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**The Depression of Sphalerite during Carbon Pre-flotation and Lead
Flotation at the Century Mine Concentrator**

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Master of Science (Minerals Engineering)
of
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Declaration

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university. To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

Daniel Healy

March 2005

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Abstract

The differential lead-zinc flotation process has been practised since 1912, yet selectivity in the process remains a significant technical issue in many operations. The minerals processing operation at Zinifex Limited's Century Mine, which uses differential flotation, began in November 1999 and the flotation behavior of the ore remains a major research interest. The present study was aimed to determine the possible mechanisms of sphalerite recovery during carbon pre-flotation and lead flotation in this operation including identification of the variables that affect these two flotation stages and also identify depressants for sphalerite that offer better selectivity during these stages.

To achieve this aim, the study was undertaken in two stages: a review of literature related to selectivity during lead-zinc flotation, and an experimental program consisting of bench-scale flotation tests wherein the various experimental variables were systematically varied. A comparison between the data generated to those of the plant was also undertaken.

The review of literature revealed four basic mechanisms of sphalerite recovery: activation of the sphalerite surface, composite particle flotation with galena and gangue, graphitic inclusions in the mineral surface and entrainment in the froth. The depression or rejection of sphalerite on the other hand could be affected by grinding, froth washing and the use of chemical depressants including cyanides, zinc sulfate, abraded iron and iron sulfate, sodium sulfide, sodium sulfite and metabisulfite, and organic depressants derived from selective collectors.

The results from the experimental program indicate that: (a) activation of the sphalerite surface as a mechanism of sphalerite recovery during lead flotation was not significant at the Century Mine concentrator, (b) the recovery of sphalerite during the carbon pre-flotation was predominantly due to a bulk flotation action and entrainment in the froth, (c) composite particle recovery was a significant contributing factor in the recovery of sphalerite in lead flotation, and (d) mineral oxidation was only significant for galena and occurred mostly during pre-flotation, but the use of cyanide adequately counters any effect on sphalerite recovery.

The investigation on the variables that affect the pre-flotation and lead flotation circuits revealed that: (a) reducing the pulp density and the amount of frother added during pre-flotation significantly reduced the bulk flotation action and entrainment of sphalerite in the froth, (b) grinding the ore finer ($P_{80} = 40 \mu\text{m}$) reduced the recovery of sphalerite as composite particles during lead flotation, and (c) the pulp pH was best maintained at natural pH during pre-flotation and at an elevated alkaline pH (pH 9.5) during lead flotation for optimal selectivity. In terms of depressants it was found that zinc sulfate specifically depressed sphalerite during lead flotation.

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CHAPTER 1

GENERAL INTRODUCTION

Lead and zinc minerals typically co-exist as galena and sphalerite in the same ore deposit. The traditional mineral processing technique used to concentrate these minerals involves differential froth flotation where galena is first recovered by flotation whilst sphalerite is selectively depressed (Basilio et al. 1996). Sphalerite is then recovered from the lead tailings by flotation. Clearly, the selectivity in lead-zinc flotation is essential to the recovery of both lead and zinc and improving plant economics.

1.1 A Brief History of the Development of Lead-Zinc Flotation

The earliest work that led to the concentration of sulfides by flotation began in 1860 when William Haynes patented a process where pulverised sulfide minerals were separated from gangue by mixing with oil and removing the gangue with a powerful jet of water. In 1877, the Bessel brothers of Dresden, Germany, patented a flotation process to separate graphite ores by mixing pulverised graphite ore with oil and water.

The concentration of sulfide ores by flotation techniques at plant scale began in the early 1900s with silver-lead-zinc ore at a number of operations in Broken Hill. Most lead-zinc ores have since been processed whereby galena (PbS) is floated first whilst sphalerite (ZnS) and iron minerals are selectively depressed.

A particularly informative review of the Broken Hill mining industry and the development of lead-zinc flotation has been compiled by Woodward (1952, pp. 84–98) and it is summarised here. Accordingly, Charles Potter of Melbourne, Australia, patented the first flotation process in 1901 in response to zinc recovery problems at a Broken Hill mining operation. The Broken Hill deposit was discovered in 1883 and by 1889 conventional gravity methods of concentration were established to produce a product for direct smelting. These methods only recovered 45–50% of the silver and 65–69% of the lead from the ore and were not suitable for the recovery of the zinc minerals. Nearly all of the zinc and the remainder of the silver and lead would report to the tailings. In 1904 there were approximately 6.6 million tons of zinc locked in the Broken Hill tailings.

Potter's idea involved mixing hot sulfuric acid with the zinc-rich tailings. The sulfuric acid in the hot circuit (82–88 °C) reacted with the lime, manganese and other carbonate minerals present in the ore to produce copious bubbles of carbon dioxide. The carbon dioxide gas bubbles carry sulfide mineral particles as they rise causing them to float to the surface of the acid mixture where they could then be recovered. Potter operated a small plant from 1903 to 1905 at the Block 14 Co. Mine. Plant operating data from November 1903 to March 1904 showed recoveries of approximately 73% zinc and 25% lead, with a concentrate grade of 46% zinc.

Guillaume Delprat, General Manager of Broken Hill Proprietary Co. Mine, used Potter's idea in 1902 but substituted sulfuric acid with salt cake (NaHSO_4). This led to litigation for infringement of intellectual property rights brought about by Potter and continued until 1907 when both parties agreed to a merger of the two processes,

subsequently known as the Potter-Delprat process. The process continued to operate on a large scale until 1923 when all of the zinc tailings had been processed.

The Sulphide Corporation Ltd.'s Central Mine found in 1903 that the Potter-Delprat process was not very successful in treating their high carbonate-grade tailing without the cost prohibitive additions of sulfuric acid. The mine management was advised by Minerals Separation Ltd., London, of the Cattermole or Granulation process. This process mixed ore with water, acid or alkali, and a heavy oil such as oleic to agglomerate the oil coated sulfide minerals into granules. Classifiers were then used to separate the granulated minerals from the gangue. A pilot plant was operated in 1904 and a larger operation with 100 tons per day capacity began in July 1905.

A succeeding development, the Minerals Separation process, was an improvement of the Cattermole process following an observation at the Central Mine that, by reducing the addition of oleic acid to less than 1% per ton of ore, the oil coated minerals formed a froth which could be separated from the gangue by flotation. The granulation process gave way to the Minerals Separation process in October 1905 and this began the flotation process used throughout the world today.

Another variation, the De Bavay process, was developed in Broken Hill in 1904. De Bavay found that in the Potter-Delprat process, the addition of sulfuric acid caused bubble formation from the decomposition of lime and carbonates present in the feed and cleaned these oxides from the mineral surface. He further found that when de-slimes sulfide mineral particles were aerated by agitation they were coated by a film of bubbles, which caused the particles to float. The addition of heavy oils such as kerosene to the pulp assisted the recovery of the sulfide minerals reporting to the froth. The De Bavay cone was developed as the apparatus to work the process. De

Bavay operated a commercial treatment plant from 1905 to 1917 when the Minerals Separation process superseded it.

Another process, the Elmore process, was a vacuum flotation process patented in England in 1904. The process involved mixing the ore with acid and oil that was then fed into a vacuum machine. The pulp was then subjected to a drop in pressure, which caused the dissolved gases in the pulp to form bubbles that would carry sulfide mineral particles to the surface. The process was used from 1908 to 1911 at the Zinc Corporation Ltd. and from 1910 to 1913 at the Broken Hill Proprietary British Mine. The process, however, was not effective with some of the tailings dumps. Losses of 16% zinc and 30% lead were contained in the residues at the Zinc Corporation's operation. The Minerals Separation process also replaced this process.

A combined concentrate of galena and sphalerite was produced from these early flotation processes. The lead was typically removed by gravity treatment using Wilfley tables until the development of differential flotation processes in 1910 with the Horwood process. This process used a low temperature roast (400–500 °C) that would coat the galena in the bulk concentrate with an oxidised lead film. This rendered the galena unfloatable whilst the unaffected sphalerite could be floated as a zinc concentrate, leaving a rich lead tailing. The process was operated on a commercial basis at the Zinc Corporation Ltd.'s operation between April 1913 and August 1914.

Selective flotation of galena began in 1912, when F. J. Lyster discovered the possibility at the Zinc Corporation Limited Mine when a small quantity of a rich lead-silver product was obtained from the early stages of the process. Lyster first found the lead product as a frothy overflow from the dewatering cones immediately

before the Minerals Separation process flotation circuit. He then found that by utilising the first or first two cells in the flotation circuit prior to the addition of acid for zinc flotation, lead product could also be obtained. The flotation process conducted in alkaline or neutral conditions resulted in differential flotation whereby galena was recovered and sphalerite remained in the pulp.

Lyster then experimented with the use of eucalyptus oil as a frothing agent and obtained very good results. The use of eucalyptus oil allowed the process to be carried out at low temperatures removing the need to heat the pulp. The first metal recoveries by this process between September 1912 and March 1913 were approximately 81% lead and 17% zinc in a lead concentrate grade of 56.0%, with the remainder of the zinc reporting to the de-leaded tail. Lyster's process was the first true differential flotation process developed. It was patented in September 1912.

Bradford discovered in 1912 that copper sulfate salt was suitable for activating depressed sulfide minerals making them amenable to flotation. Later, Bradford also discovered that thiosulfate, sulfites and bisulfites are chemicals capable of liberating reducing gas (sulfur dioxide) in the presence of sulfuric acid that depresses sphalerite during galena flotation. The Broken Hill Proprietary Co. Ltd. Operations from September 1916 to November 1923 used the sulfur dioxide and copper sulfate processes. Later practices of recovering sphalerite in alkaline or neutral pulp were only made possible by the use of copper sulfate.

In 1913, Owen discovered that by introducing a stream of finely divided air bubbles into the pulp it was possible to sequentially float galena and sphalerite. The use of frothing agents and aeration during agitation significantly reduces the power and reagent required for flotation and the process was used at several mines including the

Junction North N.L. Co. operation. By 1916 the differential flotation of galena from sphalerite was well established.

One of the most important discoveries was made in October 1923 when Keller and Lewis of Minerals Separation Ltd., San Francisco, found a use for the alkyl sulfur derivative of carbonic acid now known as xanthate. Xanthates were shown to have extremely effective collecting properties for sulfide minerals. The reagent was first used in Broken Hill in 1925 and it became the collector used in both lead and zinc flotation circuits. Alkyldithiophosphates, commonly known as aerofloats[®] (Mining Chemicals Handbook 1986, pp. 63–64), were identified by Whitworth in 1926 as an alternative to xanthates and sodium aerofloat was used in Broken Hill operations for zinc flotation from April 1932 to November 1944.

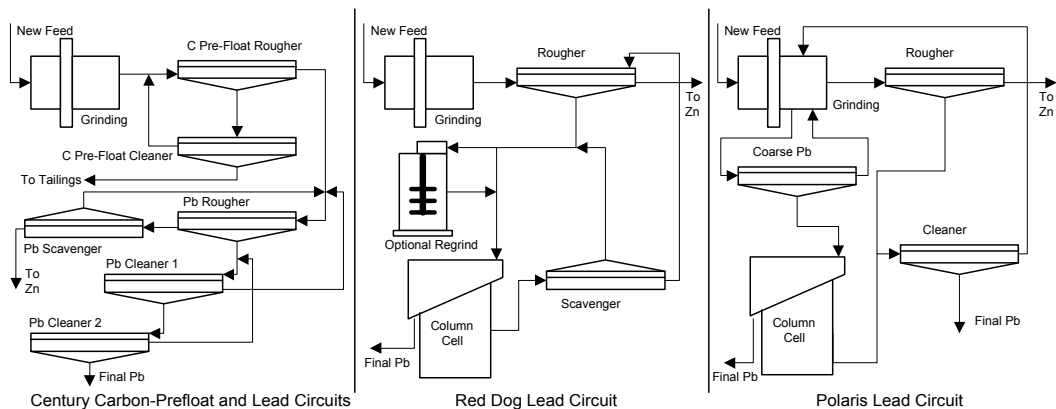
These reagents are still currently used in flotation processes. Frothers such as pine oil, methylisobutylcarbonyl (MIBC) or higher alcohols are used to establish a stable froth so that air bubbles carrying mineral particles to the surface do not burst. Collectors such as alkyldithiocarbonates (xanthates) or alkyldithiophosphates are used to adsorb to the sulfide mineral particle surface and to make it hydrophobic. Conditioners such as lime are added to adjust the pH of the pulp to improve selectivity. Depressants such as cyanide ions added during lead flotation, are used to make sphalerite and iron mineral surfaces less responsive to collectors. Activators, such as copper sulfate added during zinc flotation, adsorb to the sphalerite surface and make it more responsive to collectors. This means that Lyster's basic idea of differential flotation remains unchanged.

Most of the world's lead and zinc is produced from sulfide ores where flotation is used to separate and concentrate the minerals of the metals before they are extracted.

Mineral processing operations that use the selective flotation process include all of the world's major lead-zinc mining operations. These include, for example, Century, Broken Hill and Mount Isa Mining Operations in Australia, and Red Dog, Polaris, Sullivan and Brunswick Mining Operations in North America.

A comparison of the lead flotation circuits for the world's three largest lead-zinc mining operations as of 2000 namely Century, Red Dog, and Polaris is shown in Figure 1.1.

Figure 1.1 Lead Flotation Circuits of the Lead-Zinc Flotation Flowsheets of Century, Red Dog* and Polaris*



**The circuits for Red Dog and Polaris were taken from Zielinski et al. (2000).*

Common to these circuits are the main stages of grinding, lead rougher and lead cleaner. However, significant individual differences among the circuits exist including the presence or absence of pre-flotation, lead scavenger flotation, type of flotation cells and regrinding mills. These differences are dictated by the nature of the ore that each operation processes. Similar commonalities and differences could be observed among the various lead-zinc operations around the world.

Although the selective flotation process has been practiced since Lyster's patent in 1912, the mechanism of the action of various flotation reagents used to improve selectivity during lead flotation is not yet well understood. Investigators seeking alternative reagents have largely depended on empirical testing owing to the complexity of the chemistry of sulfide mineral flotation (Wang and Forssberg 1995). Even at an operation with good ore grade control there are differences in ore content, mineral oxidation, particle size, impurities, composite mineral particles, pulp pH and redox potential (E_h) which can affect flotation response (Clarke 1998).

1.2 Description of the Century Mine Operation

Currently owned by Zinifex Ltd., the Century Mine operation is located in Northwest Queensland, Australia. It is situated approximately 250 kilometers north-northwest of Mount Isa and within 150 kilometers of the Gulf of Carpentaria at 138° 36' E longitude, 18° 43' S latitude. The Century deposit is comprised of sphalerite, pyrite and galena confined in black shale layers. Quartz, sericite and siderite are the principal non-sulfide gangue minerals (Waltho and Andrews 1993).

Exploration and mining in the area around the Century deposit has been intermittently occurring for over 100 years. The first mining lease in this area was pegged in 1887 over what is now the Silver King vein deposit. A total of 43 other veins were discovered by prospectors within 10 years of Silver King and the area was proclaimed the Burketown Mining Field. Lead, zinc and silver was produced from the field. From the late 1940's mining companies have explored the area. A mining company, CRA, had tenements granted in 1987, almost precisely 100 years from the discovery of Silver King and named the area "Century".

CRA announced the discovery of the Century deposit on 17 September 1990. Resource definition drilling identified a geological resource of 118 million tonnes averaging 10.2% zinc, 1.5% lead and 36 g/t silver (Waltho and Andrews 1993). A small plant, known as the Batch Sampling Plant, was operated using flotation, with ultra-fine grinding in the zinc circuit, to initially process Century ore for use in smelting trials.

Pasminco Ltd. announced on 24 September 1997 that it had completed the acquisition of the Century deposit. It further developed the site by 6 November 1999, to become the first company to process Century ore through a large-scale operation including a large open pit mine and the differential lead-zinc flotation process. The project's construction plans itemised capital expenditure at \$888 million. Knowledge about the flotation behaviour of Century ore was limited to the batch sampling plant, and research and development at laboratory and pilot scale. Consequently, the Century Mine is regarded as a Greenfield site. Pasminco Ltd. went into administration and was restructured as Zinifex Ltd. in May 2004, who now owns the operation.

Appendix 1.1 shows an aerial photograph of the Century Mine pit, taken facing south in September 2003. The image gives a good idea of the size of the pit after 4 years of mining. The open pit mine has been developed to expose the upper zone and some of the lower zone ores. The mining operation moves approximately 7.8 million bank cubic meters (BCM) of ore and waste rock each year. The run-of-mine (ROM) pad and the approach to the concentrator is shown on the left side of the image.

Appendix 1.2 is an aerial photograph of the Century Mine concentrator area taken facing east in April 1999, prior to the commencement of concentrate production. The

image shows the ore stockpile, concentrator, reagent facility and product handling areas and gives an indication of the magnitude of the operation. The path of the 300-km underground concentrate pipeline, which transports both zinc and lead concentrates to gulf community of Karumba for de-watering and shipping, is also evident at the top center of the image. The crusher, ROM pad and open cut pit, which are not clearly shown, are located forward of the conveyors shown at the bottom of the image.

Appendix 1.3 is a photograph of the concentrator grinding area taken during construction and shows the 2-stage grinding process including semi-autogenous grinding (SAG) followed by ball mill grinding. Two cyclone nests, each containing 26 cyclones, are shown positioned above the mills. At full production, the grinding circuit is capable of grinding 5 million tonnes of ore per annum to an 80% passing particle size of 58 microns. This equates to a grinding rate of 570 tonnes of ore per hour and the flotation feed produced is approximately 30% solids.

Appendix 1.4 is a photograph of the northern side of the concentrator showing the carbon pre-flotation, lead flotation and zinc primary flotation circuits. Carbon pre-flotation is commonly known ‘pre-flotation’ and will be referred to this herein for brevity. The pre-flotation process is specifically aimed at removing a significant amount of the carbonaceous minerals contained in the ore, which would otherwise dilute the lead and zinc concentrates. The carbonaceous minerals float in this process due to their natural flotation properties and only a frother (200–300 g/t MIBC) is required to be added to the pulp at pH 7.0–8.5 to establish a stable froth. The pre-flotation circuit currently consists a roughing stage of seven 100-m³ flotation cells.

The lead flotation circuit consists a rougher–scavenger stage, consisting six 100-m³ flotation cells, followed by two cleaner flotation stages, which consists a total of five 50-m³ flotation cells with froth washing systems. The reagents added to the circuit include approximately 50 g/t MIBC, 270–300 g/t sodium isopropyl xanthate (SIPX) and lime sufficient to adjust the pulp pH to 8.5. Dextrin (200 g/t) is added during the roughing stage to depress carbonaceous minerals not recovered during the pre-flotation stage, which would otherwise dilute the final lead concentrate. The use of cyanide occurs earlier in the process flowsheet and is added during the grinding process (300 g/t) to depress sulfide minerals other than galena.

These circuits are directly related to the current study. Approximately 300 000 tonnes of pre-flotation concentrate and 100 000 tonnes of lead concentrate are produced each year. The pre-flotation concentrate reports to the final tailings, whilst the lead concentrate is transported by pipeline, pumped in between zinc concentrate and water batches, to the Karumba port facility for de-watering and export. Surplus lead concentrate that cannot be pumped to Karumba within the pumping schedule is de-watered on site in an evaporation dam and the dried product is transported to Karumba by triple road-trains.

Appendix 1.5 is a photograph of the southern side of the concentrator. The image was taken on commencement of production on 25 October 1999 and shows the last four stages of a five-stage cleaning circuit. The closest flotation cells shown produce the final zinc concentrate that is transported by pipeline to the Karumba port facility for de-watering and export. Approximately 800 000 tonnes of zinc concentrate are produced each year. Froth washing trays are also shown on the closest cells. An ultra

fine grinding circuit is located at the end of the flotation banks, but is not clearly visible on the image.

Appendix 1.6 is a photograph of the Outokumpu[®] 200 m³ capacity OK-200 flotation cell, which was installed during 2002 to increase capacity in the primary zinc circuit. All other flotation cells at the Century Mine concentrator are Outokumpu[®] 50 m³ and 100 m³ cells. The OK series flotation cell is round as opposed to the traditional rectangular banks (Denver[®] D-R cell). Launderers are positioned around the edge of the cell and around the impellor shaft. The OK impellor design consists a number of vertical slots that taper downwards and a horizontal disc encloses the top of the impellor. As it rotates the impellor acts as a pump drawing in new slurry at the base of the cell and expelling it outward where it comes into contact with air expelled from the base of the rotor in the rotor-stator clearance (Wills 1992, p571). The aerated slurry then moves into the surrounding cell volume. The OK flotation cell design provides large cell volumes whilst occupying a minimum floor space and often banks containing only two large cells have been successfully operated, as is the case for primary zinc rougher flotation at Century Mine.

The process flowsheet, first established in 1999 is shown in Appendix 1.7. Now fully operational, the Century Mine's annual production averages 5 million tonnes of ore producing over 800 000 tonnes of zinc concentrate and 100 000 tonnes of lead concentrate. The mine's concentrator ramped up to full annual production capacity of 500 000 tonnes of zinc metal contained in concentrate in August 2002. The designed zinc recovery of 82.5% was achieved later in January 2003. The current process flowsheet is shown in Appendix 1.8.

Burgess et al. (2003) has provided a detailed account of the ramp up to full production. Accordingly, significant changes were implemented to improve zinc recovery during the development period. These include grinding and mine-to-mill process control strategies to maintain stability and reduce feed variation; a lower pulp density strategy, including increased capacity in the pre-flotation and primary zinc circuits; froth crowders, froth cameras and reagent control strategies; and improved plant availability, including longer operating periods between plant maintenance shutdowns and the installation of a post-grinding vibratory screen. In addition, froth washing has also been implemented as a secondary concentration means in the lead cleaner, zinc rougher and final zinc cleaner flotation circuits. The main changes can be seen in the mine's current concentrator flowsheet shown in Appendix 1.8 when compared with the Mine's concentrator flowsheet at the commencement of operations shown in Appendix 1.7.

1.3 Aims of the Study

This study was aimed to explore methods of improving the selectivity in lead-zinc flotation by improving the depression of sphalerite particularly at Zinifex's Century Mine concentrator. Specifically it was aimed to:

- review studies related to selectivity in lead-zinc flotation;
- identify the mechanisms involved in sphalerite recovery during pre-flotation and lead flotation;
- determine the variables that affect the flotation of sphalerite during pre-flotation and lead flotation;
- identify depressants for sphalerite that offer better selectivity during pre-flotation and lead flotation;

- generate data that are directly relevant to Zinifex's Century Mine concentrator; and
- contribute to the knowledge and understanding of the effect of depressants on the recovery of sphalerite during pre-flotation and lead flotation.

