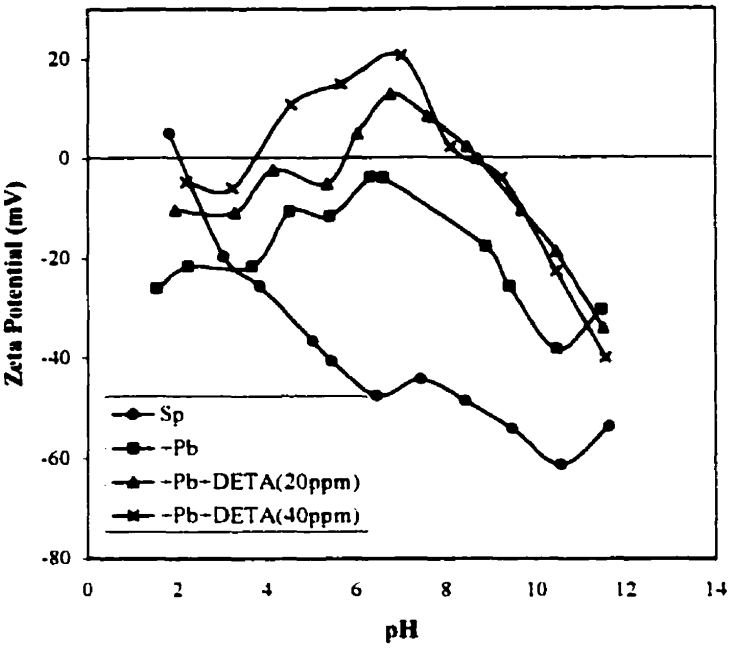

Figure A.3 Effect of DETA concentrations on zeta potential of sphalerite

The results suggest that DETA is adsorbed on the surface of sphalerite, and adsorption is enhanced by the presence of Pb. It is suspected that DETA interacted with Pb ions forming a complex on the surface of sphalerite. This complex may inhibit the Pb activation effect. This is similar to the case of Pb-pyrite (Sui et al, 1997a), but different from the case of Ni/pyrrhotite where adsorbed Ni ions were removed by DETA (as a soluble Ni-DETA complex) which returned the zeta potential of Ni-treated pyrrhotite to that of pyrrhotite alone (Xu et al., 1997).

A.4.1.3 With dextrin

As shown in Figure A.4, addition of dextrin resulted in an increase in zeta potential of clean sphalerite. This suggests adsorption of dextrin as a positively charged species. For Pb-contaminated sphalerite, the value of zeta potential did not significantly increase in the presence of dextrin (about the same trend) compared to its absence, except at ca. pH 10-12. This is attributed to the formation of a chemical complex with lead through interactions with lead hydroxide which is in agreement with the findings of Liu and Laskowski (1989a).

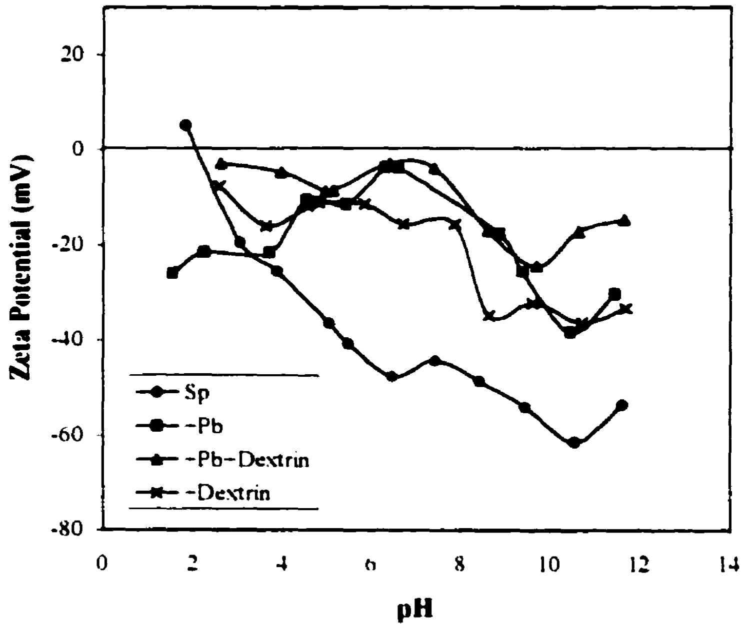

Figure A.4 Zeta potential of sphalerite in the presence of Pb and/or dextrin

A.4.1.4 With carbonate

In the presence of 600 ppm carbonate, the zeta potential of sphalerite did not change significantly compared to that of sphalerite alone (Figure A.5). This is because HCO_3^- and CO_3^{2-} are negatively charged and are not readily adsorbed on the negatively charged mineral surface.