1.4 Research Methodology

As the first step of this study, a review of literature was undertaken to gain a good understanding of lead-zinc flotation in general and the depression of zinc during pre-flotation and lead flotation in particular. The findings of this review were then used to design an experimental program to investigate the key recovery mechanisms for the reporting of the sphalerite into the lead concentrate and determine the optimum conditions for depressing sphalerite.

The first part of the experimental program dealt with reproducibility tests to develop practical skills in carrying out flotation tests and establish a baseline, i.e. a basic test flowsheet and reagent scheme comparable to that of the concentrator. The concentrates produced in the baseline flotation tests were sized and the sized fractions assayed to determine the dominant recovery mechanisms during laboratory flotation.

The optimum conditions for depressing the sphalerite was determined by investigating the effect of primary grinding, pulp density, pH and frother addition on the selectivity of the flotation process at various stages of the process flowsheet. This was then followed by a series of tests that explored the use of zinc sulfate and iron sulfate, either alone or in combination with sodium cyanide, as alternatives to the

current practice of using sodium cyanide alone to improve selectivity and reduce reagent costs at Zinifex's Century Mine concentrator.

The results of the experimental program at this point of the study were used to rank the key recovery mechanisms for the reporting of sphalerite in the pre-flotation and lead flotation concentrates.

In order to generate data that are directly relevant to Zinifex's Century Mine concentrator, ore test samples were obtained from this operation.

1.5 Significance of the Study

The data generated from this study will directly benefit the processing of lead-zinc ore at the Zinifex's Century Mine concentrator. At full production, the concentrator will be producing 250 000 tonnes of pre-flotation carbon concentrate containing, on average, 11% zinc and 100 000 tonnes lead concentrate per annum containing, on average, 4% zinc. This represents a combined loss of 31 500 tonnes of zinc metal per annum. A reduction in zinc losses of even only 1% due to the reporting of sphalerite to both products would amount to an annual increase of 3 500 tonnes in zinc metal recovery. This would represent approximately US\$3 million in increased production of zinc concentrate. Clearly this is a substantial benefit for the operation.

In addition, the data generated in this study would also be relevant to other lead-zinc flotation operations, particularly those with a mineralogy that is comparable to Century's ore and have a pre-flotation stage in the process flowsheet.

Further, the results of this study will contribute to the overall understanding of the flotation of galena and sphalerite.

1.6 Scope and Limitations

This study investigated the selective depression of sphalerite during the pre-flotation and lead flotation using zinc sulfate, iron sulfate and sodium cyanide including their combinations. The results were then used in an attempt to determine the mechanisms involved in the flotation of sphalerite during these unit processes. There was no attempt to either increase the recovery of the carbon or lead although clearly for practical purposes these would have been desirable results. Thus, the recovery of these species and other significant components of the ore were monitored in all flotation tests.

CHAPTER 2

REVIEW OF STUDIES ON SELECTIVITY IN LEAD-ZINC FLOTATION

The undesirable reporting of sphalerite to the pre-flotation and lead concentrates during the lead-zinc flotation process is well known. This literature review was undertaken to gain a good understanding of this phenomenon and explore methods of inhibiting it.

2.1 Activation of Sphalerite during Pre-flotation and Lead Flotation

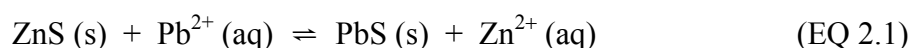
According to Wills (1992), activation of the sphalerite surface during pre-flotation and lead flotation can occur through interactions with metal ions, metal hydroxides, metal xanthates and galena fines. After activation, the collector added during lead flotation such as xanthate adsorbs to the sphalerite surface and produces a very insoluble metal xanthate that provides the surface with a “water repellent envelope”. A sphalerite surface, cleaned of metal ions or galena fines, is not strongly hydrophobic in the presence of xanthate as zinc xanthate has a relatively high solubility and thus, inhibits its flotation. Activation of the surface may also result in the formation of elemental sulfur or polysulfide species on the sphalerite surface that can enhance hydrophobicity and assist its recovery.

2.1.1 Activation of Sphalerite Surface by Metal Ions

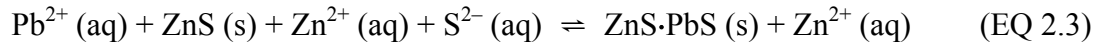
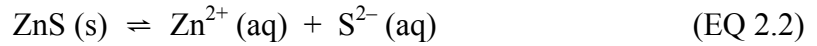
The activation of sphalerite by metal ions has been observed as early as 1913, during the early developments of the differential flotation process when Bradford discovered the use of soluble copper salts as a means of enhancing and activating the flotation of sphalerite. It was recognised in 1960 by Rey and Formanek that activation also occurred when sphalerite misreported to the lead concentrate during the processing of oxidised lead ores. Accordingly, oxidation products such as lead ions are released from the sulfide minerals during grinding and aeration. Ores with an acid gangue such as high siliceous ores were shown to exhibit a higher selectivity compared with those with a basic gangue (limestone based ores) that are easily oxidised. The presence of soluble lead minerals such as anglesite (PbSO_4) also markedly increased the recovery of sphalerite during lead flotation.

It has been proposed (Ralston and Healy 1980a, Von Reeken et al. 1989, Clarke 1998) that the activation of sphalerite surface by metal ions in acidic media occurs in two ways: one is by ion exchange whereby the zinc ions from sphalerite at the surface of the mineral are replaced by metal ions such as lead (II) (Ralston and Healy 1980a). The other is by adsorption whereby the activating ion such as lead (II) is adsorbed on the mineral surface and thus activates the mineral itself.

The activation by ion exchange may be represented by the following equation (EQ 2.1):



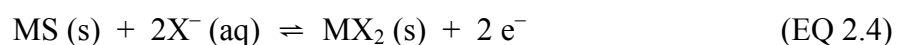
Another proposed ion exchange reaction involves the dissolution of ZnS (EQ 2.2) resulting in the precipitation of lead sulfide on the sphalerite surface (EQ 2.3) (Ralston and Healy 1980a):



Zinc sulfide is sparingly soluble and at pH values above 6 the release of zinc (II) has been found to be below the detection limits of ICP (Clarke 1998). As zinc sulfide dissolution (EQ 2.2) would be minimal, the extent to which the precipitation reaction occurs and hence the role it plays in sphalerite activation would be small compared with the direct Pb^{2+} reaction shown in EQ 2.1.

Other metal ions such as silver, cadmium, mercury, bismuth, gold and cesium behave similarly and may replace Zn^{2+} on the sphalerite lattice surface (Von Reeken et al. 1989). Copper ions are still added during zinc flotation to recover sphalerite by activation and subsequent adsorption to the collector. The replacement of zinc ions on the sphalerite surface by other metal ions enables sphalerite to act essentially like the sulfide mineral of the metal during flotation (Von Reeken et al. 1989).

The interaction between collectors, such as xanthate, and sulfide minerals is a surface chemistry phenomenon. Martin et al. (1990) have described the mineral surface-xanthate interaction as an electrochemical process with an oxidation reaction between xanthate and the mineral surface (EQ 2.4) and a reduction of oxygen in the pulp (EQ 2.5):

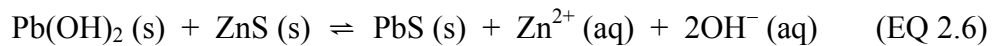




where MS represents the metal sulfide and X^- represents xanthate. Zinc xanthate is very soluble, whereas other metal xanthates such as copper (II) or lead (II) xanthate are insoluble. When the sphalerite surface has been activated by these metal ions the chemical adsorption of xanthate is stable, hydrophobicity increases and flotation can occur.

2.1.2 Activation of Sphalerite Surface by Metal Hydroxides

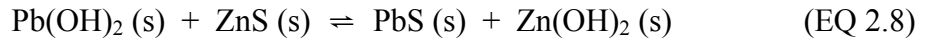
More often, sulfide mineral flotation is carried out in alkaline media, as collectors such as xanthates are stable under these conditions and the corrosion of cells and pipe work is reduced (Wills 1992, p. 520). Ralston and Healy (1980b) observed that the activation of sphalerite is affected by the pH of the solution. Accordingly, M^{2+} species are dominant in the pulp at pH values up to pH = 6.5. However, at higher pH values $\text{M}(\text{OH})_2$ becomes dominant and the mechanism is complicated by hydrolysis effects. They proposed that in mildly alkaline media a slow ion exchange reaction proceeds after the adsorption of lead hydroxide ($\text{Pb}(\text{OH})_2$) to the sphalerite surface as shown in EQ 2.6:



or after the slow dissolution of lead hydroxide as shown in EQ 2.7 followed by a simple exchange reaction (i.e. EQ 2.1 or EQ 2.2 and EQ 2.3):



They also speculated that at pH values high enough for zinc hydroxide ($\text{Zn}(\text{OH})_2$) to form at the mineral surface, the ion exchange proceeds as shown in EQ 2.8:



The mechanisms proposed by Ralston and Healy (1980b) were based partly on the observed variations in the kinetics of activation with variations in pH. Ralston and Healy performed activation studies using synthetic cubic zinc sulfide and soluble analytical grade copper (II), cadmium (II) and lead (II) salts in a sealed system. They used various ion-selective electrodes, in conjunction with Atomic Absorption Spectrophotometry, to determine copper (II), cadmium (II) and lead (II) ion uptake. Metal ion uptake was found to be rapid at first followed by a second slow activation step. The metal ion uptake followed a logarithmic dependence on time except for lead (II) ions, where there was no well defined rate equation for the second step.

Popov et al. (1989b) also observed marked variations in the kinetics of activation with variations in pH. The longer activation time necessary to reach a near-equilibrium condition in an alkaline medium, compared to the time required in an acidic medium, is due to different mechanisms of activation. They carried out Hallimond tube flotation tests using natural sphalerite mineral specimens together with zeta potential and IR spectrum measurements. When potassium ethylxanthate and lead ions were added during flotation tests, IR absorption bands for lead-ethylxanthate were observed after 15 minutes at pH = 5 to 6 and after 40 minutes at pH = 8 to 9. These results were in agreement with the mechanism of activation in acidic medium where an exchange reaction as shown in EQ 2.1 would be generally faster than the mechanisms for activation in an alkaline medium that involve a surface reaction. The results from IR spectroscopy were correlated with zeta potential measurements and they suggested that the mechanism of activation at an

alkaline pH occurred by a mechanism that does not lead to any significant change in the surface charge of sphalerite.

Clarke (1998) found that whilst the ion exchange mechanism is likely for copper (II) activation, lead (II) activation is more likely to proceed only by adsorption to the sphalerite surface. Experimental results from EDTA extraction testwork and XPS analysis showed differences between lead (II) and copper (II) activation mechanisms. Clarke found that whilst lead (II) was adsorbed to the sphalerite surface there was little or no release of zinc (II) into the pulp other than that which was due to the natural dissolution of sphalerite. In the case of copper (II) activation a 1:1 exchange of copper (II) for zinc (II) was found. Differences in the charge shifting of XPS spectra of lead (II) activated sphalerite are higher than that for copper (II) activated sphalerite experiments suggesting that the lead-zinc exchange does not occur or is very small during lead (II) activation.

Clarke postulated that the larger ionic radii of the lead (II) ion (0.118 nm) is much greater than zinc (II) ions (0.075 nm) and this limits its ability to exchange into the sphalerite lattice. Copper (II) ions (0.073 nm) have a radii smaller than that of zinc (II) ions and hence an ion exchange can proceed more easily. The kinetics of sphalerite activation by silver (I) ions is similar to copper (II) activation in that it has a logarithmic dependence with time (Gaudin et al. 1957). However, silver (I) ions in the pulp have an ionic radii of 0.115 nm (CRC Handbook of Chemistry and Physics 1999, p. 12.14) which is similar to lead (II) and should accordingly have difficulty fitting into the sphalerite lattice. Other possible activating metal ions such as cadmium (II), cesium (III), mercury (I), mercury (II), bismuth (III) and gold (I) are also heavier elements than copper (II) and zinc (II) and their larger ionic radii,

ranging from 0.095 nm to 0.137 nm (CRC Handbook of Chemistry and Physics 1999, p. 12.14), is also likely to inhibit exchange into the sphalerite lattice if Clarke's postulation was correct.

These "minor" elements known to contribute to the activation of sphalerite are typically found in parts-per-million levels at Century Mine and most other complex sulfide mineral deposits where sulfur, lead, zinc, iron and often copper are the major elements comprising the mineralisation. The role "minor" elements play in sphalerite activation would presumably be small compared with the major metals of lead and copper.

2.1.3 Activation of Sphalerite Surface by Lead Xanthate and Galena

Fines

Just as lead hydroxide can adsorb to the sphalerite surface it has been suggested that lead xanthate or galena (PbS) fines may adsorb or adhere to the sphalerite surface (Morey 1997). Insoluble metal xanthates are formed when the xanthate used as the collector during lead flotation reacts with ions, such as lead ions, in the pulp (Wills 1992, p. 504). Galena fines are formed during the crushing and primary grinding process.

The effectiveness of the collector during lead flotation is reduced by interactions with lead ions as the lead xanthate product may also adsorb onto the sphalerite and gangue mineral surfaces, resulting in those particles reporting to the concentrate along with galena particles. The alkaline conditions used as early as the grinding circuit prior to flotation can precipitate free metal ions in the pulp as relatively

insoluble hydroxides reducing the possibility of metal xanthate formation (Wills 1992, p. 504).

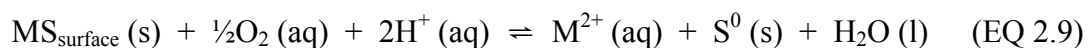
The activation of sphalerite by adhesion of galena (PbS) fines present in the pulp by hetero-coagulation (Morey 1997) is also known as carrier flotation. Carrier flotation occurs when fines adhere to coarse particles through hydrophobic flocculation and the resultant coated coarse particle is amenable to flotation (Song et al. 2000). Flocs are formed from fine particles through an interaction with xanthate whilst the pulp is stirred or agitated. Mineral fines rendered hydrophobic by xanthate can coagulate when they collide with sufficient energy to form larger hydrophobic flocs, which have an increased probability of colliding with air bubbles.

Flotation by flocculation is a way of improving the flotation response of mineral fines through an increase in particle size and hence an increase in the probability of collision with air bubbles at a favorable contact angle. However, when the flocculation process is not selective to galena fines during lead flotation, other mineral particles, such as sphalerite fines or coarse sphalerite particles, can become more amenable to flotation. Selective floc flotation is possible by adding special dispersants and controlling pH to prevent hetero-coagulation from occurring. Typically sphalerite and gangue particles do not have stable interactions with xanthate during lead flotation and flocculation through hydrophobization is less likely to occur. However, coarse sphalerite particles that only have small galena inclusions may interact sufficiently with xanthate to become subject to hetero-coagulation and hence become more likely to float.

2.1.4 Elemental Sulfur and Polysulfides on the Sphalerite Surface

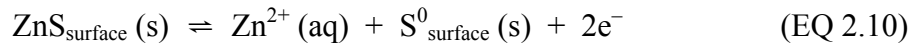
Elemental sulfur and polysulfide species can form on the metal deficient sphalerite surface after the interaction of metal ions during activation. The metal ions responsible for activation come from the oxidised mineral lattice and recycled plant water. The presence of elemental sulfur or polysulfide species on the sphalerite surface increases hydrophobicity and the floatability of the mineral particle.

Oxidation of sulfide minerals in the presence of dissolved oxygen and acidic media to form elemental sulfur may be represented by (EQ 2.9):

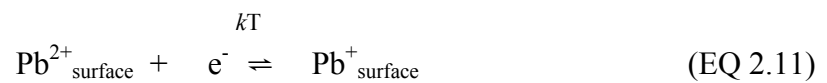


Studies by Ralston et al. (1981) support this mechanism, using a mass spectroscopic method. For example, they detected elemental sulfur at the sphalerite mineral surface. A series of activation tests were performed at specified pH values for 30 minutes, whereby high purity synthetic zinc sulfide was conditioned with copper (II), lead (II) and cadmium (II) solutions. Tests were carried out in darkness and under normal light. Samples were collected using a 20-cm³ syringe, filtered through a 0.22 µm Millipore filter and dried in a vacuum dessicator over silica gel. A Finnigan 1015 electrostatic mass spectrometer was used with a solid probe inlet to introduce dried solid samples packed in capillary tubing into a vacuum system where they were vaporized and directed into the ion source.

Ralston et al. (1981) proposed that elemental sulfur is formed on a sphalerite surface after irradiation with UV light or activation by metal ions such as copper (II), cadmium (II) and lead (II). When unactivated sphalerite is irradiated with UV light, elemental sulfur (S⁰) formation proceeds as shown in EQ 2.10 (Ralston et al. 1981):



After activation, for example the activation of the surface by lead (II) ions, elemental sulfur has been detected both in the dark as well as normal light, indicating that thermal energy (kT) is sufficient to allow redox reactions to proceed. Ralston et al. (1981) proposed that after the interaction of lead (II) with the sphalerite surface, elemental sulfur is formed through the following redox reaction, i.e. the reduction of Pb^{2+} to Pb^+ and the oxidation of S^{2-} to S^0 :



When the metal deficiency on the sulfide surface becomes extensive, a restructuring may occur to form a polysulfide, such as S_8 rings, on the mineral surface. S_8^+ was detected by the mass spectrometer in Ralston et al. (1981) experiments.

Enhanced elemental sulfur formation would occur under UV radiation due to metal ions on the mineral surface, as shown by EQ 2.11 and EQ 2.12, occurring jointly (Ralston et al. 1981). Some operations, such as the Cannington Mine, have flotation circuits that are not sheltered from direct sunlight and weather. Whilst the Century Mine concentrator has a roof above all parts of the flotation circuit, the pulp can be at temperatures up to 60 °C during primary grinding. Such conditions allow formation of elemental sulfur on the sphalerite surface if activation by metal ions is a major factor affecting selectivity.

Metal ions are released into the pulp as a result of oxidation of mineral surfaces. The extent of oxidation of minerals in base metal flotation can be determined by

extracting slurries with ethylenediaminetetra-acetic acid (EDTA) (Rumball and Richmond 1996). An EDTA extraction of plant samples from the Hellyer Lead-zinc Mine by Rumball and Richmond (1996) showed that the base minerals are typically fresh before milling, mildly oxidised during milling, but extensively oxidised during flotation. The recovery of sphalerite has been shown to be considerable during the late stages of lead flotation, particularly in the lead roughing bank of cells (Rey and Formanek 1960; Basilio et al.1996) where the base minerals have been extensively oxidised.

The differential flotation of lead-zinc ores is typically carried out in alkaline media. Lime or other pH modifiers are usually added as early as the primary grinding circuit. In an alkaline medium, metal ions are precipitated as solid metal hydroxides which are less likely to interact with the collector and extends the reaction time required to activate the sphalerite surface as discussed earlier.

A natural or collector-less flotation effect can occur due to enhanced hydrophobicity from the presence of elemental sulfur on the sphalerite surface. Operations, like Century, which consist of a pre-flotation circuit prior to lead flotation to remove naturally floating carbon minerals, may lose sphalerite to the pre-flotation concentrate due to this effect when only frother is added to the pulp. Depressants added during grinding, such as cyanide, may however react with elemental sulfur formed on the sphalerite surface to form thiocyanates (Prestidge et al. 1997). At Century Mine, zinc recovery in the pre-flotation concentrate is typically 5–7% compared with approximately 1–2 % recovery during lead flotation.

2.2 Sphalerite Recovery Associated with Mineral Texture, Liberation and Froth Conditions

Zinc losses can also be attributed to locked particles and mechanically entrained fines that report to the pre-flotation and lead concentrates. Sphalerite recovery during pre-flotation and lead flotation can be due to complex composite flotation with galena and gangue, carbonaceous inclusions, or entrainment as a function of water recovery. Mineral texture and liberation after grinding and froth control determines the extent of sphalerite recovery through these mechanisms.

2.2.1 Complex Composite Flotation with Galena and Gangue

Complex composite flotation occurs when a particle containing a sphalerite grain that is in composite with galena or sulfide gangue minerals adsorbs to the collector causing the particle to report to the concentrate. Recovery problems increase with finely disseminated ores where there is a close mineralogical association between sphalerite, galena and sulfide gangue minerals such that these minerals will still be together on most particles after grinding. To achieve high recoveries and acceptable concentrate grades, regrinding is often required during the flotation process to reduce the number of composite particles and improve sphalerite liberation. Some operations re-grind the pulp before or during cleaner flotation in an attempt to reduce the composite mineral particles to sizes where the valuable minerals are liberated.

Mineral liberation studies by Petruk (1995) examined some of the relationships between mineral textures and flotation in experiments with Brunswick Mine ore. Accordingly, the ease of liberating mineral grains is dependent upon grain size, crystallinity and bonding between mineral grains. Mineral grains with straight grain

boundaries and weak bonds between other minerals are easily liberated and readily concentrated into high-grade concentrates. Mineral grains that have re-entrant boundaries and strong bonds with neighboring minerals are not easily liberated and will not produce high-grade concentrates, even with regrinding. Minute random inclusions in large grains will not be liberated unless they occur along planes of weakness.

To successfully process an ore by flotation, the ore must be ground fine enough to liberate minerals so that they can be selectively concentrated while maintaining a grind size that is not too fine. Reducing the grind size to very fine sizes has the potential to introduce other problems that need to be resolved in the flotation process. For instance, the finer the grind size, the higher the plant running costs owing to increases in energy usage in grinding and the reagents used in flotation due to an increase in particle surface areas. Testwork by Frew et al. (1995) on the effect of re-grinding on flotation found that the recoveries of gangue minerals are not always decreased by size reduction alone and efforts need to be directed at improving flotation following grinding. They performed flotation tests in a 2.7 L Denver laboratory cell using samples collected from five lead-zinc concentrators, where samples were taken before and after regrinding. No attempts were made to optimise flotation performance and the same controlled conditions and reagent additions were used to compare the flotation performance when re-grinding was included in the flotation test.

2.2.2 Sphalerite Flotation due to Carbonaceous Inclusions

The flotation of sphalerite due to carbonaceous inclusions is well recognised in the base metals mining industry. Carbonaceous minerals, such as graphite and calcite, and phyllosilicate minerals, such as talc, are often present in sulfide ore bodies. These minerals have natural flotation properties and can report to a concentrate without the addition of a collector. When these minerals are included as fine grains in the surface of a sphalerite particle, the particle can exhibit these natural flotation properties and report to the concentrate.

Lead-zinc mining operations which have high-carbon or high-talc bearing ores often use a pre-flotation stage to float most of the naturally hydrophobic minerals before lead flotation to avoid dilution of the lead concentrate. Operations such as Century and Cannington in North-west Queensland continue to operate pre-flotation circuits. Operations such as Mount Isa Mines and Woodlawn have operated pre-flotation circuits in the past. Woodlawn has ceased operations, whilst Mount Isa Mines now operates a heavy medium separation plant and processes the slimes separately from the coarser material during lead flotation. Zinc recoveries during pre-flotation can be partly attributed to carbonaceous inclusions in the sphalerite particles. When these recoveries are high the economic benefit of having a pre-flotation stage is questionable.

A combined optical and QEM–SCAN analysis of pre-flotation concentrate obtained from pilot plant testwork with Century Mine ore (Butcher and Gottlieb 1999a) revealed that some sphalerite particles contained micron sized (<1–2 microns) inclusions of graphite and quartz. The test sample analysed by QEM–SCAN included the C4 and C5 cyclosized fractions of the pre-flotation concentrate, which usually

consist of fine (approximately +7–12 microns) liberated mineral particles. A photomicrograph of sphalerite particles is shown at Appendix 2.1 and the brownish grey–grey black phases on the particles have been identified as graphite. The same study obtained back-scattered electron micrographs of sphalerite particles, which are shown in Appendix 2.2, and the dark areas on each particle were mainly found to consist of graphite. Some particles of pyrite in the test sample were also found to contain inclusions of graphite and quartz and the textures of these inclusions were very similar to those found in sphalerite. However, other sphalerite particles were found to be completely free of inclusions, indicating that sphalerite recovery during pre-flotation cannot be solely attributed to graphitic inclusions and that other mechanisms such as entrainment in the froth also have a role in sphalerite recovery.

2.2.3 Sphalerite Flotation due to Entrainment

Flotation due to entrainment occurs when sphalerite or gangue particles are mechanically carried into the froth. These particles are transported from the pulp region to the concentrate by physical transportation in the water that reports to the concentrate. According to Klassen and Mokrousov (1963, pp. 377–381), the thickness of aqueous films between air bubbles in the froth and the amount of water draining between the air bubbles play an important role in determining how much mineral is physically recovered by this mechanism. This process is not just limited to sulfide mineral flotation. It has also been observed in the flotation of coals and oxide ores.

Entrainment is a function of water recovery and the rate of recovery of free gangue of size i by entrainment (Lynch et al. 1980, p. 74) is:

$$\text{RRFG}_i = \frac{\text{RRW} \times \text{CF}_i}{\text{MWP}} \times \text{MFGP}_i \quad (\text{EQ 2.13})$$

where RRFG_i and MFGP_i are the rate of recovery and mass of free gangue respectively,

RRW is the rate of water recovery (mass/time), and

MWP is the mass of water in the pulp volume.

CF_i is the transportation efficiency factor:

$$\text{CF}_i = \frac{(\text{Mass of free gangue per unit weight water})_{\text{concentrate}}}{(\text{Mass of free gangue per unit weight water})_{\text{pulp}}} \quad (\text{EQ 2.14})$$

The efficiency of transportation factor approaches 1 for small particles ($< 5 \mu\text{m}$) with low specific gravity and reaches 0 for larger particles ($> 50\mu\text{m}$). Table 2.1 shows typical transportation efficiency factors for siliceous gangue:

Table 2.1 Typical CF_i Values for Siliceous Gangue (Lynch et al. 1980, p. 74)

<i>Size Fraction (μm)</i>	+150	+75	+44	+33	+23	+16	+11	
	-210	-150	-75	-44	-33	-23	-16	-11
CF_i	0	0	0.03	0.04	0.11	0.24	0.44	0.83

Further concentrating the targeted mineral in the froth (secondary concentration) can be achieved by spraying the surface of the froth with water. Fine particles, most of which are mechanically entrained in the aqueous film between air bubbles are washed away, while large hydrophobic mineral particles adhered to the air bubbles remain in the froth (Klassen and Mokrousov 1963, pp. 378–381). The “froth washing” process, by spraying the optimum amount of water into the froth, results in an improvement in concentrate quality and an increase in recovery. Sufficient water

needs to flow through the froth to displace the “dirty” mineral-entrained aqueous film between air bubbles, otherwise the clean water will simply mix and be recovered with the “dirty” water and the desired change will not be realized. On the other hand, excessive froth washing may have a deleterious effect on the froth where the increased flow of water can cause the air bubbles to collapse.

A froth washing system is used at Century on flotation cells in the lead and zinc cleaner flotation circuits. Appendix 2.3 shows the froth washing trays without the wash water running and the porous rubber screens, which deliver the water evenly across the froth, can be seen. Appendix 2.4 shows the water supply distribution to the froth washing trays. The water is supplied tangentially to the tray at a high velocity to ensure that pulp deposits or residues do not block the holes in the tray through which the wash water flows. This provides a reliable and even distribution of wash water.

Concentrate quality during pre-flotation or lead flotation may be improved by froth washing if sphalerite and gangue minerals mechanically trapped between air bubbles are sufficiently displaced. Lead recovery may be increased due to the retention of coarse galena particles that might normally be lost towards the top layer of the froth (Klassen and Mokrousov 1963, pp. 378–381). Towards the top of the froth column the bubbles normally increase in size as they combine together; a decrease in surface area results and competition for sites on the bubbles often results in coarser particles being displaced. However, froth washing decreases the size of bubbles in the upper froth layers allowing a larger portion of the coarse particles to remain in the froth (Klassen and Mokrousov 1963, p. 382).

Maintaining equilibrium of water recovery, whereby “dirty” water containing mineral particles is kept in lower section of the froth and pulp, whilst clean water is recovered may be more easily achieved in flotation techniques that have deep froth zones, such as column flotation. Column flotation techniques, including more modern technologies such as the Jameson cell often effectively utilize froth washing. A schematic drawing of the Jameson flotation cell is shown in Appendix 2.5. The Jameson cell is a pneumatic flotation machine that uses air entrained in a turbulent pulp addition to achieve flotation. The main advantages of the Jameson flotation cell compared with the conventional column flotation cell is that the height of the column is reduced to approximately 1 m and the flotation column can be self-inducing with respect to air supply (Wills 1992, pp. 561–562).

Another advantage of column flotation techniques is that they can be introduced quickly into a flotation plant as an additional cleaning stage at a significantly lower capital cost than conventional or tank mechanical cells. Some of the world’s largest lead-zinc mining operations, including Red Dog and Polaris (Zielinski 2000) use column cells in the lead cleaner flotation circuit. The application of Jameson cell technology in cleaner flotation for the pre-flotation circuit has been tested at pilot scale in the Century Mine concentrator and remains under consideration as a cost effective method of reducing sphalerite losses to the pre-flotation concentrate.

2.3 Depression of Sphalerite during Pre-flotation and Lead Flotation

Sphalerite is commonly depressed during pre-flotation and lead flotation using inorganic depressants, either alone or in combination. Cyanide is commonly used in sulfide mineral flotation to achieve the separation of complex poly-metal sulfide ores, particularly when the depression of pyrite and other iron sulfides is also involved (Wang and Forssberg 1995).

Zinc sulfate has been used in a number of operations to depress sphalerite and has been shown to have best countered sphalerite activation in test work and plant operation. Iron sulfate has also been shown and used at plant scale as an alternative to zinc sulfate. Other reagents, such as sodium sulfide and organic depressants, have also been used as depressants in laboratory testwork and possibly at plant scale.

2.3.1 Depression of Sphalerite using Cyanide

Cyanides are widely used in sulfide mineral flotation due to the high degree of selectivity achieved. Cyanide is generally the preferred depressing agent, particularly when lime or soda ash (sodium carbonate) is used to regulate alkalinity and the presence of pyrite is significant. Cyanide eliminates metal xanthates from the surface of zinc and iron minerals and has been used for some time to dissolve surface metal ions from activated sphalerite. A sphalerite surface free of metal xanthates is not likely to float due to the solubility of zinc xanthate.

Mitrofanov observed in 1928 an interaction between sphalerite and cyanide which produced a dark film, zinc cyanide ($Zn(CN)_2$), on the mineral surface (Klassen and Mokrousov, 1963, p. 307). It was believed that this film coating the mineral surface could explain the depressing action of cyanide. It has since been proposed by

numerous authors (Wark and Cox 1934; Gaudin et al. 1957; Elgillani and Fuerstenau 1968; Wang and Forssberg 1995) that cyanide depresses sulfide minerals in at least one of two ways and forms insoluble metal cyanide complexes. One is by reacting with metal xanthates at the mineral surface. The other is by reacting with activating ions that are either present in the pulp or adsorbed to an activated mineral surface.

It has been reported that cyanide selectively solubilizes metal xanthates on the mineral surface (Klassen and Mokrousov 1963, pp. 307–310). Xanthates of different metals were shown to have varying solubilities in cyanide solutions. Metal xanthates such as those of lead, thallium, bismuth, antimony, arsenic and tin form neither strong cyanide complexes nor insoluble simple compounds. Minerals containing these metals strongly interact with xanthates in the presence of cyanide and it is common to find these metals recovered as impurities in base metal concentrates. Metal xanthates such as those of copper, platinum, mercury, silver and cadmium are more soluble in cyanide solutions, but a large amount of free cyanide is necessary to depress these minerals activated by these metals during flotation.

Metal xanthates such those of zinc, iron, gold, nickel and palladium are readily soluble in cyanide solutions and traces of free cyanide are sufficient for depression during the flotation of ores containing these minerals. Solubility of xanthates has also been shown to depend on the length of the hydrocarbon chain. The longer the hydrocarbon chain, the less pronounced are the differences between different metal xanthates and the selective depressing action of cyanide during flotation is decreased.

Wang and Forssberg (1995) studied the solution electrochemistry of sulfide-xanthate-cyanide systems and proposed that depression of sulfides by cyanide is caused by one or more of the following processes:

- cyanide dissolves metal xanthates to form metal-cyanide complexes or combines with surface metal ions to prevent the formation of metal xanthates;
- cyanide reduces the redox potential of the flotation pulp and consumes oxygen in the flotation pulp to prevent the chemisorption and oxidation of xanthate;
- cyanide is preferentially adsorbed on the sulfide mineral surfaces as cyano-metal complexes to inhibit the adsorption of xanthate and its oxidation on the mineral surface; and
- cyanide reacts with elemental sulfur and polysulfides to form thiocyanate, thereby removing the hydrophobicity of the surface.

They also performed thermodynamic stability calculations using SOLGASWATER software and thermodynamic data obtained from literature. Pyrite and copper, nickel, zinc, cadmium-sulfides were considered and pE–pH stability diagrams were plotted for each metal–xanthate–cyanide–water system. Electrochemical measurements were performed in cyclic voltammetry experiments with pyrite crystals and platinum electrodes in the presence of sodium cyanide (6×10^{-3} M) and sodium perchlorate (0.1 M) at pH 10.5 and confirmed the effect of cyanide on the pyrite surface. Other cyclic voltammetry experiments, investigating pyrite depression by cyanide (Janetski et al. 1977) have supported the formation of surface species after interaction of the pyrite surface with cyanide.

There have been findings from experimental work with sphalerite that have been different to those with iron sulfides. Khin Maung Win (1966) found no trace of

cyanide complexes on sphalerite surfaces in IR spectroscopy experiments. In their work, natural (particle size $< 1 \mu\text{m}$) and synthetic samples of high purity sphalerite were conditioned for 15 minutes in solutions of 500 mg/L NaCN; 2.5% potassium ethyl xanthate (PEX); 0.5% CuSO_4 ; and 2.5% potassium amyl xanthate (PAX) with and without 0.5% CuSO_4 added. Flotation tests were also carried out on collector (PEX) adsorbed activated (CuSO_4) sphalerite, with and without the addition of 500 mg/L of NaCN conditioned for 15 minutes before flotation. The mixtures after each test were filtered, dried under vacuum and pressed into potassium bromide discs for IR spectroscopy analyses.

He found no detectable amounts of PEX, PAX or cyanide on the pure unactivated sphalerite surface. Sphalerite activated with copper sulfate was found to adsorb xanthate. Sphalerite previously conditioned with copper sulfate and PAX and then conditioned with cyanide were found to have adsorbed no detectable amount of xanthate. Sphalerite and PAX studies found weak adsorption of the collector on the sphalerite surface. However, on addition of excess cyanide the adsorbed PAX was removed. In all cases no adsorption of cyanide to the sphalerite surface was noticed. There may be a weak physical adsorption of cyanide on sphalerite in solution during the experiments with pure sphalerite in the presence of cyanide, which was subsequently lost during the sample preparation for IR spectroscopy.

More recent studies by Prestidge et al. (1997) have supported these findings through experiments involving the cyanide treatment of copper(II) activated zinc sulfide. Cyanide was found to remove copper hydroxide and copper polysulfide species from the surface, whilst photoelectron spectroscopy showed no detectable sign of cyanide complexes on the sphalerite surfaces. In their study zinc sulfide samples were

conditioned with copper nitrate and cyanide solutions for 30 minutes at pH 9. Samples were introduced into the spectrometer as concentrate slurries to preserve the chemistry of the solid-liquid interface. The absence of cyanide complexes on the zinc sulfide surface was different from Wang and Forssberg's proposition where cyanide was adsorbed on iron sulfide surfaces as cyano-metal complexes. Prestidge et al. (1997) proposed a sequence of ligand exchange mechanisms for the action of cyanide on copper activated sphalerite surfaces as follows:

- a ligand exchange between hydroxide and cyanide ions;
- decomposition of surface copper (II) cyanide to form copper (I) cyanide and cyanogens;
- further complexation with cyanide leading to a range of anionic copper (I) cyanide complexes;
- copper extraction as anionic copper cyanide complexes; and
- polysulfides, or sulfur-like components, form thiocyanate.

Cyanide is a powerful complexing agent and similar mechanisms can be proposed for other species which can affect sphalerite activation, such as lead (II) ions and hydroxides.

The adsorption of cyanide to iron sulfide surfaces to inhibit the adsorption of xanthate (Wang and Forssberg 1995; Prestidge et al. 1993a) is in contrast to the effect cyanide has on galena and sphalerite surfaces (Prestidge et al. 1997). Whilst the presence of cyano-species on the surface of pyrite has been confirmed by electrochemistry (Wang and Forssberg 1995) and by IR and photoelectron spectroscopy (Prestidge et al. 1993a), this was found to be in contrast with galena and sphalerite surfaces from photoelectron spectroscopy studies (Prestidge et al.

1997). There is no competitive adsorption between cyanide and xanthate for the mineral surfaces of galena and sphalerite as evident with pyrite and pyrrhotite surfaces (Prestidge et al. 1993b). Instead the cyanide reacts with any adsorbed metal ions, metal xanthates or sulfur products on the mineral surfaces leaving a “mineral-rich surface” which is more acceptable to xanthate adsorption. Galena then readily floats whilst sphalerite, which does not readily float without previous activation, is depressed since zinc xanthates with short hydrocarbon chains are more soluble.

2.3.2 Depression of Sphalerite using Zinc Sulfate

Zinc sulfate is a depressant used in pre-flotation and lead flotation to depress sphalerite by readily dissociating in the process water to contribute the cation Zn^{2+} to the pulp. Zinc sulfate reduces the cyanide requirement in the lead-zinc flotation process by supplementing it. Numerous studies on zinc sulfate as a flotation reagent have been cited in literature, since 1928 (Klassen and Mokrousov 1963, p. 307) to more recent work by Clarke (1998). It is now well recognised that zinc ions alone will not depress sphalerite and that the depressing action only occurs in the presence of hydroxyl ions at alkaline pH (Klassen and Mokrousov 1963, p. 304).

Since Lyster developed the selective lead-zinc flotation process in 1912, flotation has been conducted at alkaline pH (Read 1968). At pH 5.2, zinc hydroxide begins to precipitate and Malinkovsky (1946) has shown that from pH 5.5 to pH 7.4 the depressing action of zinc hydroxide on sphalerite recovery increases with increasing alkalinity.

The mechanism of depression by zinc hydroxide is however different to that of cyanide. Three mechanisms have been proposed:

- adsorption of zinc hydroxide to the sphalerite surface preventing the adsorption of activating metal ions, metal hydroxides or xanthates;
- the creation of unfavorable pulp equilibrium conditions for activation of sphalerite by metal ions to occur; and
- ion exchange with any heavy metal sulfides formed on the activated sphalerite surface to release the activating metal ions into the pulp.

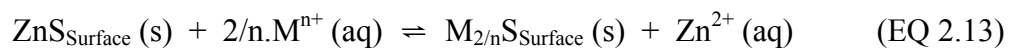
The adsorption of zinc hydroxide to the sphalerite surface to inhibit activating metal ions from getting to possible adsorption sites is different to the mechanism of depression by cyanide, which “cleans” the sphalerite surface of activating metal ions. Zinc hydroxide adsorbed to the sphalerite surface similarly prevents the adsorption of xanthate resulting in depression, as the interaction with xanthate is relatively weak. However, not all zinc xanthate may readily dissociate. Metal xanthates with a longer hydrocarbon chain have a decreased solubility and when such xanthates are chosen as the collector the selective depression of sphalerite may be more difficult.

Livshitz and Idelson (1953) have shown that zinc hydroxide adsorbs not only on the sphalerite surface, but also on the surfaces of other mineral particles. Experiments with increasing additions of quartz to a sphalerite–quartz mixture have shown that zinc hydroxide is consumed through a decrease in its effectiveness as a sphalerite depressant. When not agitated, the mixture showed similar results, showing that the increase in sphalerite flotation was not affected due to mechanical removal of adsorbed zinc hydroxide by the “abrasive action” of moving quartz particles (Klassen and Mokrousov 1963, p. 306). An increase in zinc sulfate additions to increase the zinc hydroxide concentration, again improved the depression of

sphalerite, suggesting that the presence of quartz in the mixture adsorbed most of the zinc hydroxide particles originally present.

The selective action of zinc hydroxide adsorbing to mineral surfaces is also observed with other mineral particles, such as galena and chalcopyrite, whose ability to float does not seem to be affected by the presence of zinc hydroxide in the pulp. This is demonstrated at plant scale, where zinc sulfate additions show a considerably stronger depression of sphalerite than for galena or chalcopyrite. It is possible that even whilst zinc hydroxide may adsorb to the galena or chalcopyrite surface, the interaction between these minerals, xanthate and air bubbles is still strong enough to allow the mineral to readily float (Klassen and Mokrousov 1963, p. 306). Zinc hydroxide adsorbed to the sphalerite surface, which may otherwise only weakly interact with xanthate, maintains a high degree of hydrophilic character.

Von Reeken et al. (1989) has suggested that the addition of zinc sulfate to the pulp enhances sphalerite depression by creating unfavorable pulp equilibrium conditions for activation to occur. The action of zinc sulfate on metal ions, M^{n+} , adsorbed to the sphalerite surface is based on the equilibrium reaction:



It is a common practice to increase zinc sulfate additions when the depression of sphalerite is insufficient. Accordingly, Von Reeken et al. (1989) suggest that the object of increasing and maintaining the zinc ion concentration is to shift the equilibrium of (EQ 2.13) to the left. In plant practice, where new feed, air and reagent additions are constantly entering the flotation cell, it may be questionable that pulp equilibrium conditions can control the activation mechanism for sphalerite.

With high shear from the impellor stirring the pulp it is difficult to imagine that the mere presence of an excess of zinc ions will not allow free metal ions in the pulp from interacting with the sphalerite surface. Von Reeken et al. (1989) also concedes that if metal ions adsorb to the surface before the addition of zinc sulfate then it is questionable as to whether the reaction can be forced to the left considering that the rate of solid state reactions at ambient temperatures are normally very slow.

El-Shall et al. (2000) have proposed that the reaction (EQ 2.13) can be forced to the left for lead ions on the sphalerite surface, by the addition of zinc salts. They suggested that zinc sulfate depresses lead-activated sphalerite as shown by the reaction:



They believe that depression by zinc (II) ions is a reverse reaction to lead activation by a direct ion exchange mechanism. This, however, contradicts the findings from other studies, which suggest that ion exchange does not occur for sphalerite activation by lead ions or hydrolysis products. Essentially, this is the same mechanism of depression proposed by Von Reeken et al. (1989). As discussed in section 2.1, Clarke (1998) argued that activation by lead (II) species is only by adsorption to the sphalerite surface whereas copper (II) and silver (I) activation involves an ion exchange reaction with zinc (II) ions in the sphalerite lattice. El-Shall et al. (2000) may be correct in finding that zinc ion addition to the pulp can affect the adsorption of lead ions, but the mechanism suggested may not be correct as it is based on the reversal of an ion exchange mechanism for activation. The results from El-Shall et al. (2000) support the depression of sphalerite at pH values between pH 7.5 and pH 9.0, above which colloidal zinc hydroxide ($\text{Zn}(\text{OH})_2 (\text{s})$) forms in

significant concentrations and the effectiveness of zinc sulfate is questionable. This is in contrast to earlier studies cited by Klassen and Mokrousov (1963, p. 304) and more recent studies by Clarke (1998) that propose that zinc hydroxide precipitate is capable of depression through a different mechanism as discussed earlier.

The main advantage of using zinc sulfate at plant scale is the reduced cyanide requirement (Wills 1992, p. 517). Normally, up to 200 g/t zinc sulfate and 150 g/t sodium cyanide are added to grinding and flotation circuits. The cyanide requirement can be reduced to below 100 g/t and some American mines have used zinc sulfate alone. The flotation of sulfide minerals is very complex and the Grund Concentrator in Tasmania, Australia, typically used 900 g/t of zinc sulfate to achieve satisfactory selectivity during lead flotation (Von Reeken et al. 1989) with no cyanide use reported. Run-of-mine ore at the Grund operation during 1989 which typically graded 5.2% Pb and 9.6% Zn, was processed with the addition of 934 g/t zinc sulfate and produced lead concentrate containing 62.6% Pb and 3.0% Zn. Reducing cyanide usage also reduces the environmental impact of tailings as well as reducing the amount of copper sulfate required during the subsequent zinc flotation circuit, contributing to savings in reagent use. Excessive cyanide use not only locks free metal ions in the pulp but will also form strong complexes with gold and silver, resulting in these metals reporting to the tailing.

Table 2.2 shows the typical pH, use of depressants and zinc recoveries in pre-flotation and lead flotation circuits for operations located near Century in North-west Queensland. The Century Mine concentrator currently operates its pre-flotation and lead flotation circuits between pH 7.5–8.5 and has discontinued zinc sulfate additions after finding that additions during grinding and lead roughing had little effect on

sphalerite recovery. The characteristics and response to changing flotation conditions of sphalerite are very complex and differ from one ore to another. Other Australian operations have also not successfully used zinc sulfate in the process flowsheet. Operations such as Broken Hill, Elura and Rosebery mines do not use zinc sulfate and continue using cyanide alone.