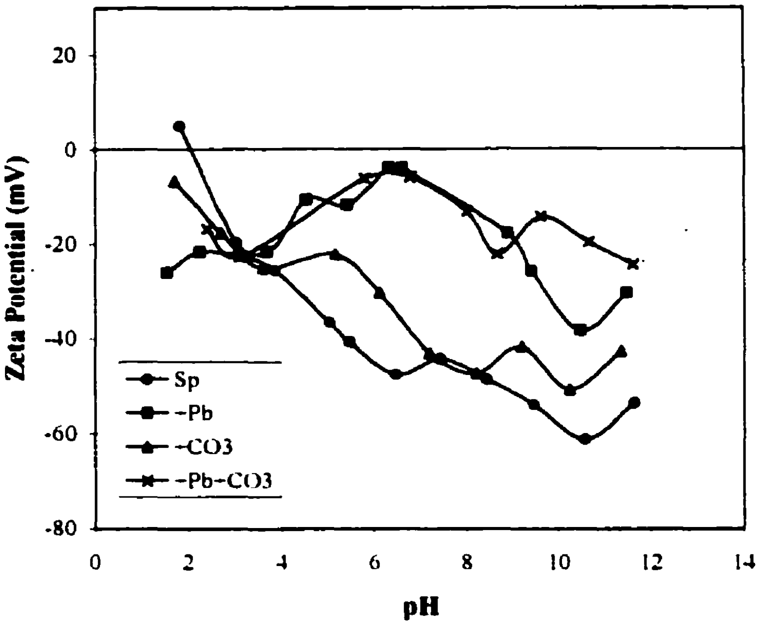

Figure A.5 Zeta potential of sphalerite in the presence of Pb and/or carbonate

Addition of carbonate also did not greatly vary the value of the zeta potential of Pb-contaminated sphalerite (Figure A.5), except at ca. pH 9.5-10.5. This suggest that carbonate is precipitated as $PbCO_3$ or $Pb_2(OH)_2CO_3$, reducing the number of negative charged species such as plumbate ($HPbO_2^-$ or $Pb(OH)_3^-$) on the surface. The same explanation can be given for the increase in zeta potential in the absence of Pb (Sp alone) suggesting that the zincate ions, $Zn(OH)^{3-}$ and $Zn(OH)_4^{2-}$ are converted to solid species ($Zn(OH)_{2(S)}$) reducing the negative charge (Finkelstein and Allison, 1976).

The trend in zeta potential curve in the presence of 600 ppm and even up to 6000 ppm carbonate is almost the same as that for Pb-contaminated sphalerite alone (Figure A.6), suggesting that carbonate did not clean Pb from the surface as it did in the case of silica

(Rashchi et al., 1998).

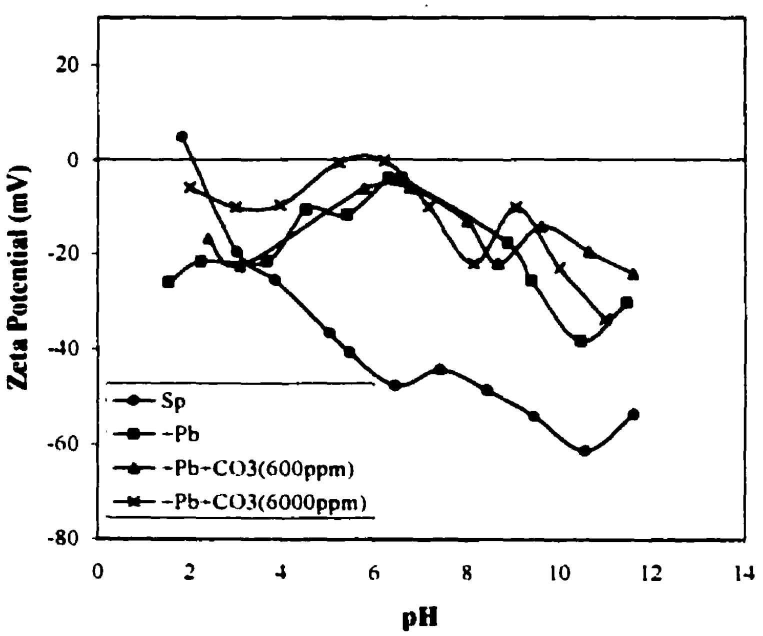

Figure A.6 Effect of carbonate concentrations on zeta potential of sphalerite

A.4.2 Xanthate Adsorption

A.4.2.1 Sphalerite

As shown in Figure A.7, xanthate adsorption on sphalerite was significantly increased after sphalerite was treated with Pb compared to clean sphalerite. Addition of all depressants led to a significant decrease in xanthate adsorption. The order of decrease was DETA+dextrin > dextrin > sodium bicarbonate > DETA.