Table 2.2 Typical pH, Depressants and Zinc Recoveries in Pre-flotation and Lead Flotation Circuits for Operations in North-west Queensland

Mining Operation	pH	NaCN (g/t)	ZnSO ₄ (g/t)	SMBS ^α (g/t)	Zn Recovery (%) ^β
Century Mine	7.5–8.5	300	—	—	5–6
Mount Isa Mines	8.0	160	250–300	—	6
Cannington Mine	6.5–7.0	—	1000	700	8–9

α SMBS represents sodium metabisulfite

β Total Zn recovery for both pre-flotation and lead flotation concentrates, where applicable

2.3.3 The Depressing Effect of Iron and Iron Sulfate on Sphalerite

In 1960, Rey and Formanek found that iron abraded from steel balls and mill liners during grinding has a strong deactivating effect in the presence of a siliceous gangue. The effect of iron on selectivity in the differential flotation of lead-zinc ores has since been the subject of many investigations, particularly by those researchers seeking a better alternative depressant for zinc sulfate (Draskic et al. 1980). Iron sulfate has been used in combination with cyanide in selective lead-zinc flotation processes in Yugoslavia (Pavlica et al. 1991). It has been found in studies to also affect the kinetics of galena flotation (Popov et al. 1989a). More recently, an investigation by Zielinski, et al. (2000) has found that liberated low-iron sphalerite preferentially misreports to lead concentrates compared to sphalerite that has a more iron present as inclusions in the mineral lattice. This is particularly relevant to the processing of Century ore, which contains sphalerite with very low iron content (< 1%) compared to other ores, such as Broken Hill where sphalerite contains as much as 8–10% iron. However, the significant siderite (FeCO_3) content in Century ore may assist in reducing this effect.

The effect of iron from grinding media on selectivity is much reduced in the presence of a limestone gangue as the abrasion of iron is much less and there is a lower intrinsic activity of the iron that is present (Rey and Formanek 1960). Zinc powder has also been shown to have a similar effect to iron powder but its use is not economically feasible due to the amount required being too large for commercial use.

Yelloji Rao and Natarajan (1989) confirmed the galvanic effect of grinding media on the floatability of sphalerite. They found that the extent to which sphalerite

depression occurs due to galvanic interactions with grinding media depends on the duration of contact and the amount of oxygen and flotation reagents present during grinding. They conditioned a high purity natural sphalerite sample with and without oxygen as well as the activator and the collector in a crucible made from hyper steel grinding media before conducting Hallimond tube flotation tests using only nitrogen as the carrier gas. X-ray photoelectron spectroscopy VG Scientific ESCA-3 Spectrometer equipped with Al K alpha X-rays was used to determine the reaction products on the sphalerite surface after the galvanic interaction. Samples were washed with distilled water, acetone-dried and stored in a vacuum desiccator prior to analysis.

The presence of oxygen was found to be detrimental to flotation recovery reducing it to 30% as opposed to 87% in the presence of nitrogen and activator (10^{-3} M CuSO_4) after 4 hours of aeration. There was no advantage found by adding the collector during the galvanic contact. However, the addition of the activator alone during contact or with a higher concentration after contact enhances flotation recovery. They suggested that the redox reactions occurring during contact are represented by the following equations:



where EQ 2.15 represents the anodic dissolution of iron from the ball material and EQ 2.16 represents the cathodic reduction of oxygen on the sphalerite mineral surface. ESCA observations indicated that the zinc (2p) spectra was lower for galvanically interacted sphalerite than that of a fresh sphalerite sample. A strong iron

(2p) peak at 710.5 eV was also observed for galvanically interacted sphalerite, whereas the fresh sphalerite sample did not register any iron (2p) peak. Even after conditioning with activator (10^{-6} to 10^{-5} M CuSO_4), relatively intense iron peaks were still observed. Although the higher activator concentration (10^{-5} M CuSO_4) showed the lowest iron peak intensity and both concentrations had iron peak intensities lower than experiments with galvanic contact in the absence of an activator. These observations clearly indicated that copper activation modifies the galvanically interacted surface.

A few tests were carried out where the sphalerite sample was conditioned with the activator in the presence of oxygen, and iron powder or iron sulfate was added prior to flotation. It was found that the effect of iron sulfate on depressing sphalerite flotation was not as significant as when the mineral was contacted with grinding media or iron powder. The decrease in sphalerite flotation recovery after conditioning with iron sulfate (25 g/L) was 25%, whereas the decrease in recovery after conditioning a similar amount of mineral with grinding media or iron powder (1:1 iron–sphalerite ratio) was 60–70%. The ESCA spectra for the sphalerite surface after each experiment supported these results. The zinc (2p) peak intensity for sphalerite contacted with iron sulfate was not significantly affected compared with that for a natural sphalerite sample. Galvanically interacted sphalerite had significantly lower zinc peak intensity and a stronger iron peak was observed, suggesting further iron contamination of the sphalerite surface.

The presence of iron in the sphalerite lattice has also been shown to affect the extent to which sphalerite misreports to the lead concentrate. An investigation by Zielinski, et al. (2000) analysing samples from three North American lead-zinc mines has

found that liberated low-iron sphalerite preferentially misreports to lead concentrates compared to high-iron sphalerite. Ore feed and lead concentrate samples were collected from Red Dog, Pollaris and Sullivan concentrators for comparative studies. Samples were sized using screens and a Warman cyclosizer and the sized fractions produced were then resin mounted, polished and coated with a thin Pd-Au layer for microscopic analyses by SEM (Leo Stereoscan 440) and EDS (Oxford ISIS with germanium detector). The iron content of sphalerite in each sample was estimated using these techniques. In all sized fractions and at all three concentrators, it was found that liberated sphalerite reporting to lead concentrate had a lower iron content than the sphalerite in the ore feed.

The authors believe that the liberated sphalerite misreporting to the lead concentrate during lead flotation would most probably be due to activation by metal ions and have suggested two mechanisms for the effect of solid solution of iron in the sphalerite lattice on selectivity:

- iron in the sphalerite lattice inhibits the adsorption of activating metal ions, such as lead ions, and hence low-iron sphalerite can adsorb significantly more lead ions per unit of surface area; and
- the presence of iron in the sphalerite lattice could lead to a faster oxidation of the mineral surface, coating possible adsorption sites and hence lowering cation adsorption capability in high-iron sphalerite whilst non-oxidised low-iron sphalerite could still adsorb metal ions.

The use of the depressing effect of iron on the sphalerite surface has been investigated on a laboratory scale with iron sulfate experiments in an attempt to replace commonly used zinc sulfate. Draskic et al. (1980) has confirmed the

depressing action of iron sulfate through experiments using modified Hallimond tubes. The results have shown that sphalerite can be depressed over a pH range of 3 to 10 using a reagent combination of iron sulfate-sodium cyanide in a molar ratio of 2:1 or more. Whilst the results from Hallimond tube tests can be related to floatability, as frothers were not used it is doubtful whether the method truly simulates flotation at the industrial scale.

The effective use of iron sulfate in place of zinc sulfate has however been confirmed at plant scale at a number of operations in Yugoslavia (Pavlica et al. 1991). Operating data from these plants show that the consumption of iron sulfate and sodium cyanide is considerably lower than reagent use with zinc sulfate and sodium cyanide. Avoiding the use of zinc sulfate and reducing the amount of cyanide required also reduces the consumption of the activating agent copper sulfate during zinc flotation after the lead flotation stage. Whilst sodium cyanide is an extremely effective flotation reagent, its discharge in the tailings effluent can cause serious environmental concerns, as cyanide salts are highly toxic. The use of cyanide can also result in considerable losses of silver and gold due to the strong leaching and complexing effect of cyanide with these precious metals. Specific silver minerals in the ore may also be depressed by cyanide. Authors such as Calic et al. (1996) and Popov et al. (1989a) clearly believe that by replacing the depressant combination of zinc sulfate-sodium cyanide with the combination of iron sulfate-sodium cyanide, the amount of cyanide required is decreased.

Five flotation plants in Yugoslavia, namely the Leposavic, Trepca, Lece, Veliki Majdan and Sasa plants, have changed from using zinc sulfate-sodium cyanide to iron sulfate-sodium cyanide to successfully depress the zinc and iron sulfides during

lead flotation. In general the iron sulfate:sodium cyanide ratio used in most of the plants is 2:1. This compares favorably with results from Hallimond tube flotation tests by Draskic et al (1980) and Popov et al (1989a). High iron sulfide contents can increase cyanide in the iron sulfate:sodium cyanide ratio to 1:1 and may require magnetic separation processes (to remove pyrrhotite) to be added to the plant as has been the case at Veliki Majdan. Less than half the amount of cyanide is consumed compared to operations using zinc sulfate–sodium cyanide. It should be noted however, that magnetic separation would also remove grinding media iron, which could explain the requirement to increase iron sulfate usage for sufficient depression to occur at these operations.

Metallurgical performance has also improved for most of these eastern European operations with less zinc reporting to the lead concentrate and an improved recovery of silver. Other reagent uses, in particular copper sulfate, have also been significantly reduced across all of the plants. Reproducing the advantages of iron sulfate–sodium cyanide as a replacement for zinc sulfate–sodium cyanide still remains difficult with some ores. Many plants in Western countries continue to use the classic depressant combination of zinc sulfate–sodium cyanide or cyanide alone despite the advantages experienced in Yugoslavia. However, it is not clear in the literature whether the depressants iron–iron sulfate have been tested in Western lead-zinc mining operations. It is possible that an increased use of iron sulfate may create other problems for stability in flotation plants including a detrimental effect on pulp pH control.

Even if the reagent combination of iron sulfate–sodium cyanide alone is less selective in depressing sphalerite in Century ore, its effectiveness in the depression

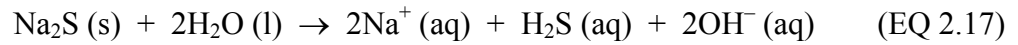
of iron sulfides, such as pyrite, may warrant its use in combination with zinc sulfate. This may further reduce the cyanide added during the process, thus the value in studying it.

2.3.4 Sphalerite Depression by Alternative Inorganic Salts

A number of inorganic salts have been reported as regulators for sphalerite, as well as a number of other minerals found in lead-zinc ore bodies, such as naturally hydrophobic minerals. The work of investigators seeking alternatives to cyanide for sphalerite and pyrite depression has explored the use of depressants containing divalent sulfur in the form of readily soluble sulfide salts, such as sodium sulfide and sodium metabisulfite. Lime is another commonly used regulating reagent in flotation of sulfide minerals, to control pH conditions at which different sulfide minerals float as well as contribute to the depression of pyrite. Other inorganic salts, such as sodium chloride, calcium chloride, and sodium sulfate have been used to promote the flotation of naturally hydrophobic minerals, such as coals, and their presence during the lead-zinc flotation process may have implications in the processing of ores with a high carbonaceous content.

The depressing action of sodium sulfide on galena and sphalerite appears to be particularly strong. Investigators seeking to achieve the cyanideless depression of galena and sphalerite have succeeded in test work where sodium cyanide was replaced by alkaline salts, such as sodium sulfide, which contain sulfide ions that depresses sulfide minerals by its sulfidising action (Calic et al. 1996). Whilst galena and sphalerite are both depressed, selective flotation is then possible by selective activation of each mineral using lead acetate and copper sulfate, respectively.

Sodium sulfide hydrolyses in aqueous solutions according to the following equation (EQ 2.17):



The hydrogen sulfide then dissociates to form hydrosulfide and divalent sulfur ions (EQ 2.18 and 2.19):



In the flotation of sulfide minerals with xanthates, both the hydrosulfide and sulfide ions have a particularly strong effect on the process (Klassen and Mokrousov 1963, p. 311).

The depression of galena and sphalerite by the sulfidising action of sodium sulfide is analogous to the flotation of sulfide minerals without any interaction with oxygen. Sulfide minerals do not interact well with xanthates when oxygen is completely absent from the pulp (Klassen and Mokrousov 1963, p. 317). Oxygen adsorbed on to mineral surfaces results in a decrease in surface hydration. If oxidation of the mineral surface is not too extensive, the surface can then react with collectors, such as xanthates. One possible explanation for the improved mineral-collector interaction in the presence of oxygen is that the surface is coated with oxygen, which weakens the bonds between ions in the surface layer and hence increases the chemical activity of the mineral surface (Klassen and Mokrousov 1963, p. 319). Sodium sulfide acts as a sulfidising agent in this process and transforms the surface into a form that does not strongly interact with xanthate. Galena or sphalerite that has been depressed by

sodium sulfide will regain floatability once sufficient time is allowed for dissolved oxygen in the pulp to react with the sulfide (Klassen and Mokrousov 1963, p. 317).

In more recent studies by Calic et al. (1996), the depression of sphalerite using iron sulfate (6.5×10^{-5} M) and sodium sulfide (1.3×10^{-4} M) with xanthate collection has been shown to be satisfactory between pH 5.5 to 10.5. Galena is also depressed under these conditions and full depression occurs above pH 7.0 for molar ratios of iron sulfate:sodium sulfide of 1:2. Selective flotation of galena was then achieved by lead acetate addition (7.5×10^{-5} M) in the pH range 6.8 to 8.5 with either a potassium ethyl xanthate (PEX) or potassium amyl xanthate (PAX) collector. Lead acetate selectively activates the galena surface making it amenable to flotation whilst the sphalerite remains depressed (Calic et al. 1996). Sphalerite can be activated and floated in the usual process with copper sulfate activation in the pH range 9.0 to 9.5.

The depression of sulfide minerals using sodium sulfide is widely recognised. Sodium sulfide is also known as a reagent that, under certain conditions, activates non-sulfide or oxidised sulfide minerals of non-ferrous metals. The amount of oxidised minerals that constitute the gangue in the pulp that may float during flotation with sodium sulfide use is uncertain. If more gangue reports to the lead concentrate then this will dilute the grade of the concentrate. The ability of sodium sulfide to promote gangue flotation and temporarily depress galena and sphalerite may however be of benefit to plants that incorporate a pre-flotation circuit to remove naturally floating gangue minerals before lead flotation. A decrease in lead and zinc losses to the pre-flotation concentrate, which typically reports to the mine tailings, would improve overall lead and zinc recoveries providing the depression effect on galena sufficiently deteriorates during lead roughing and scavenging.

The selective activation of pre-depressed galena by lead acetate is also uncertain. Popov et al (1989a) observed that lead acetate addition to a galena suspension conditioned with iron sulfate-sodium cyanide in the pH range 5.5 to 7.0 leads to an increase in the flotation recovery of galena, but not as good as when it has not been previously depressed. The successful activation of galena by the addition of lead acetate to the pulp to achieve good recoveries after iron sulfate-sodium sulfide depression may be analogous to the iron sulfate-sodium cyanide system observed by these investigators. It may otherwise be that a better galena recovery is observed. However, in such a case, the selective recovery of galena is also doubtful, as it is well known that lead ions and hydrolysis products can contribute to sphalerite activation and subsequently interact with the collector as mentioned previously (Section 1.1).

Sodium sulfite (Na_2SO_3) and sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), also known as MBS, are finding increasing use as a sulfide mineral depressant which is used alone or in combination with cyanide or zinc sulfate (Mining Chemicals Handbook 1986, p. 89). The Cannington Mine uses MBS (700 g/t) in combination with zinc sulfate (1000 g/t) as depressants during the talc pre-flotation and lead flotation stages of the operation. The difficulty using sodium sulfite and MBS, particularly during lead flotation, is that both galena and sphalerite can be depressed. The depressing effect of sulfite ions derived from sodium sulfite or MBS is similar to that of sodium sulfide whereby the sulfite ion reacts with the oxygen adsorbed onto the mineral surface causing surface hydration. It also reacts with any metal ions that may have adsorbed to the mineral surface causing surface activation. Both effects reduce the possibility of a strong interaction with xanthate.

Grano et al. (1997) have reported that MBS decreased galena recovery due to the decomposition of xanthate by the sulfite ion derived from MBS. They suggested that the galena flotation recovery could be restored by including an aeration stage prior to xanthate addition due to a decrease in the concentration of any unreacted sulfite ions after aeration. This indicates that the sulfite ion has the potential to depress both galena and sphalerite during pre-flotation in the Century process and its depressing effect on galena is likely to deteriorate with sufficient aeration of the pulp occurring prior to lead flotation. In practice the sulfite ion in alkaline conditions is known to be an effective sphalerite depressant, but it has been reported by Pattison (1983) that near neutral pH conditions have enhanced sphalerite flotation. Both pre-flotation and lead flotation are conducted at neutral to mildly alkaline (pH 8.5) conditions at Century and the use of MBS would need to be carefully implemented.

Lime is another regulating reagent typically used in sulfide mineral flotation for the purpose of pH control and pyrite depression. Lime is added to the pulp to regulate pH conditions at which different sulfides most effectively float in an effort to enhance selectivity. Lime is different to other basic salts, such as sodium hydroxide, in that it also has an effect on the pyrite surface that inhibits the interaction between the mineral and xanthate and thus becomes amenable to flotation. Once added to the pulp, lime interacts with the pyrite surface and free ions in the pulp to form a layer which can consist of ferric hydroxide ($\text{Fe}(\text{OH})_3$), goethite ($\text{FeO}(\text{OH})$), calcium sulfate (CaSO_4) and calcium carbonate (CaCO_3) rendering the pyrite surface hydrophilic (Klassen and Mokrousov 1963, p. 336). When sphalerite or other sulfide minerals are associated with pyrite as composite particles in the pulp, then they too may be depressed through this mechanism. It is also possible that calcium may be deposited on other gangue minerals, such as quartz. Whilst the hydrolysis products

of lime can act as a mineral depressant, the formation of Ca(OH)^+ can have an activating effect on quartz.

Inorganic salts, such as sodium chloride, calcium chloride and sodium sulfate have been used to promote the flotation of naturally hydrophobic minerals, such as coals, in the absence of other reagents such as frothers. The salts disrupt the properties of any hydrated layers and on surfaces which would only be weakly hydrated initially and assist in the stability and mobilization in the contact between the mineral particle, air bubble and pulp solution (Klassen and Mokrousov 1963, p. 338). Inorganic salts are typically found in lead-zinc ores as gangue constituents and oxidation products from sulfide minerals. They are sometimes present in significant concentrations in the raw water supplied to the plant. Their presence during the lead-zinc flotation process may have implications in the processing of ores with a high carbonaceous content, particularly if valuable minerals such as sphalerite and galena have close mineralogical associations with the carbonaceous material. If valuable minerals are successfully liberated from carbonaceous minerals during grinding, then salts such as zinc sulfate and iron sulfate may play a larger role, not only in depressing sphalerite during flotation, but also in improving the carbon mineral recovery during pre-flotation by increasing the electrochemical potential of the pulp.

2.3.5 Sphalerite Depression by Organic Reagents

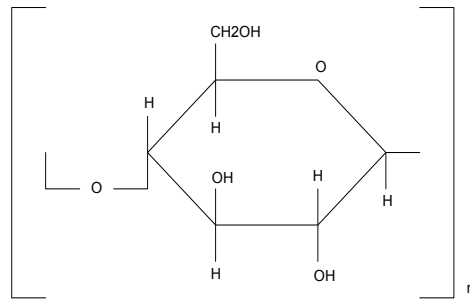
Organic depressants of sphalerite have been used with collectors offering better selectivity than xanthates or aerofloats (alkyldithiophosphates). There are also organic reagents that are used as gangue mineral depressants, which can depress particles of sphalerite in composite with these minerals.

A replacement of cyanide by the organic depressant, dimethyldithiocarbamate, has been confirmed by laboratory and plant tests (Glembotsky et al. 1995). Dimethyldithiocarbamate (DMDC) is a variant of the optimal radical in the dithiocarbamate molecule, which prevents the flotation of sphalerite in flotation processes that use a dithiocarbamate collector. A summary of the data from test work (Glembotsky et al. 1995) shows the advantages of DMDC-technology compared to cyanide-technology and its performance in commercial tests at the Russian Sherova Gora Plant. The conclusions of the paper are that there is an unmistakable depressing effect of dimethyldithiocarbamate against zinc sulfides in the treatment of polymetallic ores.

The use of dialkyldithiocarbamates at plant scale is generally regarded as insignificant due to their prohibitive cost. At the time of the current study, reagent costs for dialkyldithiocarbamates were AUD\$4000 per tonne compared with xanthates at AUD\$1600 per tonne. Significant economic benefits obtained from improvements in selectivity and collector efficiency are required to justify dialkyldithiocarbamate use.

Organic depressants that are commonly used in industry include gangue depressants. Starch, tannin, quebracho, carboxymethyl cellulose (CMC), guar or dextrin are often added in small amounts during lead flotation to depress carbonaceous or phyllosilicate mineral particles remaining in the pulp (Wills 1992, p. 519). These reagents form colloidal particles in the pulp that can deposit on to mineral surfaces preventing flotation similar to the effect of a slime coating. The addition of large quantities of these reagents will also depress all minerals, as they are not as selective as inorganic depressants.

Starch is a mixture of poly glucose, whose short chains are represented by:



During rapid heating or in the presence of acids, starch breaks down into smaller molecules called polysaccharides or dextrans (Klassen and Mokrousov 1963, p. 343). Dextrinated starch is more soluble than the original form of starch and is frequently used in flotation. The selective adsorption of starch and similar reagents, such as dextrans, depends on the character of the mineral, type of starch, pH and electrolytes present (Klassen and Mokrousov 1963, p. 343). The amount of adsorbed starch increases with concentration and the thick films formed on the mineral surface contain hundreds of maltose groups (Klassen and Mokrousov 1963, p. 344–345).

Starch depresses the flotation of non-sulfide minerals during flotation with an anionic collector, such as xanthate, by forming these thick hydrated films on the mineral surface. When sphalerite, pyrite or other minerals are in composite with carbonaceous minerals or silica the use of these depressants can also inhibit sphalerite recovery during lead flotation. In experiments by Dolivo-Dobrovolsky and Rogachevskaja in 1957, sphalerite and chalcopryrite have also been observed to be depressed in the presence of xanthate during lead flotation, with the greatest effect at pH 8.0–8.5 (Klassen and Mokrousov 1963, p. 345). The adsorption of starch can be selective by changing the composition of polar groups. Operations using starch or similar type depressants will carefully choose the form of starch that will give them the most selective results for mineral depression.