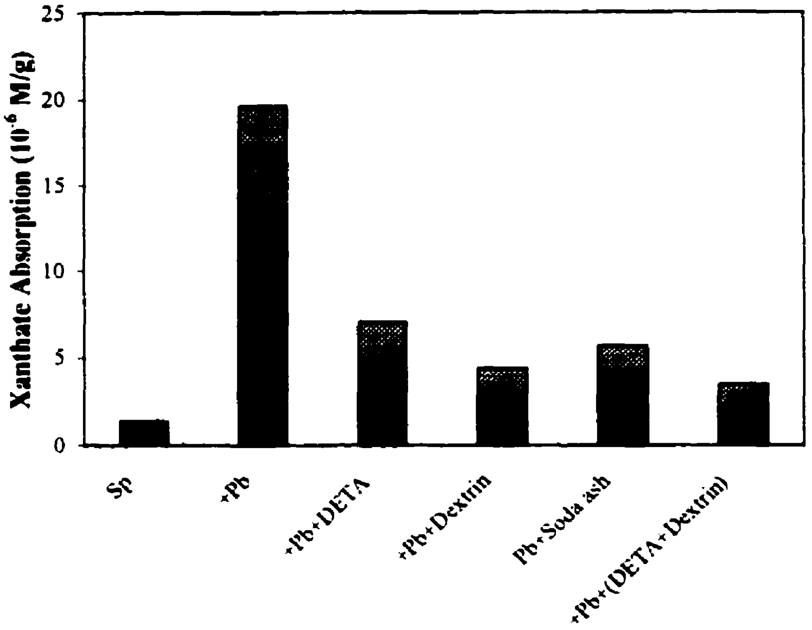

Figure A.7 Xanthate adsorption on sphalerite in the presence of Pb and Pb+DETA, dextrin, sodium bicarbonate, and DETA+dextrin

A.4.2.2 Pyrite

Xanthate adsorption on Pb-contaminated pyrite was not significantly increased compared to clean pyrite (Figure A.8). This may be because Pb activation of pyrite is dependent on pulp potential. Further study on the effect of depressants on Pb-contaminated pyrite should be conducted under controlled potential.

The preliminary study showed that addition of all reagents suppressed xanthate adsorption on pyrite with the order of "depression strength" being DETA > DETA+dextrin = dextrin > sodium bicarbonate.

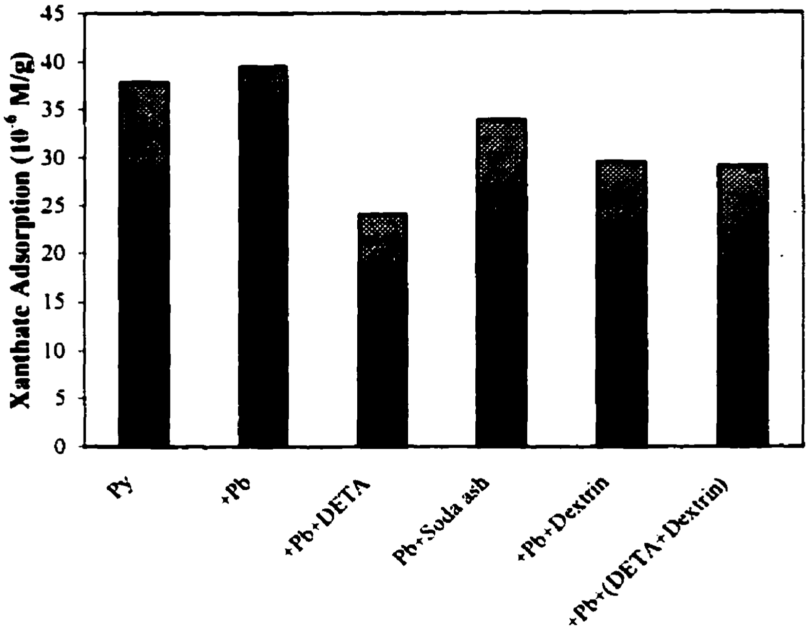

Figure A.8 Xanthate adsorption on pyrite in the presence of Pb and Pb+DETA, dextrin, sodium bicarbonate, and DETA+dextrin

A.4.2.3 Galena

The desirable reagent in the present context is one that depresses sphalerite and pyrite but does not significantly affect galena floatability. Therefore, adsorption tests were conducted on galena, with the results given in Figure A.9.

Xanthate adsorption on galena was increased after addition of Pb ion. Subsequent addition of sodium bicarbonate did not significantly affect xanthate adsorption, while all the other depressants retarded xanthate adsorption. The order of depression strength is dextrin > DETA > DETA+dextrin > sodium bicarbonate.

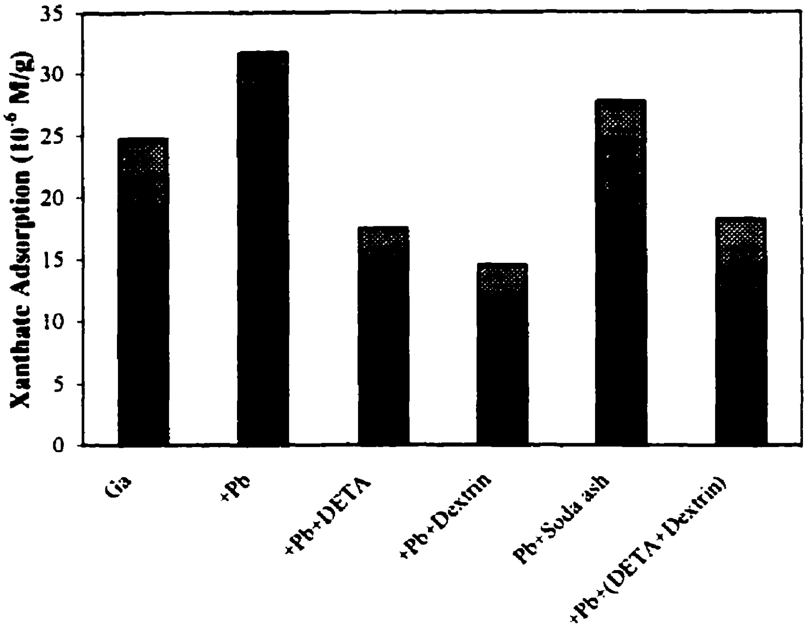

Figure A.9 Xanthate adsorption on galena in the presence of Pb and Pb+DETA, dextrin, sodium bicarbonate, and DETA+dextrin

A.5 Discussion

The results from zeta potential measurements suggest that all reagents tested adsorbed on Pb-contaminated sphalerite to form either complexes or precipitates. Those species may "block" Pb ionic species, thereby, making them less available for xanthate adsorption which, as demonstrated, was significantly decreased.

Tests on the three minerals showed that dextrin and dextrin+DETA worked well to suppress xanthate adsorption on sphalerite; however, they also decreased xanthate adsorption on galena. Sodium bicarbonate also inhibited xanthate adsorption on sphalerite and did not significantly affect that on galena; however, it did not retard xanthate uptake on pyrite. At this stage the best depressant for selective depression of sphalerite and pyrite in galena flotation appears to be a combination of DETA and dextrin. The depressant effect of DETA +dextrin may be attributed to formation of DETA-Pb and dextrin-Pb surface complexes. Further study by surface analysis techniques is required.

In this study, the pH for conditioning minerals with reagents was ca. 6 - 8 (natural pH). The effect of theses reagents, especially dextrin, does depend on pH. Hence, it is recommended that future work be conducted at different pHs.

A.6 Conclusions

Sphalerite

1. Dextrin was adsorbed on the surface of sphalerite in both the absence and presence of Pb ions. The presence of dextrin decreased xanthate adsorption by 75%. This, together with the dextrin being hydrophilic, should mean a reduction in floatability.
2. Similar to dextrin, DETA was adsorbed on the surface of sphalerite in both the absence and presence of Pb ions. Again xanthate adsorption was reduced significantly (ca. 60%). The action of DETA on Pb-sphalerite is similar to that for Pb-pyrite but different from that for Ni or Cu-pyrrhotite where DETA solubilized and removed metal ions from the pyrrhotite surface.
3. Carbonate may interact to form Pb-carbonate surface species which inhibited xanthate adsorption.

Pyrite

Xanthate adsorption on Pb-contaminated pyrite was not significantly increased compared to clean pyrite probably due to the high pulp potential. Addition of all the reagents suppressed xanthate adsorption on pyrite.

Galena

Addition of carbonate did not affect xanthate adsorption significantly, while DETA and dextrin reduced xanthate adsorption.

Overall

The order of "depression strength" of reagents for the minerals, sphalerite, pyrite, and galena are different. At this stage, the most selective depression of sphalerite and pyrite relative to galena appears to be with a combination of DETA and dextrin.

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APPENDIX B

LEAD SPECIES DISTRIBUTIONS DIAGRAMS

Species concentration for the following, Pb^{2+}, $PbOH^{+}$, $Pb(OH)_{2(aq)}$, $Pb(OH)_3^{-}$, $Pb(OH)_4^{2-}$, $Pb_3(OH)_4^{2+}$, and $Pb(OH)_{2(S)}$ were calculated by "EQUILCOM" (Sui and Huang, http://equilcom.minmet.mcgill.ca/equilcom). Figures B.1, B.2, B.3, B.4, B.5, and B.6 show the results as a function of pH for initial Pb concentrations of 2, 10, 50, 100, 200, and 400 ppm, respectively.