2.4 Summary of the Chapter

This review of studies on the selectivity in lead-zinc flotation found that the undesirable reporting of sphalerite to the pre-flotation and lead concentrates may be attributed to several factors including:

- activation of sphalerite by metal ions, which involves the adsorption of metal ions such as lead (II) to the sphalerite surface under acidic pulp conditions providing a surface coverage, which can more strongly interact with a collector such as xanthate;
- activation of sphalerite by metal hydroxides, which involves the adsorption of metal hydroxides such as lead hydroxide to the sphalerite surface under alkaline pulp conditions, which can also more strongly interact with the collector;
- activation of sphalerite by galena fines or lead xanthate, which occurs if these species collide with sphalerite particles sufficiently to complete adsorption and recovery;
- formation of elemental sulfur or polysulfides on the sphalerite surface, which occurs due to the oxidation of surface S^{2-} to S^0 in the presence of acidic media or an interaction of metal ions such as lead (II) increasing the hydrophobicity of the sphalerite particle;
- complex composite particle flotation, where a particle of sphalerite in composite with galena and gangue is able to interact with the collector sufficiently to cause recovery;
- graphitic inclusions or adsorption onto the sphalerite surface, that enhances the hydrophobicity of the sphalerite particle; and

- entrainment of sphalerite particles in the froth leading to physical transportation in the water that is recovered.

The depression of sphalerite during lead-zinc flotation was found to be possible by the use of several reagents including:

- cyanides, such as sodium cyanide, which eliminates metal xanthates, elemental sulfur and polysulfides from the sphalerite surface thereby removing the hydrophobicity of the surface;
- zinc sulfate, which readily dissociates forming zinc hydroxide in alkaline conditions, which can be adsorbed to the sphalerite surface thereby preventing the adsorption of activating metal ions, metal hydroxides or xanthates;
- iron abraded from grinding media and iron sulfate can galvanically interact or dissociate and adsorb onto the sphalerite surface, respectively, and together with any iron contained in the sphalerite lattice, can contaminate the surface and inhibit the adsorption of activating metal ions, metal hydroxides or xanthates;
- other inorganic salts such as sodium sulfide, sodium sulfite and sodium metabisulfite that increase surface hydration by acting as a sulfidising agent and thus, transforming the surface to one that is not extensively coated with oxygen sufficient to react with xanthate;
- pH regulators and gangue depressants such as lime and dextrin which can depress pyrite and carbonaceous mineral particles, which may be in composite with sphalerite; and
- organic depressants, which involves the use of more selective collectors such as alkydithiocarbamates and variants of the dithiocarbamate molecule can create

more selective flotation conditions, but they are known to be significantly more expensive.

CHAPTER 3

MATERIALS AND METHODS

3.1 Century Mine Ore and Plant Samples

The Century Mine ore samples used in this study were collected from the run-of-mine (ROM) pad. The ore samples were prepared into a 102-kg composite, which was split into 1-kg representative test portions suitable for use in flotation tests. Randomly selected test portions were further prepared for chemical and mineralogical analysis. Plant samples used in this study were collected from various sampling points in the Century Mine concentrator and used directly in flotation tests.

3.1.1 Collection and Preparation of Century Mine Ore Samples

A 180-kg ore sample was initially obtained by collecting approximately 10-kg samples from 17 different sites across the Century Mine ROM pad. Appendix 3.1 is photograph of the ROM pad area, where the ROM pad is visible behind the crushing plant and concentrator stockpile reclaim area. The Century Mine deposit is divided into upper and lower zones and the stockpiles on the left side of the image represent the upper zone material, which is blended with the lower zone ore shown right side. Blending is carried out in practice by crushing every 3 truckloads of upper zone ore with 5 truckloads of lower zone ore. The head grade therefore contains on average 37.5% upper zone ore and 62.5% lower zone ore. A Century Mine geologist assisted in the collection of two separate samples that would be typical of the upper and lower zone ore mineral grades.

Each 10-kg sample was passed through a laboratory jaw crusher (Labtech Essa[®], Nugget). A 200-g test portion was split from each ore sample using a riffle (Labtech Essa[®]). The 200-g test portion was then prepared and assayed following the procedures in Section 3.1.2 and Section 3.7. The available sample weights and assay data were used in a mass-balance to determine the ore sample weights required to produce a composite sample representative of the Century Mine concentrator feed.

The 10-kg samples were again taken and then passed through a riffle (Labtech Essa[®]) to produce a sub-sample at the approximate weight determined for the composite. Each sub-sample was then weighed on a two-place balance (AND[®] HF6100) and the weight was adjusted by grab sampling to remove excess sample or add sample from the riffle's reject fraction. The weighed ore samples were collectively transferred to three large plastic buckets. The crushed material was passed through a 1.77 mm screen. Any oversized material was passed through the jaw crusher again and then through the 1.77 mm screen. This procedure was repeated until all oversize material passed through the 1.77 mm screen. The crushed material (<1.77 mm) was collected in three large plastic buckets.

The contents of each bucket (~34 kg) were passed through the rotary sample divider (Labtech Essa[®] RSD020) to split the entire crushed ore sample into 6 fractions. Alternate bins in the rotary sample divider were then combined and transferred back into the three plastic buckets. This procedure was repeated four times to mix the entire 102-kg sample and split it into six 17-kg sub-samples.

Five of the 6 sub-samples (17 kg) were combined, transferred to the rotary sample divider and split into six 14-kg fractions. Each of the six fractions produced were

placed aside in separate aluminium trays. The 14-kg fractions were transferred to the rotary sample divider and split into six 2-kg fractions. The 2-kg fractions were split in half using the riffle, recombined and then split in half again to produce 1-kg test samples.

The remaining 17-kg sample was transferred to the rotary sample divider and split into six fractions. Five of the 6 fractions were combined, transferred to the rotary sample divider and split into six fractions (2.4 kg). One of the fractions was passed through a riffle three times to remove approximately 300 g of sample, which was placed aside. The six fractions were recombined, transferred to the rotary sample divider and split into six 2-kg fractions. The 2-kg fractions were split in half using the riffle, recombined and then split in half again to produce 1-kg test samples. The remaining (~2.8 kg) was combined with the 300 g fraction. The combined 3-kg sample was transferred to the rotary sample divider and split into six fractions. Alternate bins were combined to produce three 1-kg test samples.

A total of 87 test portions were produced, each weighing approximately 1.18 kg. All test portions were transferred to polyethylene bags. Each polyethylene bag was weighed on the two-place balance, which had been tared with an empty polyethylene bag. Each polyethylene bag was labelled with an identification number and the net weight of the test portion recorded. Each bag was purged with industrial grade nitrogen gas (99% purity, BOC gases[®]) and double sealed with a heat sealer (Better Packaging[®]). The sealed test portions were stored in a refrigerated storeroom (3 °C).

3.1.2 Preparation of Test Samples for Chemical Analysis

Ten 1-kg test portions were randomly selected from the batch. Each test portion was passed through a riffle three times to remove a 150-g assay fraction. Each 150-g assay fraction was pulverised for 3 minutes using an LM2 Labtechnics Mill[®] and a 400 cm³ Labtechnics[®] grinding set. The grinding set was cleaned with 100 g of –5 mm blue-metal road base (highly siliceous) material before the first assay fraction was milled. The pulverised assay fractions were transferred to 3” × 5” paper Geochem[®] sample bags (Seismic Supply-Kaltex[®]) and labelled with a sample identification number. The procedure followed was the standard procedure at the Pasminco Century Mine Laboratory (1999).

The ten unpulverised fractions (~1030 g) were transferred to a polyethylene bag and the net weight determined using a two-place balance.

The packaging procedure described previously was repeated for storage with the remainder of the Century Mine test samples.

3.1.3 Preparation of Test Samples for Mineralogical Analysis

A 1-kg test portion was randomly selected and prepared for use in mineralogical studies. The sample was passed through a rotary sample divider (Labtech Essa[®] RSD020) to split the contents into 6 fractions. These fractions were recombined and the procedure repeated to thoroughly mix the sample. The sample was passed through the rotary sample divider a third time and alternate bins were combined to produce three 400-g fractions. The net weight of each fraction was determined using the two-place balance and recorded accurate to ±0.01 g.

Two of the fractions were dry screened to remove the $-850+425\ \mu\text{m}$ material, representing the unbroken characteristics of the ore for scanning electron microscope (QEM–SCAN) analysis and a duplicate sample for chemical analysis. The sample was added to a nest of $1180\ \mu\text{m}$, $850\ \mu\text{m}$ and $425\ \mu\text{m}$ screens fitted to a screen shaker (Rotap[®]). The screen shaker was operated for 20 minutes. The contents of the $425\ \mu\text{m}$ screen were transferred to a polyethylene sample packet. The net weight of the sample was determined using a two-place balance. The sample was sent to CSIRO Mineral Laboratories, Clayton, Victoria, for scanning electron microscope analysis.

The sizing procedure was repeated to produce a duplicate $-850+425\ \mu\text{m}$ fraction for chemical analysis. The duplicate sample was transferred to a $400\ \text{cm}^3$ grinding set (Labtechnics[®]) and pulverised using a LM2 Labtechnics Mill[®] for 3 minutes. The sample was then transferred to a $3'' \times 5''$ paper Geochem[®] sample bags.

The remaining fraction was transferred to a polyethylene sample bag, purged with nitrogen and sealed as described in Section 3.1.1. The sample was kept as a reserve and stored in a refrigerated container with the test samples.

3.1.4 Collection and Preparation of Century Mine Plant Samples

Flotation feed samples were collected from the overflow of the primary grinding cyclones using the sampling apparatus shown in Appendix 3.2. Other plant streams were collected as they passed through the multi-stream analyser (MSA) sampling points shown in Appendix 3.3 using the sampling apparatus shown in Appendix 3.4. Prior to the commencement of sampling at the MSA sampling points, the automatic

sampler was isolated and the access hatch removed. Both sampling locations had steady flowing streams of pulp that were accessible to the sampling apparatus.

The sampling apparatus was steadily moved across the stream to evenly cut the stream. This procedure was first carried out to clean the apparatus and the sample collected was discarded. The procedure was repeated until 2.5 L of pulp was collected and transferred to a 10-L plastic bucket using a Marci-Scale Density Bucket (1 L) with a 500-mL increment marking.

All 10-L plastic buckets containing collected samples were covered with a layer of polyethylene sheeting and sealed with an elastic band. The sample was carried to the metallurgical laboratory near the concentrator for laboratory testwork. The sample was agitated in the bucket for two minutes to ensure that no solids had settled. Immediately after stirring the contents of the bucket, the entire sample was poured in to the 2.5-L flotation test cell for laboratory flotation testwork.

3.1.5 Determination of the Pulp Density of Plant Test Samples

Before the commencement of the testwork, a 2.5-L plant sample was washed with tap water into a 300-mm diameter Amdel pressure filter and filtered through a double layer of Postlip filter paper. The interior walls of the pressure filter were washed with tap water and the sample filtered again to remove most of the excess water. The wet filter paper and filter cake was weighed on the two-place balance, which had been tared with two clean pieces of filter paper to determine the net wet weight of the filter cake. A 20% cake moisture content factor was used to determine the approximate mass of solids and reagent additions required in the testwork.

The filter papers and filter cake were then dried in an oven at 105 °C for at least 12 hours. The filter cake was then removed from the oven and cooled to room temperature. The dry filter papers and filter cake were weighed on the two-place balance tared with two clean pieces of filter paper to determine the net weight of the dry filter cake. This weight was used to more accurately calculate the reagent additions (g/t) that were added to the pulp during the testwork.

The filter cake was removed from the filter papers by shaking. The filter cake was transferred to a rubber mat (50 cm × 50 cm) and the agglomerates crushed with a stainless steel rolling pin. The sample was mat-rolled 20 times and a 100-g grab sample (assay fraction) was cut out using a rectangular shaped scoop. The 100-g assay fraction was passed through a 300 µm test screen using a rubber stopper. The assay fraction was transferred to a paper Geochem[®] sample bag. The remaining sample was sealed in a polyethylene bag and stored as a reserve sample.

3.2 Grinding Calibration Test Procedure

Century Mine Ore test samples were milled for flotation tests using an Amdel LRM2000[®] laboratory ball mill, following Pasminco Century Mine Laboratory Procedures (1999). Grinding conditions required to produce an 80% passing size of 58 microns were established by a series of grinding calibration tests.

A 1.00-kg sample of Century Mine ore, 400 mL of water and 10.0 kg of graded mild steel ball charge were sealed inside the stainless steel Amdel LRM2000[®] laboratory ball mill and the mill operated for 24 minutes. The pulp was quantitatively transferred to a plastic 20-L plastic pail using a ½ inch (12.7 mm) aperture test screen. The contents of the pail were quantitatively transferred to a 10-L Amdel

pressure filter and filtered using a double layer of Postlip filter papers. The filter papers and filter cake were dried in an oven (105 °C) for 12 hours. The filter papers and filter cake were cooled to room temperature and weighed. The filter cake was removed from the filter papers by shaking and transferred to a rubber mat (50 cm × 50 cm). The agglomerates were crushed with a stainless steel rolling pin. The sample was mat-rolled 20 times and a 100-g sample was taken using a rectangular shaped scoop.

The 100-g sample was quantitatively transferred to a 38 µm test screen mounted on top of a bucket and the sample was wet screened to remove the $-38\ \mu\text{m}$ material. The contents of the collection bucket ($-38\ \mu\text{m}$) were quantitatively transferred to a 10-L Amdel pressure filter and filtered using a double layer of Postlip filter papers. The filter papers containing the $-38\ \mu\text{m}$ material were placed below infrared drying lamps (General Electric, 275 W) for 30 minutes to dry. The dried filter papers were weighed on the two-place balance, which had been tared with a two clean filter papers to determine the net weight of the $-38\ \mu\text{m}$ fraction.

The oversize fraction ($+38\ \mu\text{m}$) was quantitatively transferred to a 350 mm × 260 mm × 45 mm aluminium tray by washing with a minimum amount of water. The tray was placed below the infrared drying lamps until the sample was dry. The dry sample was dry screened using a nest ($\sqrt{2}$ series) of 150 µm, 106 µm, 75 µm, 53 µm, and 38 µm test screens (Labtechnics[®], 200 mm diameter) fitted to a screen shaker (Rotap[®]). The screen shaker was operated for 20 minutes. The contents of each test screen were transferred to aluminium trays using a small paintbrush. Each fraction

was weighed on the two-place balance, which had been previously tared with the aluminium tray to determine the net weight for each sizing.

The grinding and sizing procedures were then repeated with another 1.00-kg sample with a grinding time of 29 minutes.

A size distribution curve was plotted for each grinding time to determine the 80% passing size from each sizing. A linear plot of the 80% passing sizes against grinding time was used to determine the time required to achieve an 80% passing size of 58 μm .

The grinding and sizing procedure was repeated with a third 1.00-kg sample using the estimated grinding time to confirm the sizing. A 300-g grab sample was also collected from the confirmation grind product for sizing and the sized fractions were assayed as described in Section 3.7.

3.3 Preparation of Solutions

The solutions used for grinding, flotation test, surface chemistry and chemical analysis procedures were prepared using analytical grade reagents unless otherwise indicated. The deionised water used to prepare solutions for surface chemistry tests had a conductivity of 1.0 $\mu\text{S}/\text{cm}$ (TPS[®] 900-C conductivity meter).

3.3.1 Flotation Test Solutions

Tap water was used in the laboratory flotation tests to dilute the test sample to volume in the flotation cell and quantitatively transfer samples to the pressure filter. The lead, zinc, iron and copper contents of Century laboratory tap water are shown at Appendix 3.5.

Dilute solutions (1% w/w) of sodium cyanide, zinc sulfate 7-hydrate, and iron (II) sulfate 7-hydrate (BDH AnalaR[®]) were prepared by weighing 1.00 g of solid reagent into a beaker and adding 99 mL of tap water using a measuring cylinder. The solution was stirred until all solids had dissolved. This has been the standard procedure at Century's laboratory.

Dilute solutions (1% w/w) of sodium isopropyl xanthate (SIPX–Tieling, China) and dextrin (Coogee Chemicals) were prepared by repeating the procedure using samples of technical grade reagent. The SIPX sample was stored in a refrigerated container (3 °C) when not in use.

All solutions were prepared immediately prior to commencement of a flotation test and residual solutions were discarded afterwards.

3.3.2 Surface Chemistry Test Solutions

A 0.1-M ethylenediaminetetra-acetic acid solution was prepared by transferring 37.0 g of ethylenediaminetetra-acetic acid disodium salt (BDH AnalaR[®]) to a 1-L volumetric flask. Deionised water was added to dissolve the salt and dilute to volume (1 L). Sodium hydroxide pearl was added to adjust the pH to 7.5 (Horiba[®] D22 pH meter).

3.4 General Flotation Test Procedures

The Century Mine laboratory flotation test procedure consisted of grinding the test portion (Section 3.4.1), a pre-flotation circuit (Section 3.4.2) and a lead flotation circuit (Section 3.4.3). The laboratory process flowsheet for the flotation testwork is shown in Appendix 3.6. A primary zinc flotation test procedure (Section 3.4.4) was carried out after lead flotation when required.

The primary grind was carried out to produce the required 80% passing size for the testwork. A pre-flotation circuit was used to float the organic carbon and graphitic material in the test portion. The pre-flotation circuit tailing was used in the lead flotation circuit to produce lead concentrates as well as lead tailings that would normally constitute the feed sample for zinc flotation test work. After all flotation tests, the test products were weighed, prepared for chemical analysis and, in some cases, a size distribution analysis.

3.4.1 Primary Grinding Procedure

The sample was milled in the laboratory ball mill used in the grinding calibrations. A 1.00-kg sample of Century Mine ore, 400 mL water-reagents and 10.0 kg of graded mild steel ball charge were sealed inside the stainless steel grinding mill. A 30-mL aliquot of 1% w/w sodium cyanide solution was part of the 400 mL of water-reagents added to the mill before grinding. The sample was then ground for a grinding time determined from the grinding calibrations data to produce the required 80% passing size. The pulp was quantitatively transferred from the mill and ball charge to a plastic 10-L bucket using a ½ inch (12.7 mm) aperture test screen and washing with

tap water. The contents of the bucket were quantitatively transferred into a 2.5-L flotation test cell and diluted to volume with tap water.

3.4.2 Pre-flotation Circuit Test Procedure

The 2.5-L flotation cell from the primary grinding procedure was fitted to the flotation machine (Labtech Essa[®]) with an impeller as shown in Appendix 3.7. The pulp was conditioned for 3 minutes at 750 rotations per minute (rpm). The pulp pH was adjusted during conditioning by the addition of calcium oxide (BDH AnalaR[®]). The calcium oxide was weighed to determine the amount added to the pulp. A 1.25-mL aliquot of methylisobutylcarbinol (MIBC–Orica, Technical Grade) was added to the pulp.

After conditioning, the airflow was adjusted to 8 L per minute. Once a stable froth had formed, the froth was scraped from the surface of the pulp using even strokes. A pre-flotation rougher concentrate was collected for 3 minutes. The pre-flotation rougher concentrate was quantitatively transferred to a 1.5-L flotation cell and diluted to volume with tap water.

The pre-flotation rougher concentrate was the feed for cleaner flotation. The same flotation procedure as the proceeding step was followed except that the amount of methylisobutylcarbinol was reduced to 0.25-mL and the conditioning time was 1 minute. Two pre-flotation cleaner concentrates were collected: the first after 0.5 minute and the second after a further 1.0 minute of flotation.

The pre-flotation cleaner tail sample was quantitatively transferred to a 10-L Amdel pressure filter and filtered using a double layer of Postlip filter papers. The filtered sample was weighed on the two-place balance tared with a clean double layer of

filter papers and the net weight of the wet filter cake was recorded. The filtered sample was quantitatively transferred to the 2.5-L flotation cell containing the pre-flotation rougher tail by shaking and washing the filter papers with a minimum amount of tap water.

3.4.3 Lead Flotation Circuit Test Procedure

The pre-flotation tailings contained in the 2.5-L flotation cell were the feed for lead rougher-scavenger flotation. The flotation machine was operated as described in Section 3.4.2 except that: 20 mL of 1% w/w dextrin solution (Coogee Chemicals, Technical Grade) was added and the pulp was conditioned for 1 minute; and 27.5 mL of 1% w/w SIPX solution and 0.15 mL of MIBC were added to the pulp, and the pulp was conditioned for a further 1 minute during which calcium oxide was added to adjust the pulp pH to pH 8.5.

The flotation technique was repeated for 3 minutes to collect a combined lead rougher-scavenger concentrate. The lead rougher-scavenger concentrate was quantitatively transferred to a 1.5-L flotation test cell and diluted volume with tap water.

The lead rougher-scavenger concentrate was the feed for the first stage of lead cleaner flotation. The flotation machine was operated as described in Section 3.4.2 except that: 8-mL aliquots of 1% w/w sodium cyanide solution and 1% w/w dextrin solution were added and the pulp was conditioned for 1 minute; and 5 mL of 1% w/v SIPX solution and 0.15 mL of MIBC were added and the pulp was conditioned for a further 1 minute. The flotation technique was repeated for 2 minutes to collect the lead first cleaner concentrate. The lead first cleaner concentrate sample was

quantitatively transferred into the 1.5-L flotation test cell and diluted to volume with tap water.

The lead first cleaner concentrate was the feed for the second stage of lead recleaner flotation. The flotation machine was operated as described in Section 3.4.2 except that: 5.0 mL of 1% w/w SIPX solution and 0.10 mL of MIBC was added and the pulp was conditioned for 1 minute. The flotation technique was repeated for 2 minutes to collect three second recleaner concentrates; each collected after separate time intervals of 0.33 minute, 0.67 minute and 1 minute.

3.4.4 Primary Zinc Flotation Test Procedure

When primary zinc flotation tests were required, the lead flotation circuit rougher-scavenger tailing was retained in the 2.5-L flotation cell. The lead flotation first cleaner tailing sample was filtered. The filtered sample was weighed on the two-place balance to determine the net weight of the wet filter cake. The filtered sample was quantitatively transferred to the 2.5-L flotation cell containing the pre-flotation lead flotation rougher-scavenger tail by shaking and washing the filter papers with a minimum amount of tap water. The 2.5-L flotation cell was diluted to volume with tap water and fitted to the flotation machine with the impeller.

The combined lead rougher-scavenger and lead first cleaner tailings were used as the feed for zinc rougher flotation. The flotation machine was operated as described in Section 3.4.2 except that: 6 mL of 1% w/w copper sulfate solution was added and conditioned for 3 minutes, and 20 ml of 1% w/w SIPX and 0.15 mL of MIBC was added and conditioned for 2 minutes during which calcium oxide was added to adjust the pulp pH to pH 9.0. The flotation technique was repeated to collect two zinc

rougher concentrates; the first after 0.5 minute and the second after a further 1.0 minute.

The zinc rougher tail sample was the feed for zinc scavenger flotation. The sample was retained in the 2.5-L flotation cell and diluted to volume with tap water. The flotation machine was operated as described in Section 3.4.2 except that 4 mL of 1% w/w copper sulfate solution was added and conditioned for 1 minute, and 20 ml of 1% w/v SIPX and 0.10 mL of MIBC were added and conditioned for a further 1 minute during which calcium oxide was added to adjust the pulp pH to pH 9.0. The flotation technique was repeated to collect two zinc scavenger concentrates: the first after 1.5 minutes and the second after a further 2.5 minutes.

3.4.5 Preparation of Test Products for Analysis

The flotation test products such as concentrates and tailings samples were quantitatively transferred to separate filters and filtered.

All filter papers and filter cakes were oven dried (105 °C) for 12 hours. The filter cakes were then removed from the oven and allowed to cool to room temperature. The filter papers and filter cakes were weighed on the two-place balance, which had been tared with a clean double layer of filter papers, and the net weight was recorded.

Each filter cake was removed from the filter papers by shaking. The filter cakes were transferred to a rubber mat and crushed with a rolling pin. The broken up filter cakes were then passed through a 200 µm screen (Labtech Essa[®]) using a rubber stopper. These were then mat rolled 20 times on a rubber mat to mix the sample. Samples less than 20 g were transferred to a plastic sample vial. Samples greater than 20 g were

grab sampled using a stainless steel rectangular shaped scoop to remove a fraction for chemical analysis and retain the remaining fraction as a reserve sample. Both fractions were transferred to paper Geochem[®] sample bags (Seismic Supply-Kaltex[®]) and labelled.

3.5 Size Distribution Analysis

Size distribution analyses of flotation test samples were performed using test screens and a cyclosizer (Warman[®]), which had been extended to include a pre-cyclone stage. The fractions produced from the sizings performed using screens, cyclosizer and pre-cyclone were also prepared for chemical analysis.

3.5.1 Test Screening Procedures

All test samples required to be screened were first filtered, dried and passed through a 200 µm test screen following the procedures for the preparation of test samples (Section 3.4.5). A 100-g fraction was cut out from the sample using a rectangular scoop and weighed on the two-place balance.

The sample was wet screened through a 38 µm screen mounted on top of a plastic bucket. The undersize product was filtered through a double layer of filter papers. The filter papers and filter cake were dried using the infrared drying lamps (General Electric[®], 275 W) for approximately 30 minutes. The filter papers and filter cake were cooled to room temperature and weighed on the two-place balance tared with two pieces of filter paper to determine the net weight for the sizing.

The oversize fraction was quantitatively transferred to a 350 mm × 260 mm × 45 mm aluminium tray using a small paintbrush. The tray was placed below the infrared

drying lamps for approximately 30 minutes. The dried sample was dry screened using a nest ($\sqrt{2}$ series) of 150 μm , 106 μm , 75 μm , 53 μm , and 38 μm test screens (Labtechnics[®]) fitted to a screen shaker (Rotap[®]). The screen shaker was operated for 20 minutes. The contents of each test screen were transferred using a small paintbrush to 120-mm filter papers used as weighing boats. Each fraction was weighed on the two-place balance tared with a single filter paper to determine the net weight for each sizing. Each fraction was then transferred to a plastic sample vial.

3.5.2 Cyclosizer Procedure

The $-38 \mu\text{m}$ fraction from the wet screening procedure was used as the test portion in the cyclosizer procedure. The sample was weighed on a two-place balance, transferred to a 250-mL beaker and mixed with approximately 150 mL of tap water on an overhead stirrer for 10 minutes.

The cyclosizer procedure had two stages: a pre-cyclone stage to remove a C7 fraction, followed by a cyclosizer stage, which included a centrifuge on the cyclosizer discharge to collect C1 to C6 fractions. Appendix 3.8 is a photograph of the pre-cyclone apparatus, Warman[®] cyclosizer and centrifuge. The pre-cyclone apparatus is shown in front of the cyclosizer and consists a cyclone, pump and holding tank, which are used to separate the C7 fraction from the sample prior to cyclosizing. The cyclosizer consists five inverted cyclones that are used to separate and collect the C1 to C5 fractions. Any material passing the last cyclone (minus C5 fraction) is collected and concentrated in the centrifuge shown on the floor to the right of the cyclosizer.

The pre-cyclone apparatus consisted a holding tank, small cyclone, cyclone underflow cutter and a Sunflo[®] high-pressure centrifugal pump connected to mains pressure water line via a water pressure regulator valve. The tap water flow was adjusted to approximately 200 kPa and the holding tank was half filled with water. The pump was turned on and the system was operated for 15 minutes. The sample was added to the holding tank whilst the cyclone overflow was directed in to the holding tank to recombine with the underflow stream. After 1 minute, the overflow stream was directed into the overflow collection line and the overflow was collected in a 20-L plastic bucket positioned below the apparatus. Clean tap water was added to the holding tank during the procedure to maintain the water level. The underflow stream was directed through the underflow cutter and collected in a 1-L plastic beaker positioned below the holding tank. Both the overflow and underflow streams were collected until a clear stream of water was visible.

The overflow product was filtered through a double layer of filter papers. The filter papers and filter cake (C7 fraction) were dried using the infrared drying lamps for approximately 30 minutes. The filter papers and filter cake were cooled to room temperature and weighed on the two-place balance tared with two pieces of filter paper to determine the net weight for the sizing.

The underflow product was left to settle in the collection beaker. The excess water was decanted and the settled material retained as the sample for the cyclosizer stage.

The cyclosizer (Warman[®]) pump was run with the instrument control valve fully open for at least 20 minutes before closing off the valve and removing the sample container. The sample was then quantitatively transferred to the cyclosizer sample container by washing with water. The sample container was then replaced on the

cyclosizer and the control valve fully opened to expel any air from the pipe work. The air was bled from each cyclone, starting from the first cyclone, by opening the apex valves one at a time. The centrifuge was turned on and the discharge from the last cyclone was directed into the cyclone. The centrifuge discharge was directed to the drain.

The sample container valve was opened slowly and regulated to discharge the sample into the stream over a 5-minute period. The control valve was then closed until the flow meter indicated the required elutriating flow. The timer-alarm was set for an elutriating time of 30 minutes. After the elutriating time had elapsed, the control valve was fully opened. Starting with the fifth cyclone, each apex valve was opened to collect each fraction in 600 mL plastic beakers. The water temperature was recorded.

The cyclosizer discharge line was removed from the centrifuge and the centrifuge was stopped. The centrifuge liner was removed and the C6 fraction collected was washed from the liner into the pressure filter and filtered through a double layer of filter papers.

Each pulp collected from the cyclosizer was allowed to stand for 20 minutes to allow the solids to settle. The excess water was decanted from each beaker and the remaining contents quantitatively transferred to 250-mL short form glass beakers (previously weighed) by washing with a minimum amount of water. The beakers and filter papers were placed in a drying oven (105 °C) for 12 hours. The beakers were then cooled to room temperature and weighed on the two-place balance to determine the net weight of the size fraction. All fractions were transferred to plastic vials using a small paintbrush. The filter papers and filter cake from the cyclosizer discharge (C6

fraction) were cooled to room temperature and weighed on the two-place balance tared with two pieces of filter paper to determine the net weight for the sizing. The filter cake samples from the pre-cyclone overflow and centrifuge were prepared as described in Section 3.4.5.

3.6 Surface Chemistry Studies

The surface chemistry studies undertaken involved the extraction of metal ions from flotation test samples by complexation with ethylenediaminetetra-acetic acid (EDTA) ions.

The EDTA extraction method had two parts; the extraction of free cations in the pulp with water and the extraction of cations adsorbed to the mineral surface with EDTA. The solid residue obtained from filtering the pulp in each procedure was dried and prepared for chemical analysis.

A test portion of 50 mL of pulp was used in the water extraction of the flotation test sample. A 50-mL syringe (previously weighed) was used to extract 50 mL of pulp from the flotation test cell as it was being conditioned. The syringe exterior was wiped clean with a paper towel and the syringe weighed to determine the weight of the test portion. The test portion was filtered through a Whatman[®] Number 2 filter paper. The filtrate was collected and filtered twice through Millipore[®] 0.45 micron filter paper. The filtrate was transferred to a sample bottle and two drops of nitric acid, 68% w/v (BDH AnalaR[®]), were added.

A test portion of 25 mL of pulp was used in the EDTA extraction of the flotation test sample. A 25-mL syringe (previously weighed) was used to extract 25 mL of pulp

from the flotation test cell as it was being conditioned. The syringe exterior was wiped clean with a paper towel and the syringe weighed to determine the weight of the test portion. A 250-mL aliquot of 0.1 M EDTA solution was added to a 400-mL glass beaker and stirred using a magnetic flea on a mechanical stirrer set at $\frac{3}{4}$ of the highest speed. The test portion was added to the EDTA solution. The stirring speed was adjusted to ensure that all solids were in suspension. The solution was stirred for 5 minutes, after which the solution was filtered through a Whatman[®] Number 2 filter paper. The filtrate was collected and filtered twice through Millipore[®] 0.45 micron filter paper, then transferred to a sample bottle.

The filtrates collected were analysed for zinc, lead and iron ion concentrations as described in Section 3.7. The solid residues collected on the filter paper in both methods were dried in a laboratory oven (105 °C) for 12 hours. The paper and dried residue was then removed from the oven allowed to cool to room temperature and weighed on a balance tarred with a clean piece of filter paper. The solid residue was prepared as described in Section 3.4.5 and analysed for zinc, lead and iron concentrations as described in Section 3.7.

3.7 Procedures for the Chemical Analysis of Samples

Samples were analysed by X-Ray Fluorescence (XRF) Spectrometry, Atomic Absorption Spectrometry (AAS) and complete combustion/infrared spectrometry (LECO SC-444DR[®] carbon–sulfur analyser). All analyses were carried out following standard Pasmenco Century Mine Laboratory analytical procedures (2000).

Two types of samples were presented for analysis: dry samples (particle size <200 µm) prepared from test products (Section 3.4.5), and aqueous solutions from surface chemistry test filtrates (Section 3.6).

XRF Spectrometry was used to routinely analyse dry samples for zinc, lead, iron, silica (SiO₂) and sulfur and the procedure is detailed in Appendix 3.9. AAS was used to analyse dry samples for silver content and aqueous solutions for zinc, lead and iron ion concentrations. The procedure for AAS including sample digestion and dilution is detailed in Appendix 3.10. The Leco SC-444DR[®] carbon–sulfur analyser was used to analyse samples for total organic and elemental carbon (TOEC) and total carbon (i.e. TOEC + carbonate carbon) contents and the detailed procedure is detailed in Appendix 3.11.

The total uncertainty (95% confidence interval), U₉₅, of Century Laboratory assays for head grade ore, low-grade ore/tailings, and lead concentrate are shown in Appendix 3.12.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Results of Preparation and Characterisation of Century Mine Ore Samples

The following results are for the sample preparation and characterisation of the Century Mine ore tests samples as described in Chapter 3. A total of 87 approximately 1-kg representative test portions were generated from the 102-kg composite sample taken from the run-of-mine (ROM) pad. Out of these representative test portions, several portions were randomly selected for chemical analyses, grinding calibration tests and assays of sized fractions.

4.1.1 Results of the Chemical Analyses of the Test Samples

The results of the generation of target grade, calculated grade and chemical analyses are summarised in Table 4.1.

Table 4.1 Calculated Head Grade of the Weighted Composite Sample

	Zn (%)	Pb (%)	Fe (%)	SiO ₂ (%)	Ag (g/t)	C (%)
Target Grade	12.3	2.3	6.5	48.0	55	4.2
Calculated Grade	12.4	2.2	5.9	51.9	73	3.3
Actual Grade	12.3	2.4	5.8	51.5	72	3.4
% Difference	< 0.1	-4.3	-10	7.3	31	-20

The target grades for the tests samples, which represent the weighted-average head grades for the plant during 2001–2002 financial year, were generated from Century Mine metallurgical accounting software (J.K. Met Account[®]). The calculated grades, which represent the desired grade of the composite sample that needs to be prepared so as to achieve test portions that have a composition comparable to that of the target grades, were generated by manipulating the masses of individual samples taken from the ROM given their assay grades shown in Appendix 4.1. The actual grades, which represent the actual composition of the tests samples, were generated from the assay results shown in Appendix 4.2. The reproducibility of the results of the head grade assay as shown by the negligible standard deviations (Appendix 4.2) clearly show that the test samples used in the present study has been split into representative test portions.

The good agreement between the values of the calculated grades and that of the target grades in terms of lead, zinc and iron indicate that the planned composite would represent the actual plant feed. As well, the good agreement between the target grade and calculated grade for these elements on the one hand and the actual grade on the other hand indicate that the sampling process followed was adequate. The weighted averages for silver and carbon were significantly different from the target grades but these were considered acceptable because plant data for these species can vary from ± 30 g/t and $\pm 1\%$ respectively and these values are well within these ranges. These results further indicate that the assumptions made in grab sampling to represent the upper zone and lower zone ores adopted in this work was appropriate. That is, the sample obtained contains 38% upper zone material and 62% lower zone material, which is consistent with the 3 trucks of upper zone ore and 5

trucks of lower zone ore blending of feed in Century's process. Clearly, these results indicate that the composite used in the present study has been prepared to closely represent the chemical and mineral content of the typical concentrator head grade at Century Mine.

It has been estimated that the lead head grade should remain consistent during the first half of the expected 20-year mine life. As the mine depth progresses the lead content in the plant head grade will start to decrease to approximately 1–1.5% as high lead grade ore from the upper part of the ore body becomes less available for blending with low lead grade ore from lower parts of the ore body. The low abundance of galena in the Century deposit and subsequent low lead head grade may reduce the presence of galena oxidation products such as lead ions and hydroxides in the pulp. Subsequently, the possibility of lead activation of sphalerite during the differential flotation process as discussed in Section 2.1 may also be reduced.

Other major deposits located near Century include McArthur River, Mount Isa and Hilton. These deposits are similar to the Century deposit in that they consist of sphalerite, pyrite and galena contained within shale layers with a high carbonaceous material content. They are different to the Century deposit as they also contain chalcopyrite, pyrrhotite, arsenopyrite and marcasite (Waltho and Andrews 1993). Pyrite is the most common sulfide mineral at other local deposits whereas Century has a much higher abundance of sphalerite. The high sphalerite abundance was confirmed by the significant zinc grade at 12.3%, which has been estimated to continue throughout the mine life. Iron at Century is predominately present as pyrite (FeS_2) and siderite (FeCO_3), with little or no other iron sulfides. The occurrence of pyrite at Century is between 3% and 5%, which is considerably less than other local

lead-zinc deposits (Waltho and Andrews, 1993). The non-sulfide mineralisation is also similar to other deposits, where quartz (SiO₂), organic and graphitic carbon (TOEC), sericite (FeSiO₃) and siderite (FeCO₃) are the main components. The results in Table 4.1 confirm that silicate minerals are the principal component of the gangue with a significant Si content reported as SiO₂ (54.7%). The results in Appendix 4.2 support the presence of carbonate minerals, such as siderite, with an inorganic carbon content represented by the 0.5% difference between total carbon and the total organic and elemental carbon (TOEC).

The test sample was analysed for trace element concentrations by ICP–OES analyses carried out at the Pasminco Cockle Creek Smelter Laboratory and the results are shown in Table 4.2.

Table 4.2 Trace Element Concentrations

Analyte	%	Analyte	%
Al	3.05	Mg	0.26
Ba	0.01	Mn	0.22
Cd	0.03	Hg	23 g/t
Ca	0.33	P	0.12
Cr	0.006	K	1.4
F	0.030	Ni	0.003
Ge	0.003	Na	0.05

Other elements that were assayed but were found to be below detection limits include: Sb below 0.05%; As, Bi, Cl, Cu, In, SO₄/S, Tl and Sn below 0.01%; Co and Se below 0.005%.

The Century Mine ore is regarded as a “clean” ore meaning it has low levels of impurity metals and this was confirmed by the present results (Table 4.2), where all

impurity metals except aluminium, manganese and magnesium have concentrations less than 100 g/t. The aluminium and potassium grades are the highest of the trace elements listed in Table 4.2, suggesting the possibility of orthoclase feldspars (KAlSi_3O_8) as another major siliceous gangue constituent. The low copper concentration confirms that only trace amounts of chalcopyrite or other copper minerals are present at Century. The low abundance of minerals containing divalent metal ions such as copper, bismuth and mercury at Century reduces the possibility of sphalerite activation by these metal ions during the differential flotation process as discussed in Section 2.1.1. Combined with the relatively low abundance of lead at Century, this suggests that sphalerite recovery during pre-flotation and lead flotation is more likely to be attributed to mechanisms other than surface activation.

4.1.2 Results of the Grinding Calibration

Grinding calibration tests were undertaken following the procedures detailed in Section 3.3 and the grind time required to produce an 80% passing size (p80) of 58 μm ($\pm 2 \mu\text{m}$) was determined to be 24 minutes.

The sizing results for the 24 and 29-minute grinding times are detailed in Appendix 4.3 and size distribution curves are shown in Appendix 4.4. The grinding time required to obtain different p80 sizes can be extrapolated from a linear plot of p80 size versus grinding time for 24 and 29-minute grinds (Appendix 4.5). The relationship between p80 (μm) and grinding time, t (minutes), is given by:

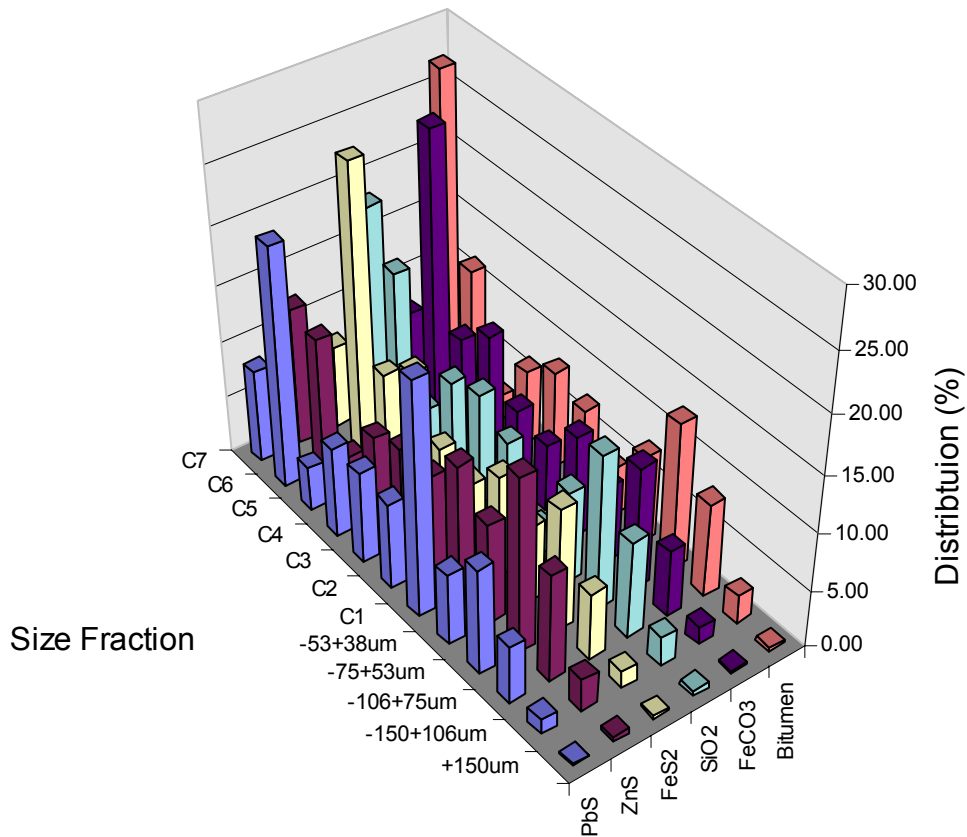
$$\text{p80} = -3.46 t + 142 \quad (\text{EQ 4.1})$$

which is useful for determining grinding times for flotation tests that examine the effect of primary grinding on flotation performance (Section 4.4.2).

4.1.3 Results of Chemical Analyses of Grind Product Sized Fractions

The mineral distribution across various particle size ranges in the primary grind product was determined by assaying the sized fractions produced from the 24-minute grind product (section 4.1.2). The distribution of the main minerals contained in the flotation feed is plotted against particle size in Figure 4.1 and the supporting data are given in Appendix 4.6.

Figure 4.1 Flotation Feed Mineral Distribution versus Particle Size*



* Where C1–C7 represent the sized fractions collected from the cyclosizing procedure.

A significant amount of each mineral (20–40%) is distributed in the C6 and C7 size fractions (approximately 1–5 μm). The fine particles in these fractions are most likely liberated and recovered in the concentrate due to entrainment in the froth,

surface activation and subsequent interaction with the collector or natural hydrophobicity. The remaining mineral distribution is roughly even through the size fractions up to 53 μm . Coarser particles greater than 53 μm represent approximately 20% of all material as the 80% passing size of the primary grind product is 58 μm and mineral distribution decreases significantly with increasing particle size. An increased distribution (10–20%) is shown in Figure 4.1 for each mineral in the –53+38 μm and C1 size fractions indicating the presence of significant amounts of composite particles. Some minerals, such as galena are known to exist in the ore as coarse grains, so that not all intermediate to coarsely sized mineral particles will be composites of multiple minerals.

4.2 Textural Analyses of the Test Samples using Scanning Electron Microscope (QEM–SCAN Analyses)

A sized fraction (–850+425 μm) was prepared following the procedure in Section 3.1.3 to represent the unbroken ore characteristics of the test samples to be used in the present study. The sample was sent to CSIRO Minerals Laboratory in Kenmore, Queensland for scanning electron microscope QEM–SCAN, also known as QEM–SEM, analyses using a standard base metal Species Identification Program (SIP) to identify minerals from low count X-ray spectra. Statistically reliable modal, grain size and mineral association data were obtained by measuring samples on the Bulk Mineral Analysis (BMA) line scan mode (widely spaced linear scans) and by processing images using a mineral suite tailored to mineralogy of the Century ore.

4.2.1 The Abundance of Main Sulfide and Gangue Minerals

The mineral distributions of the sulfide and gangue minerals in the -850+425 μm “unbroken” ore fraction are shown in Table 4.3. The results in Table 4.3 show that the sphalerite/galena ratio is approximately 6:1, which agrees with the zinc/lead ratio shown by the elemental assays and confirms that lead and zinc are present solely as galena and sphalerite and not oxide minerals. Both the galena and sphalerite at Century is exceptionally pure and this has been confirmed by electron microprobe analyses by Waltho and Andrews (1993). The same study showed that a number of Century sphalerite samples contained up to 67% Zn with less than 2% Fe and 0.2% Mn. Other lead-zinc deposits can have sphalerite (or marmatite, $(\text{Zn,Fe})\text{S}$) compositions averaging 55% Zn and approximately 10% Fe and Mn. Whilst these valuable minerals contain very low impurities in solid solution such as iron, they can have close associations with other minerals, which can continue to exist after grinding and consequently affect the flotation process. Various iron sulfides are present at other deposits. However, the results confirm that Century material only contains pyrite with below detection limit values recorded for pyrrhotite, chalcopyrite and arsenopyrite.