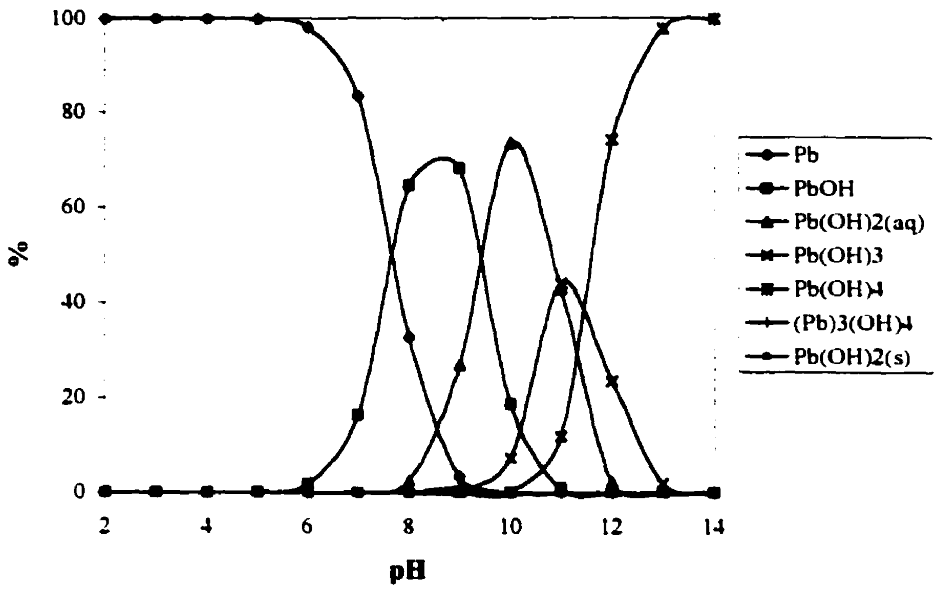

Figure B.1 Species distribution diagram for [Pb] = 2 ppm as a function of pH.

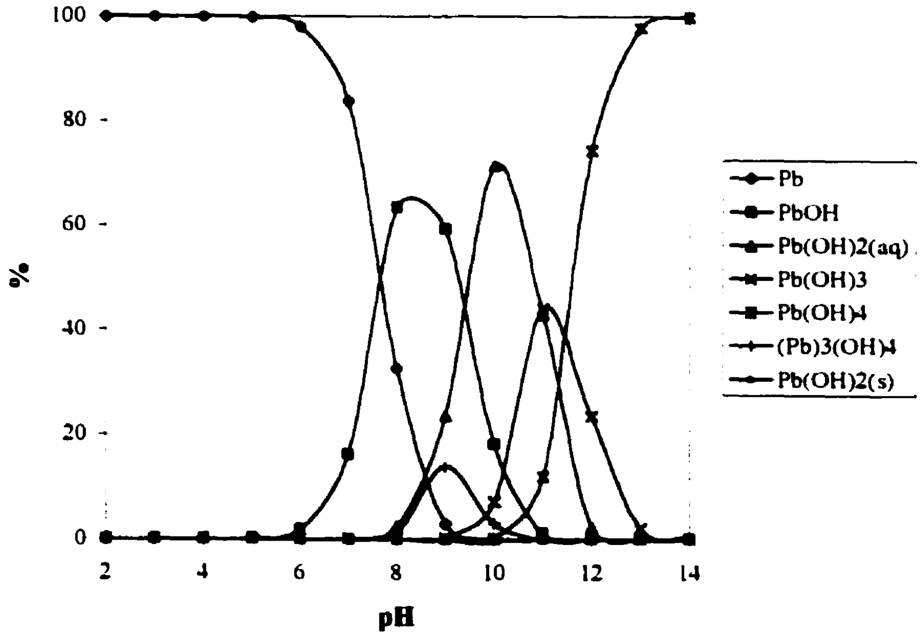

Figure B.2 Species distribution diagram for [Pb] = 10 ppm as a function of pH.

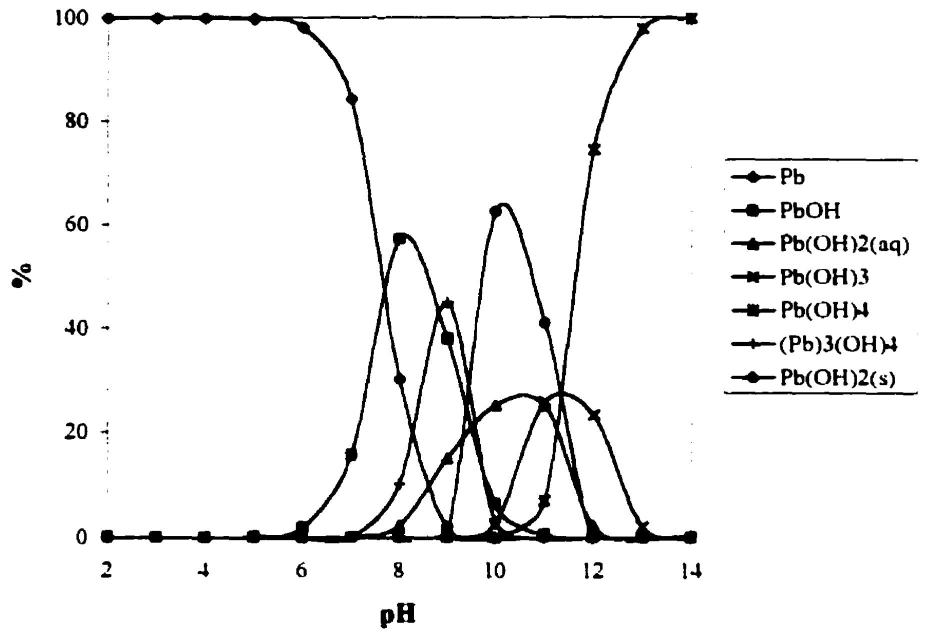

Figure B.3 Species distribution diagram for [Pb] = 50 ppm as a function of pH.

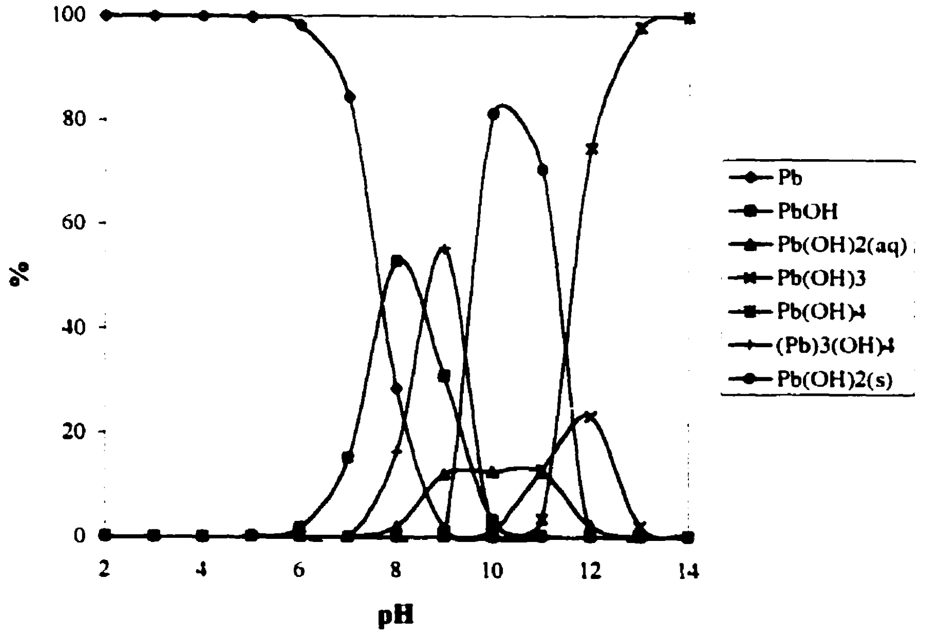

Figure B.4 Species distribution diagram for [Pb] = 100 ppm as a function of pH.

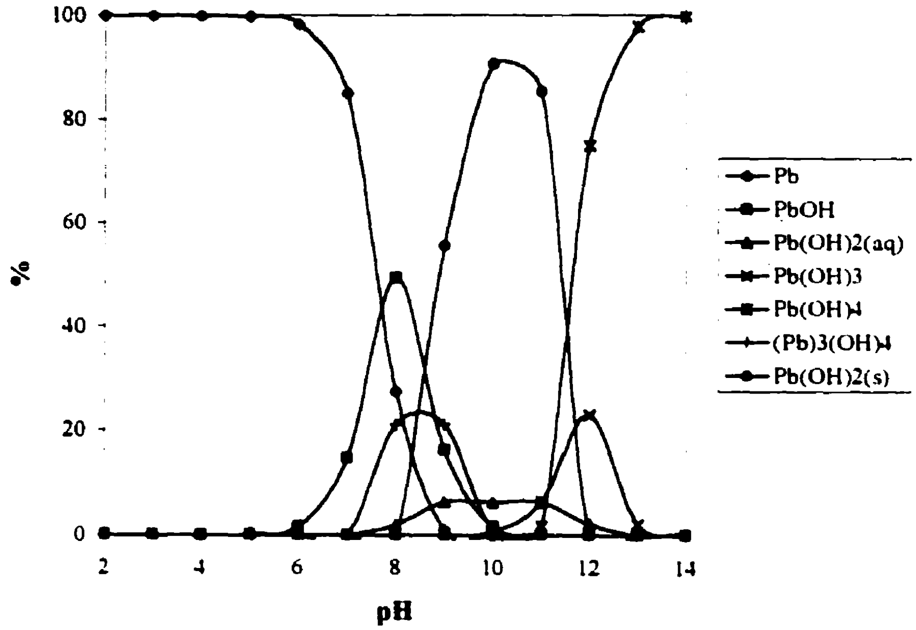

Figure B.5 Species distribution diagram for [Pb] = 200 ppm as a function of pH.