Table 4.3 Mineral Distributions of the Main Phases in the -850+425 μm ore fraction

Mineral	Distribution (Weight %)
Sphalerite	18.7
Galena	3.0
Pyrite	8.4
Pyrrhotite	Not detected
Chalcopyrite	Not detected
Arsenopyrite	Not detected
Other Sulfides	2.2
Quartz	5.2
Feldspars	42.4
Other NSG*	20.2

*Non-Sulfide Gangue.

These results show that the siliceous gangue was predominantly feldspars and not quartz (SiO_2). The orthoclase feldspar (KAlSi_3O_8) is probably the dominant feldspar mineral present because the concentrations of Al (3.05%) and K (1.4%) shown in Table 4.2 are relatively high. Lower grades for Ca (0.33%) and Na (0.05%) suggest that other common feldspars such as plagioclase ($\text{CaAlSi}_3\text{O}_8$) and microcline ($\text{NaAlSi}_3\text{O}_8$) may also be present at low concentrations. The analysis of feldspars (42.4%) by QEM-SCAN is markedly high (42.4%) considering the low total content of K, Na and Ca in the ore (1.8%) as determined by ICP analyses. The presence of quartz may be higher than the 5.2% indicated in Table 4.3. The unbroken ore fraction analysed by QEM-SCAN may not be fully representative of the ore presented for chemical analyses.

Other NSG represents the non-sulfide gangue minerals other than siliceous minerals and includes the carbonaceous matter and siderite (FeCO_3). According to Waltho and

Andrews (1993), carbonaceous matter occurs as irregular, elongate bands and as inclusions in porous sphalerite aggregates. Siderite occurs as polycrystalline aggregates ranging in size from a few microns to 100 μm in diameter.

4.2.2 Average Grain Size of Main Sulfide and Gangue Minerals

The average grain size of the main sulfide and gangue minerals is shown in Table 4.4. The data compare the grain sizes between the main phases in the unbroken ore.

Table 4.4 Average Grain Sizes of the Main Phases in the $-850+425 \mu\text{m}$ ore fraction

Mineral	Average Grain Size (μm)
Sphalerite	42
Galena	87
Pyrite	36
Pyrrhotite	10
Chalcopyrite	Not detected
Arsenopyrite	Not detected
Other Sulfides	13
Quartz	16
Feldspars	61
Other NSG	32

The results in Table 4.4 clearly show that galena (87 μm) and feldspars (61 μm) are coarsely grained minerals, whilst sphalerite, pyrite and quartz are finer (16–42 μm). A QEM–SCAN analysis of drill core material from the upper and lower ore zones at Century Mine by Butcher and Gottlieb (1999b) showed that Century ore is very finely mineralogically banded. Clear crosscutting veinlets filled with sphalerite, galena or combinations of both exist in Century Mine ore. If close mineralogical associations between sphalerite and galena or gangue are not liberated sufficiently

during grinding, then it is increasingly possible that the composite particles that result will be recovered in the concentrate by adsorption of the collector.

Quartz in particular is very fine grained (16 μm) and, according to Waltho and Andrews (1993), is found as an interstitial material within other phases such as sphalerite. This affects the zinc flotation process at Century, where ultra-fine regrinding is required to reduce intermediate sphalerite–silica particles prior to zinc cleaner flotation. However, there is no known significant effect on the pre-flotation or lead flotation processes. The other NSG, which includes carbonaceous material, is also relatively fine grained (32 μm). Any close association with sphalerite may explain the significant sphalerite recovery during pre-flotation, which is typically 4–5%.

4.2.3 Mineral Associations for the Main Sulfide and Gangue Minerals

Mineral associations were determined for sphalerite, galena, pyrite, quartz and feldspars. The percentage mineral associations for sphalerite in the unbroken ore sample are shown in Table 4.5.

Sphalerite has a large association (47%) with the background, which represents the resin used to mount the sample for analyses. Sphalerite on the outer edges of particles in the resin mount indicates that, after grinding, a significant amount of sphalerite will be liberated or will contain limited amounts of impurities. Sphalerite also has significant associations with feldspars, other NSG (such as carbonaceous minerals), quartz and pyrite, but little association with galena and other unspecified sulfides. These significant associations for sphalerite, which support the findings by

Waltho and Andrews (1993), suggest that sphalerite is present as aggregates and particles with carbonaceous inclusions.

Table 4.5 Percentage Mineral Associations for Sphalerite

Mineral	Association (%)
Background	47.1
Galena	0.5
Pyrite	8.0
Pyrrhotite	0.1
Chalcopyrite	Not detected
Arsenopyrite	Not detected
Other Sulfides	1.4
Quartz	12.1
Feldspars	17.6
Other NSG	13.2

The significant association with other non-sulfide gangue (NSG) such as carbonaceous minerals may affect the flotation process where sphalerite particles with exposed carbonaceous inclusions are naturally amenable to flotation and are likely to be recovered. The pre-flotation stage aims to recover most of the carbonaceous matter by natural flotation where only a frother is added to the pulp. This is done before lead flotation occurs to prevent contamination and dilution of the lead concentrate. Fine carbonaceous inclusions or composite particles associated with sphalerite may not be sufficiently liberated by reducing the primary grind size or by regrinding the pre-flotation rougher concentrate.

The significant association of sphalerite with feldspars, quartz and pyrite suggests that after the recovery effect of carbonaceous inclusions, significant sphalerite recovery is likely to be due to gangue recovery, possibly by entrainment of

unliberated sphalerite–gangue composites in the froth zone or ternary particles consisting of sphalerite–siliceous gangue–galena.

The low association of sphalerite with galena is most likely related to the low lead head grade in Century Mine ore. However, a reduction in the possibility of recovery due to galena–sphalerite composites may not necessarily follow as even a small amount of galena can strongly interact with the collector during lead flotation and result in flotation of the particle. It is likely that most of the sphalerite recovered during lead roughing would be present as composite particles.

The percentage mineral associations for galena in the unbroken ore sample are shown in Table 4.6. Galena has a lower association with the background, which is typical of all the mineral phases except sphalerite. The most significantly associated minerals with galena are feldspars, quartz and other NSG. Waltho and Andrews (1993) found that significant proportion of the galena at Century exists as lamellae up to 5 mm thick associated with sphalerite and fine euhedral grains within the sphalerite lamellae. This significant association with sphalerite is consistent with the present results (12.1%). However, the low lead content of Century Mine ore (2%) compared with other ores suggests that the unliberated galena-sphalerite composite particles may not be as significantly responsible for sphalerite recovery. The sphalerite recovery during lead flotation at Century is typically 1–2%.

Table 4.6 Percentage Mineral Associations for Galena

Mineral	Association (%)
Background	24.2
Sphalerite	12.1
Pyrite	3.0
Pyrrhotite	0.0
Chalcopyrite	0.0
Arsenopyrite	0.0
Other Sulfides	4.5
Quartz	16.7
Feldspars	22.7
Other NSG	16.7

The significant percentage of galena associated with gangue minerals may account for the dilution of the lead concentrate. Galena is coarsely grained with an average grain size of 87 μm (Table 4.5) and with controlled primary grinding conditions and the use of dextrin as a gangue depressant, a lead concentrate product of saleable quality is produced at Century.

The percentage mineral associations for pyrite, quartz and feldspars in the unbroken ore sample are shown in Appendix 4.7. Significant mineral associations have been observed between each mineral and the other main mineral phases, except galena. The relatively small associations of each of these minerals with galena may be due to the relatively low concentration of lead in the test sample and the presence of coarse grains of some of the galena in the test sample. The close association of these minerals with other NSG, which includes organic carbon, may explain any significant pyrite and siliceous gangue recoveries observed during pre-flotation.

4.3 Baseline Flotation Tests

Three baseline flotation tests were carried out following the standard Century Mine laboratory flotation process flowsheet, which is shown in Section 3.4. The concentrate products were then sized by wet and dry screening and extended cyclizing following the procedures in Section 3.5. The size fractions obtained were assayed (Section 3.7) and the calculated mineral recovery versus size data were plotted to determine the recovery mechanisms occurring in the process.

4.3.1 Baseline Flotation Test Results and Reproducibility

The cumulative grade and cumulative recoveries of the baseline flotation tests were calculated from the product weights and assay results. The data and a sample calculation are shown in Appendices 4.8 and 4.24. The lead grade–recovery and zinc selectivity curves are plotted in Figures 4.2 and 4.3.

The lead grades and recoveries shown in Figure 4.2 are reproducible within 3.7% absolute and 3.2% absolute, respectively. The lead second cleaner concentrate 1 sample had the highest lead grade and recovery but also the highest uncertainty. This stream has a relatively small mass (approximately 3% of the flotation feed) whilst the lead grade is high resulting in a greater uncertainty during concentrate mass collection in the flotation test as well as assay error during product analysis. The reproducibility of the lead second cleaner product weights were within 0.33% absolute and it is clear that flotation grade and lead assays for the final lead concentrate by XRF spectrometry are the greatest components of the observed uncertainty.

Figure 4.2 Baseline Flotation Tests Lead Grade–Recovery Curves

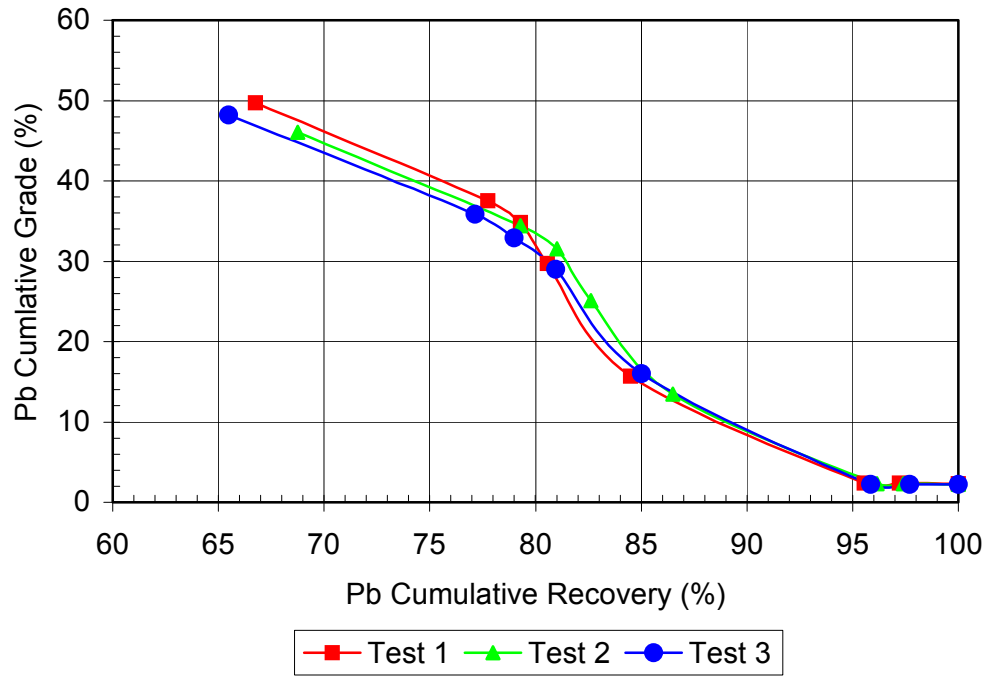
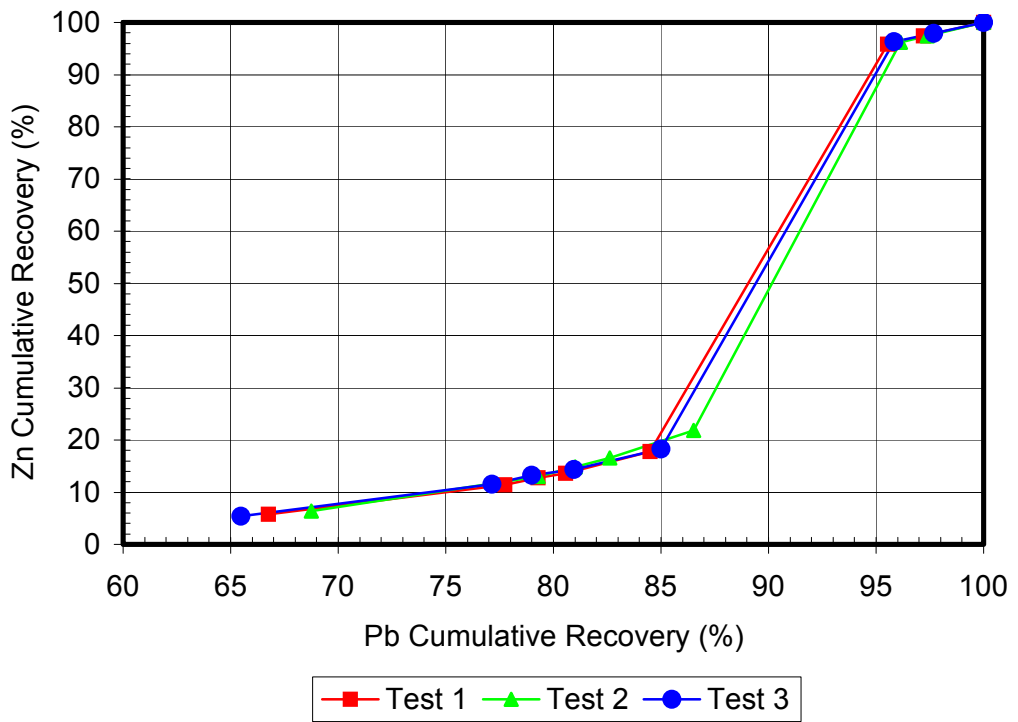


Figure 4.3 Baseline Flotation Tests Zinc Selectivity Curves



The total uncertainty of analytical results has been determined for various concentration ranges from the routine analysis of Century Mine ore, low-grade ore and lead concentrate standards and the data is shown in Appendix 3.11. The calculated total uncertainty within the 95% confidence interval, for high-grade lead analysis such as the lead contained in lead concentrate, was $\pm 1.89\%$ absolute.

The zinc recoveries, shown in Figure 4.3, are reproducible within 1.0% absolute, and the recoveries for other analytes, such as iron and silica, were also found to be within this reproducibility. The zinc recovery is equivalent to sphalerite recovery, as there are no other known zinc minerals above trace levels in the Century deposit. Figure 4.3 clearly shows a significant sphalerite recovery (5.9%) in the lead concentrate, which is more so than any of the other diluents in the flotation test. Carbonaceous minerals are also recovered (1.2%) during lead flotation but to a lesser extent. The iron and siliceous mineral recoveries in the lead concentrate are negligible.

Tables 4.7 to 4.10 show a comparison of the major grades and recoveries between the laboratory scale baseline flotation test and plant operational data, which were generated from Century Mine metallurgical accounting software (J.K. Met Account[®]). The first flotation test shown in red in Figure 4.2 was compared with typical plant grade and recoveries for the 2001–2002 financial year and for the operational period from the concentrator start-up (December 1999) to June 2003.

Table 4.7 Lead Concentrate Compared Grades and Recoveries

Stream	Weight (%)	Grade (%)			Recovery (%)		
		Pb	Zn	C	Pb	Zn	C
Pb 2 nd Cleaner Con 1	3.2	49.8	22.7	1.3	66.8	5.7	1.2
Pb Final Con 2001–2002	2.3	68.0	4.2	4.9	68.1	0.8	1.1
Pb Final Con 1999–2003	2.5	62.2	4.7	5.4	66.9	1.0	3.3

Table 4.7 clearly shows that the lead grade in the flotation test is lower than operational concentrator grades but the lead recovery compares well. The zinc grade and recovery are much higher in the flotation test and zinc was clearly the main diluent in the lead concentrate, resulting in a lower lead grade. The differences between the concentrator and the laboratory scale flotation test include flotation cell dynamics, pulp density, and the inclusion of froth washing and recirculating loads in the concentrator's lead cleaner flotation stages. The flotation test is a batch process and some of these differences cannot be overcome. Altering the flotation feed sample weight or cell volume can change the pulp density. However, the flexibility in changing these parameters in the flotation test with low lead grade in Century Mine ore is limited. If the weight of the flotation test sample is decreased, then a reduced amount of lead concentrate will be produced and this may affect reproducibility and limit the extent of sizing and chemical tests. It would be desirable to increase the cell size during laboratory pre-flotation, but a further limitation is the lack of availability of a larger cell that would operate on the flotation machine. Despite these challenges the flotation test offers a useful tool to examine the effect of changes to flotation flowsheet, where the effect on selectivity can be compared with a baseline or reference test.

Three lead concentrate samples were collected during the second lead cleaner stage of the flotation test at timed intervals of 20 s, 40 s and 60 s as described in Section 3.4.3. The second and third timed lead concentrates (40 s and 60 s, respectively) were found to consist mainly of gangue. Consequently, these streams have been combined with the lead circuit tailing streams to determine the grades and recoveries for the total lead circuit tailing as shown in Table 4.8.

Table 4.8 Lead Circuit Tailings Compared Grades and Recoveries

Stream	Weight (%)	Grade (%)			Recovery (%)		
		Pb	Zn	C	Pb	Zn	C
Pb 2 nd Cleaner Con 2	1.7	15.0	41.3	3.8	10.9	5.7	1.9
Pb 2 nd Cleaner Con 3	0.5	7.7	35.5	2.7	1.5	1.3	0.4
Pb 2 nd Cleaner Tail	1.0	3.0	11.1	4.4	1.3	0.9	1.3
Pb 1 st Cleaner Tail	6.3	1.5	8.3	4.2	3.9	4.2	7.7
Pb Scavenger Tail	82.5	0.3	11.8	3.0	11.0	78.0	74.2
Total/Weighted Average	92.0	0.7	12.2	3.1	28.6	90.1	85.5
Pb Scav Tail 2001–2002	91.6	0.6	13.0	3.8	26.3	93.8	83.2
Pb Scav Tail 1999–2003	90.7	0.6	12.4	3.6	23.7	92.8	81.5

Clearly, Table 4.8 shows that the inclusion of second and third timed lead concentrates in the total lead circuit tailing stream resulted in weighted average grades and total recoveries comparable with the lead circuit tailing observed in the concentrator. The concentrator lead scavenger tail stream represents the lead circuit tailing in a system where the first and second lead cleaner tailings are recirculated to the feed of the previous stage of flotation. The flotation tests streams shown in Table 4.8 have been combined in data analysis for any further test work that examines the lead circuit tailing, such as the mineral recovery–particle size analysis in Section 4.3.3.

The weighted average grades and total recoveries for the pre-flotation concentrates collected in the flotation test are very similar to plant data as shown in Table 4.9.

Table 4.9 Pre-flotation Concentrate Compared Grades and Recoveries

Stream	Weight (%)	Grade (%)			Recovery (%)		
		Pb	Zn	C	Pb	Zn	C
P/F Cleaner Con 1	1.9	2.1	10.4	9.6	1.7	1.5	5.3
P/F Cleaner Con 2	3.1	2.1	10.7	8.9	2.8	2.6	8.0
Total/Weighted Average	5.0	2.1	10.6	9.2	4.5	4.1	13.3
P/F Con 2001–2002	6.1	3.0	11.4	9.8	7.9	5.5	14.2
P/F Con 1999–2003	6.8	3.3	10.9	9.1	9.8	6.2	15.3

The flotation process flowsheet in the laboratory test includes a cleaner stage detailed in Section 3.4 and is comparable to the original concentrator flowsheet during commissioning in 1999. The concentrator flowsheet has since changed and the pre-flotation circuit consists of a rougher flotation stage only, where additional cells have been utilised to increase capacity. Both concentrator flowsheets are shown in Appendices 1.7 and 1.8.

The flotation test in this study is limited by cell capacity and this cleaner stage is required to selectively reduce the concentrate mass and produce a representative pre-flotation concentrate. The pre-flotation rougher stage in the flotation test is limited by variation of pulp density. This is due to the low lead grade in Century Mine ore (2–3%) and amount of sample that is required at the start of test to ensure enough lead concentrate can be collected in the last stage of lead flotation. Approximately 20 g of lead concentrate is required to be collected and this is achievable with a 1-kg test sample as demonstrated by the baseline flotation testwork.

The head grade in the flotation test is similar to the flotation feed in the plant and this is shown in Table 4.10.

Table 4.10 Baseline and Century Concentrator Head Grades

Stream	Weight (%)	Grade (%)		
		Pb	Zn	C
Head (calculated)	100	2.3	12.5	3.4
Flotation Feed 2001–2002	100	2.3	12.7	4.2
Flotation Feed 1999–2003	100	2.3	12.1	4.1

The flotation test head grade is calculated from a weighted average of grades for flotation test products and hence, these results clearly demonstrate the accuracy of the weighing and assaying of the test products. The results also show that the ore test samples closely represent the concentrator flotation feed and reaffirm the results in Section 4.1.

4.3.2 Pre-flotation Recovery versus Particle Size

The pre-flotation mineral recovery from each size range in the flotation feed is plotted against the geometric mean particle size for the pre-flotation concentrate in Figure 4.4. The total mineral recovery, with respect to the flotation feed, is plotted against particle size for the pre-flotation concentrate in Figure 4.5. The supporting data are shown in Appendices 4.9 and 4.10.