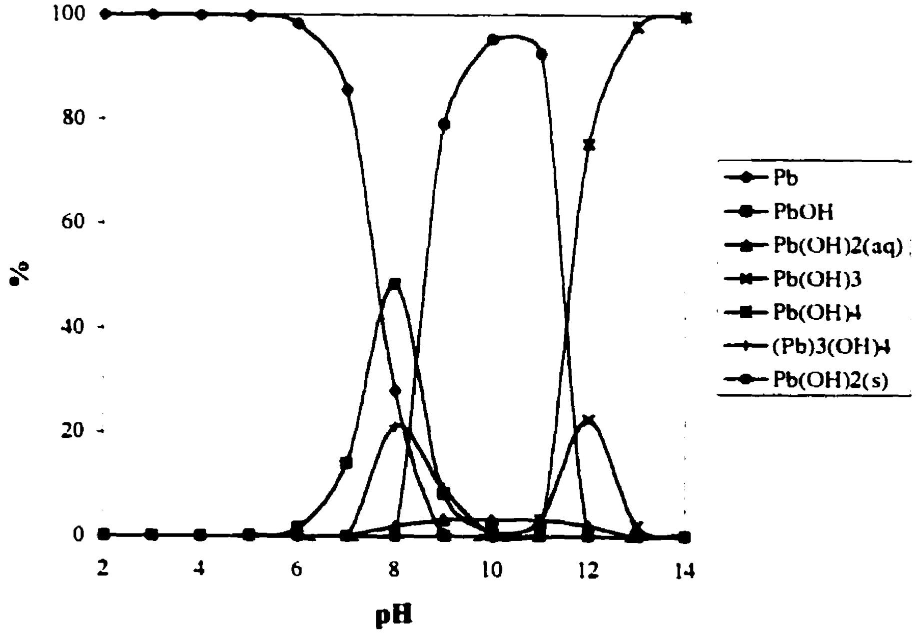

Figure B.6 Species distribution diagram for [Pb] = 400 ppm as a function of pH.

APPENDIX C

POLYPHOSPHATE CONSUMPTION PREDICTION

The calculation steps to predict the polyphosphate consumption are given below:

1. The concentration of Pb on a surface area basis given by Sui et al. (1999) and Rashchi et al. (2000)[1] is:

$$[Pb]_{surf} = 0.0167 \, . \, g \, . \, \rho \; \frac{\text{mg Pb}}{\text{cm}^2 \text{ ore}} \qquad \textbf{(C-1)}$$

   where g is fractional Pb content in the ore and ρ is the density of the ore, g/cm^3.

2. Converting to a mass of ore basis assuming spherical particles gives:

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[1] Chapter 4

$$[Pb]_{surf} = 0.0167.g.\rho \frac{\text{mg Pb}}{\text{cm}^2\text{ ore}} . \frac{6}{\rho.\bar{d}} \frac{\text{cm}^2\text{ ore}}{\text{g ore}}$$

$$= \frac{0.1g}{\bar{d}} \frac{\text{mg Pb}}{\text{g ore}} \quad (\text{ or } \frac{\text{g Pb}}{\text{kg ore}}) \qquad \text{(C-2)}$$

where d is the mean size of the ore, cm.

3. Knowing that the minimum ratio of PP/Pb to complex Pb is 1/2 (Rashchi and Finch, 2000)[2], the minimum amount of polyphosphate required to remove Pb from the surface is:

$$n_{PP} = \frac{0.1g}{\bar{d}} \frac{\text{g Pb}}{\text{kg ore}} . \frac{1}{207.2} \frac{\text{mol Pb}}{\text{g Pb}} . \frac{1}{2} \frac{\text{mol PP}}{\text{mol Pb}}$$

$$= \frac{2.41 \times 10^{-4} g}{\bar{d}} \frac{\text{mol PP}}{\text{kg ore}} \qquad \text{(C-3)}$$

4. For the polyphosphate used in this study with molecular weight of 1773.3 g/mol, the minimum amount of polyphosphate required is

$$m_{PP} = \frac{2.41 \times 10^{-4} g}{\bar{d}} \frac{\text{mol PP}}{\text{kg ore}} \times 1773.3 \frac{\text{g PP}}{\text{mol PP}}$$

$$= \frac{0.428 g}{\bar{d}} \frac{\text{g PP}}{\text{kg ore}} \qquad \text{(C-4)}$$

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[2] Chapter 6

Reference

Sui, C., Grimmelt, J.C., Rashchi, F., Rao, S.R., and Finch, J.A., "Lead ion production and sphalerite recovery in copper rougher flotation", in Proceedings of Copper 99-Cobre 99 International Environment Conference, Vol. 2, Mineral Processing Environment, Edited by B.A. Hancock and M.R.L. Pon, 1999, 145-157.

APPENDIX D

CALCULATION OF MEAN PARTICLE SIZE FROM PARTICLE SIZE DISTRIBUTION

According to the so-called Gates-Gaudin-Schuhmann formula (Schuhmann, 1940) the cumulative weight fraction of particles (Y) finer than size d can be described by

$$Y = \left(\frac{d}{k} \right)^{\alpha} \tag{D-1}$$

where d is particle size, k is termed size modulus with dimension of size, and α is termed the distribution modulus and is dimensionless. The α can be as high as about 1.5 and is usually about 0.8 (Charles, 1957). The fractional density function of the size distribution, $p(x)$, can be obtained by differentiating Eq. (D-1):

$$p(d) = \frac{dY}{d(d)} = \frac{\alpha d^{\alpha-1}}{k^{\alpha}} \qquad \textbf{(D-2)}$$

The mean size of the particles, *d*, can then be calculated from

$$\bar{d} = \int_0^k d \,.\, p(d) \,.\, d(d) = \int_0^k d \,.\, \frac{\alpha d^{\alpha-1}}{k^{\alpha}} \,.\, d(d) = \frac{\alpha k}{1+\alpha} \qquad \textbf{(D-3)}$$

For α = 0.8, Eq. (D-3) becomes

$$\bar{d} = 0.4444\,k \qquad \textbf{(D-4)}$$

A plot of Eq. (D-4) yields a straight line as illustrated in Figure D.1.

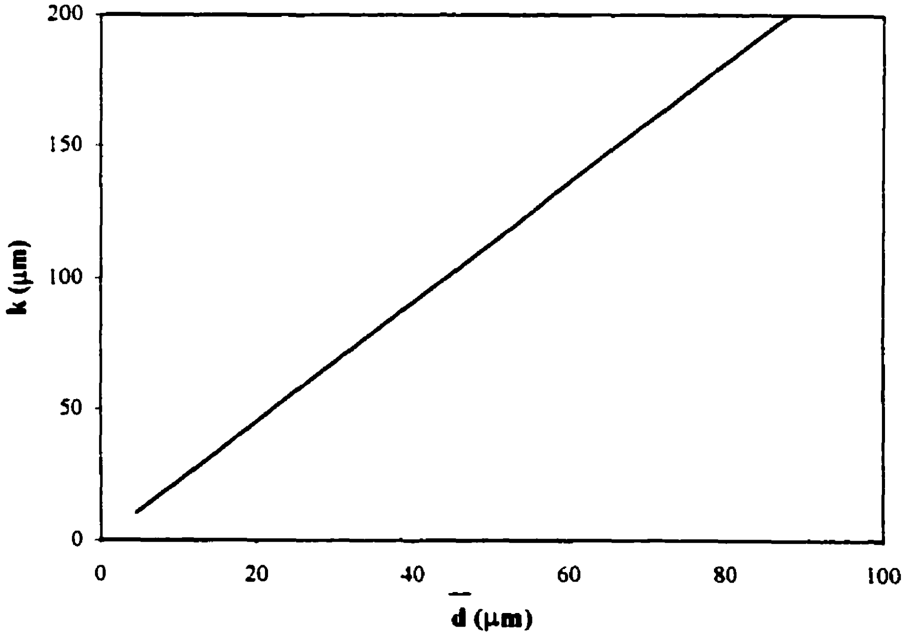

Figure D.1 Relationship between mean size and size modulus.

For 50% passing, Eq. (D-1) becomes:

$$0.5 = \left(\frac{d_{50}}{k} \right)^{\alpha} \qquad \textbf{(D-5)}$$

from which the value of d_{50} can be calculated

$$d_{50} = 0.5^{1/\alpha} . k \qquad \textbf{(D-6)}$$

Combining Eqs. (D-3) and (D-6) gives the relationship between mean size and 50% passing size:

$$d_{50} = \frac{0.5^{1/\alpha} (1 + \alpha)}{\alpha} \bar{d} \qquad \textbf{(D-7)}$$

For $\alpha = 0.8$, Eq. (D-7) becomes

$$d_{50} = 0.9460 \bar{d} \qquad \textbf{(D-8)}$$

References

Charles, R. J., "Energy-size reduction relationship in comminution", Mining Engineering, 1957, 208, 80-88.

Schuhmann, R., "Principles of comminution, I. Size distribution and surface calculations", AIME Technical Paper 1189, 1940.