Figure 4.4 Pre-flotation Concentrate Recovery (by Size) versus Particle

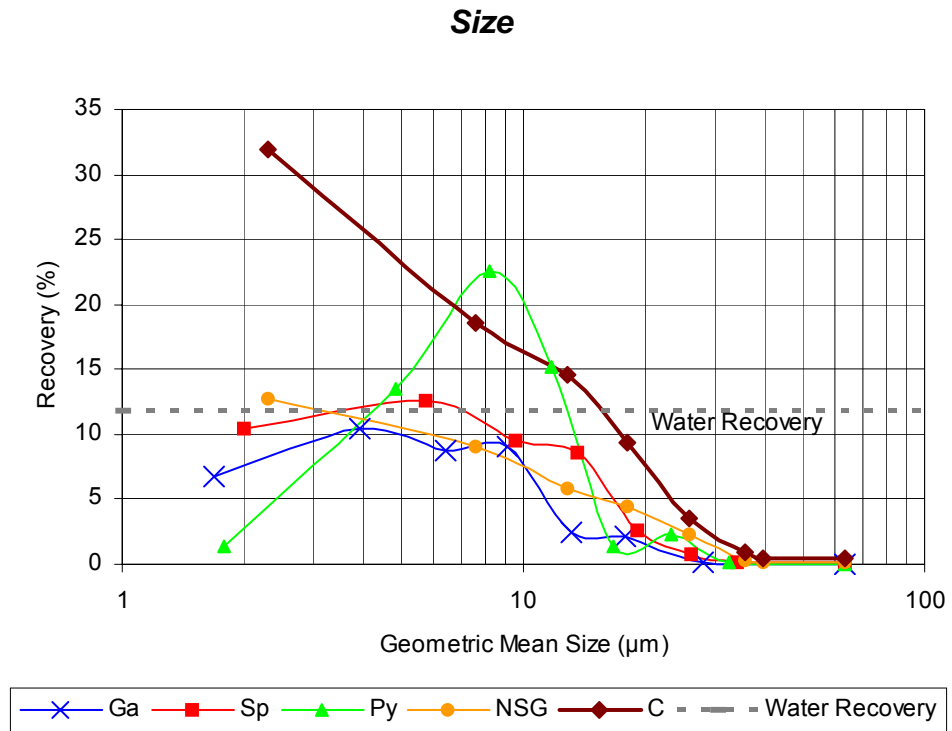
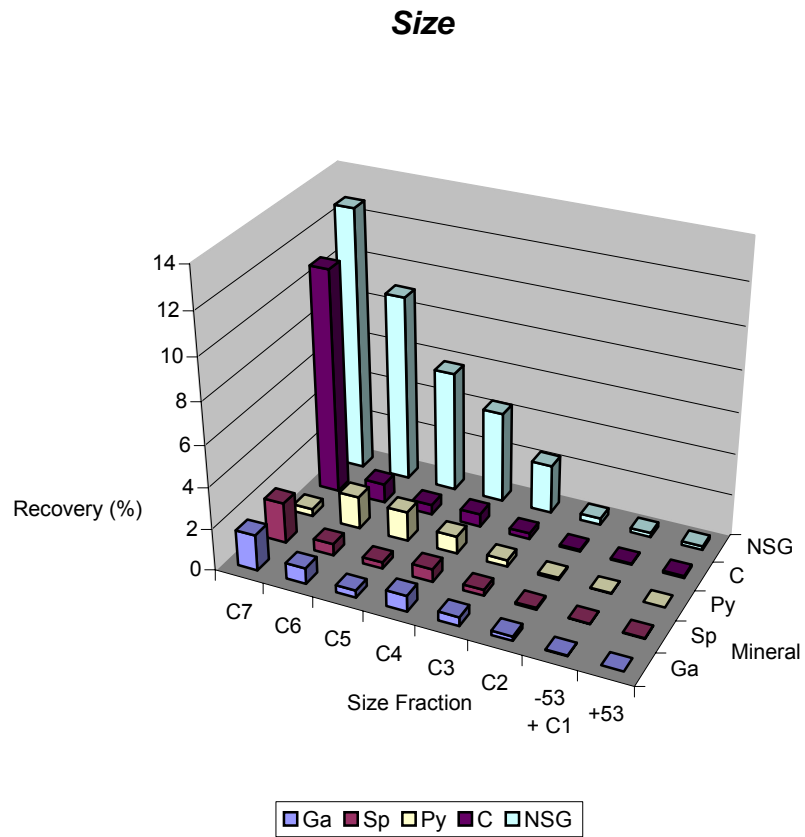


Figure 4.5 Pre-flotation Concentrate Recovery (Total)* versus Particle



* With respect to the flotation feed

The carbon recovery and its subsequent removal from the process stream prior to lead flotation is the objective of pre-flotation. Figure 4.4 shows the recovery of carbonaceous fine particles of approximately 2 μm (C7 fraction) was nearly 32%, which then decreased almost linearly with increases in particle size to 53 μm . The total carbon recovery during pre-flotation (Table 4.9) is 13% of the total carbon in the flotation feed. Figure 4.5 shows that more than 10% is recovered in the C7 fraction and nearly 1% is recovered in each of the C6–C4 fractions. These results show that as particle size increases, the recovery within each size fraction linearly decreases and approximately 70% of all carbon recovered during pre-flotation is due to the significant recovery of finely sized carbon particles of approximately 2 μm . These fine particles are most likely to be liberated from other minerals in the flotation feed. Clearly, for this to occur a significant amount of finely sized carbon particles would have been present in the flotation feed. This was confirmed in Section 4.1.3 where more than 27% of the carbon in the flotation feed was observed in the C7 size fraction and the remaining 73% was distributed almost evenly throughout the size fractions from C6 to $-106 \mu\text{m}$.

Depressing the recovery of galena and sphalerite during pre-flotation is important because once recovered here these valuable minerals are no longer available for the flotation in the lead and zinc circuits and are discarded. Galena (Ga) and sphalerite (Sp) recoveries in Figure 4.4 were all at or below water recovery indicating that 60–75% of their recoveries could be attributed to entrainment in the froth. The remainder of the recovery, particularly for the intermediate size range of around 10 μm , was probably due to composite or inclusions of graphite and non-liberated carbonaceous minerals. The recovery of sphalerite due to carbonaceous inclusions

has been identified in a QEM-SCAN study by Butcher and Gottlieb (1999). The same study shows that “inclusion-rich sphalerite” was the most common type of sphalerite found in particles of approximately 10 μm size in pre-flotation concentrates.

At plant scale, sphalerite recovery during pre-flotation (4%) is more significant than that during lead flotation (1–2%). The total galena and sphalerite recoveries in the pre-flotation concentrate are 4.5% and 4.1% respectively (Table 4.9). Figure 4.5 shows that of the total galena and sphalerite in the flotation feed, nearly 2% was recovered in the pre-flotation concentrate as C7 sized particles (approximately 2 μm) and less than 1% is recovered in each of the C6–C3 size fractions. These results suggest that galena and sphalerite are predominantly lost (approximately 70%) to the pre-flotation concentrate as fine particles which are recovered as a function of water recovery or mass recovery with the remaining losses (approximately 30%) attributed to graphitic inclusions or un-liberated particles in composite with carbonaceous minerals.

Some sphalerite hydrophobicity may have also been caused by mineral oxidation, particularly of galena, where hydrophobicity has been enhanced through the formation of elemental sulfur or polysulfides on the mineral surface (Section 2.1.4). Activating species such as lead hydroxide may also affect sphalerite recovery if significant concentrations exist in the process water which is added during grinding. However, since a significant amount of cyanide (200–300 g/t) was added to the ore during grinding, which is known to remove these oxidation products from the surface of sphalerite particles, it is unlikely that this mechanism was a factor. In addition, there was no collector added during pre-flotation, so the adsorption of activating

metal ions to sphalerite particles was not likely to have any effect on sphalerite flotation until the lead circuit, the unit process that follows. It is then that isopropyl xanthate is added as a collector which can adsorb to activated sphalerite particles and result in recovery to the concentrate.

The non-sulfide gangue (NSG) recovery is similar to carbon recovery as shown in Figure 4.4, where the recovery within each size fraction decreases almost linearly with increases in particle size to 53 μm . However, most NSG recovery is less than the water recovery and Figure 4.5 shows that of the total NSG recovered during pre-flotation, the recovery linearly decreased from 12% to 2% with increases in particle size between C7–C3 size fractions. This suggests that NSG, which is predominately comprised of siliceous minerals, is recovered either as a function of water recovery or mass recovery. A significant amount (200–300 g/t) of methyl isobutyl carbinol (MIBC) relative to other operations is added to the pre-flotation feed as a frother and this may be contributing to the increasing recovery of NSG, but also galena, sphalerite and pyrite, as particle size decreases by creating a bulk flotation of fine particles.

The only iron sulfides present in Century Mine ore is pyrite and the recovery of pyrite (Py) as shown in Figure 4.4 was consistently less than the water recovery except for the C6–C4 size fractions (5–15 μm) where there was a significant recovery for each size range (13–22%). The QEM–SCAN analyses (Section 4.2.3) show that approximately 13% of non-sulfide gangue other than siliceous minerals was associated with pyrite and that there was a significant association between siliceous minerals and the main sulfide minerals. These results indicate a clear association between pyrite and carbonaceous minerals in the 5–15 μm size range that

is sufficient to result in significant particle recovery. Figure 4.5 confirms that of the total pyrite present in the feed, the highest recovery during pre-flotation was in this size range. This recovery of pyrite during the pre-flotation stage is beneficial because without this stage, pyrite would most likely be recovered during lead flotation diluting the lead concentrate.

4.3.3 Lead Flotation Mineral Recovery versus Particle Size

The mineral recovery from each size range in the flotation feed is plotted against the geometric mean particle size for the lead concentrate in Figure 4.6. The total mineral recovery with respect to the flotation feed has been plotted against particle size for the lead concentrate in Figure 4.7. The supporting data are shown in Appendices 4.9 and 4.10.

Figure 4.6 Lead Concentrate Recovery (by Size) versus Particle Size

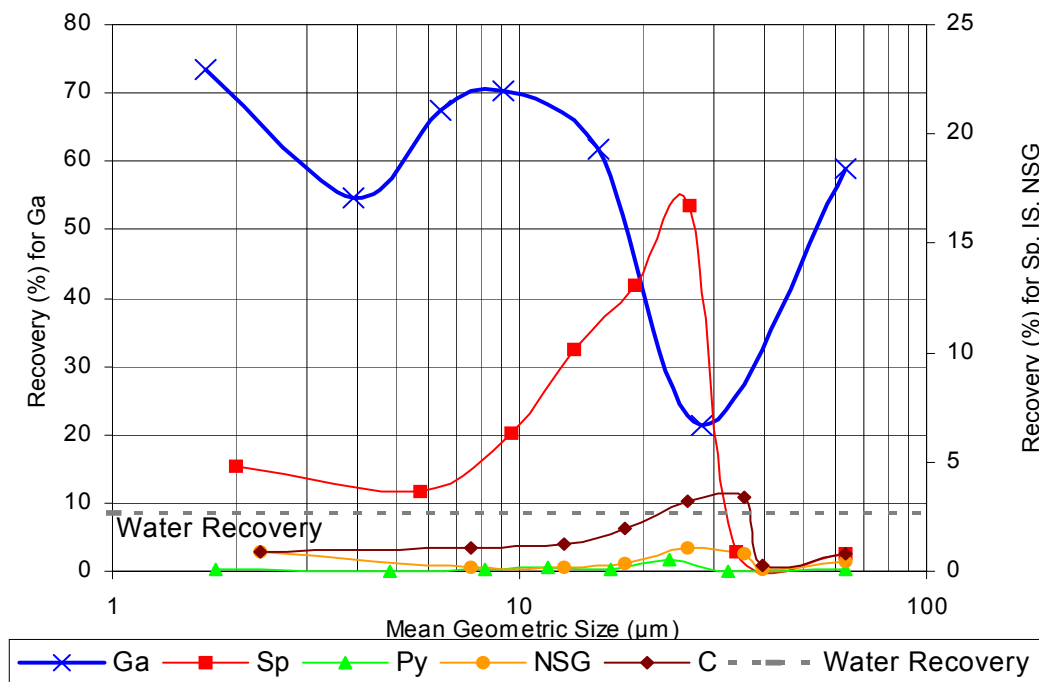
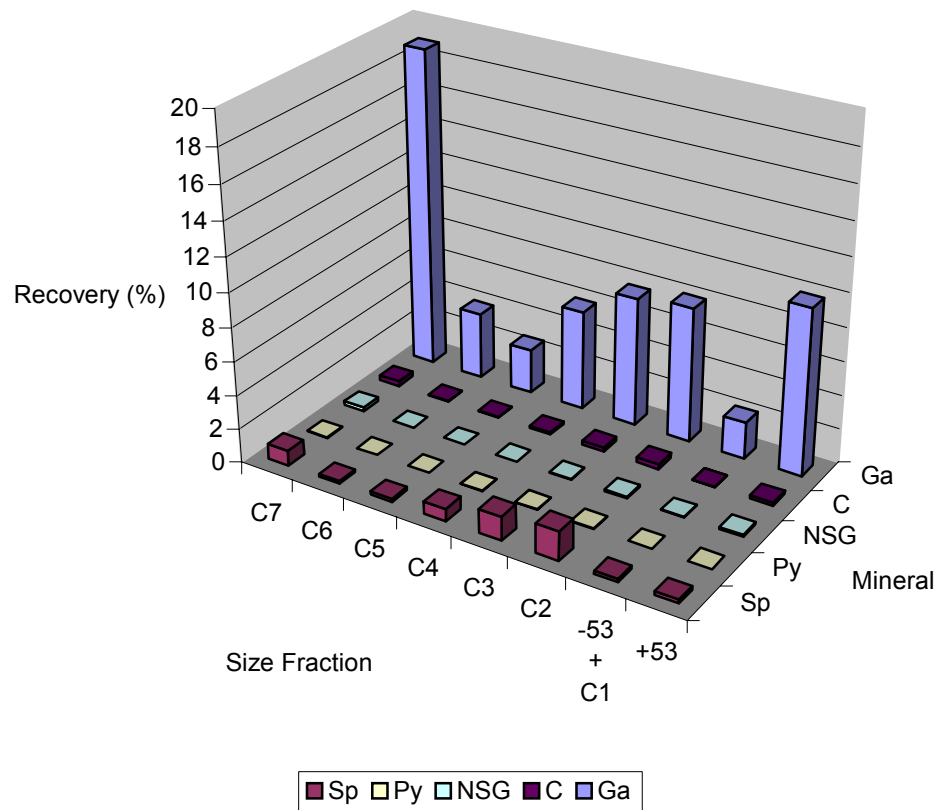


Figure 4.7 Lead Concentrate Recovery (Total)* versus Particle Size



* With respect to the flotation feed

A significant amount of galena was recovered as coarse particles as shown in Figure 4.6 by the high recovery (58.9%) for the +53 μm size fraction. This result represents the sum of all galena recovery for particle sizes greater than 53 μm . Had this fraction been further sized ($-76+53 \mu\text{m}$ and $-106+75 \mu\text{m}$ size fractions) the curve would have fallen towards zero. Coarse grains of galena are known to exist in Century Mine ore (Waltho and Andrews 1993) and the low recovery of other minerals in this size fraction (+53 μm) indicates that as much as 60% of all coarse galena is recovered without any composite particle recovery. Figure 4.7 shows that nearly 10% of the galena was recovered during lead flotation as +53 μm particles. The fine galena particle recovery shown by the C7 and C6 fractions (approximately 2–4 μm) in Figure 4.6 was relatively good (approximately 73%) indicating that the amount of

reagents and the length of residence time during lead flotation were sufficient for fine particle flotation. Figure 4.7 shows that approximately 22% of all galena in the flotation feed is recovered during lead flotation as fine particles in this size range, which are most likely liberated from other minerals.

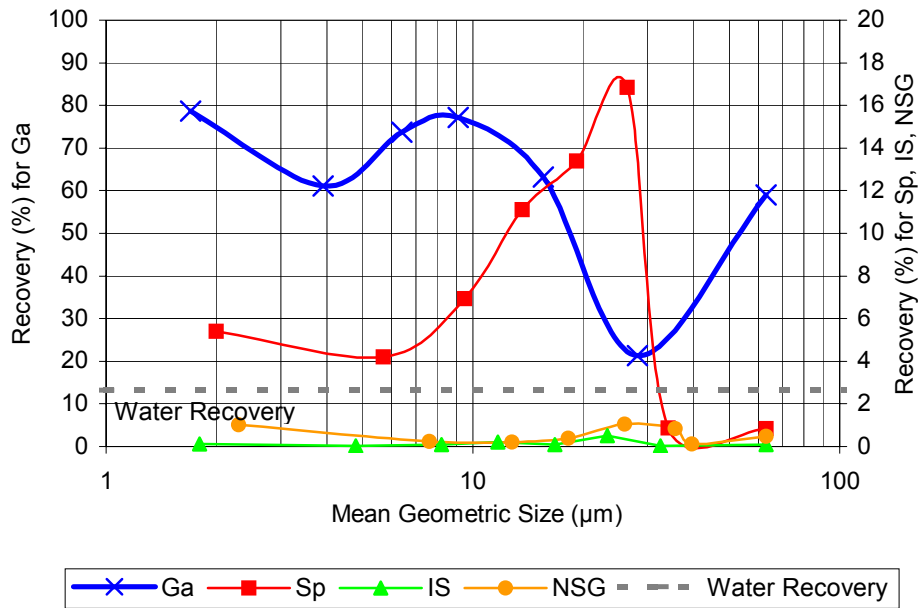
A sphalerite recovery as high as 6% occurred during lead flotation in the laboratory test. Figure 4.6 shows that the sphalerite recovery to the lead concentrate was most significant for sphalerite intermediate particles in the C4–C2 (approximately 14–26 μm) size fractions. Figure 4.7 shows that of the total sphalerite present in the flotation feed, nearly all that was recovered during lead flotation was recovered as these intermediate 14–26 μm particles. The recovery of galena and sphalerite increased, whilst the recovery of the gangue minerals was at or below the water recovery for particles in this size range. Thus, it appeared that the sphalerite recovery in this size range was due to composite particle flotation with galena. Although the carbon recovery in this size range was also above the water recovery, it could be expected that the sphalerite with sufficient carbonaceous inclusions would result in particle flotation recovery during pre-flotation. Some fine sphalerite particle flotation was observed above water recovery in Figure 4.6 for the C7 and C6 fractions (approximately 2–6 μm). Since these particles were likely to have been liberated during grinding their recovery could be attributed to surface activation and subsequent interaction with the collector or hydrophobicity due to surface oxidation.

The plant data at Century Mine indicate that, unlike the results of the laboratory scale flotation, there is no significant sphalerite recovery during lead flotation. The main differences between the plant and these laboratory tests are: (a) that the plant flowsheet includes a froth washing stage during the first lead cleaner, and (b) it

recirculates the cleaner tailings to the previous stage's flotation feed. Since the galena–sphalerite composite particles may not strongly interact with the collector it may be recirculated to the pulp by froth washing. It is also possible that these composite particles do not have sufficient residence time for collection so that they are returned to the feed of the previous flotation stage in the recirculating load, eventually leading to their recovery in the lead circuit tail.

The mineral recovery from each size range in the lead circuit feed is plotted against geometric mean particle size for the lead concentrate in Figure 4.8. The supporting data are shown in Appendix 4.9. The recovery trends in Figure 4.8 and Figure 4.6, which is with respect to the flotation feed, both indicate that sphalerite was the main diluent in the lead concentrate and sphalerite recovery during lead flotation was mainly due to its associations with galena. In Figure 4.8, sphalerite recovery as intermediate particles with respect to the lead circuit feed was more pronounced.

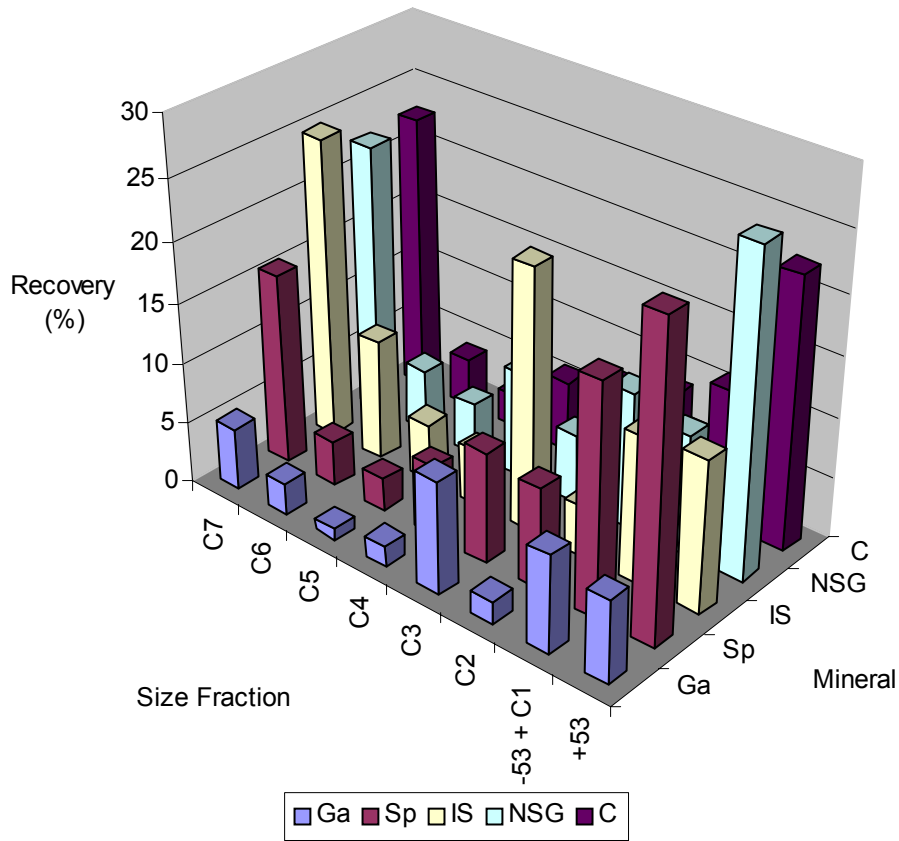
***Figure 4.8 Lead Concentrate Recovery (by Size) versus Particle Size,
with respect to the Lead Circuit Feed***



The water recovery was negligible during lead flotation. Entrainment as a function of water recovery would be less significant because the pulp density was so low due to limitations of the sample size and cleaner flotation cell volume (1500 cm³). In the plant, entrainment would also be less predominant owing to froth washing in the first lead cleaner stage. Clearly, the presence of galena–sphalerite composite particles appeared to be the main recovery mechanism occurring during lead flotation and, to a lesser extent, sphalerite surface activation and interaction with the collector was also a factor.

The total mineral recovery with respect to the flotation feed is plotted against particle size for the lead circuit tail in Figure 4.9. The supporting data are shown in Appendix 4.10.

Figure 4.9 Lead Circuit Tail Recovery (Total)* versus Particle Size



** With respect to the flotation feed*

Figure 4.9 shows that the highest loss of galena to the lead flotation tailings was in the intermediate (C3) and coarse (+C1) particles, which was most likely due to association with sphalerite or gangue minerals. Further grinding to liberate galena from such composites or reduce the +53 μm galena particles would therefore improve contact angles and the strength of their interaction with the collector and air bubbles. Nearly 6% of all galena was lost in fine particles (C7–C6) and this could be improved with better reagent control, including the use of collector and depressants.

4.4 The Effect of Grind Size and Pulp Density on Flotation

The effect of reducing primary grind size was investigated to determine if selectivity can be improved and explore its effect on primary zinc flotation. The effect of varying pulp density on the flotation feed to pre-flotation was also investigated using plant samples.

4.4.1 The Effect of Varying Primary Grind Size on Pre-flotation and Lead Flotation

Laboratory scale batch flotation tests were carried out following the procedure in Section 3.4 with primary grind sizes of 80 percent passing 20, 40 and 58 μm . The grinding times required to produce these grind sizes was determined using the data and calculations in Appendix 4.5.

Cumulative grade and cumulative recoveries were calculated from the product weights and assay results; the data is shown in Appendix 4.11. The lead grade–recovery and zinc selectivity curves for flotation tests with various grind sizes are plotted in Figures 4.10 and 4.11. The lead grade–recovery curves for the reduced grind sizes (20 and 40 μm) are comparable and both show an improvement to the baseline test (58 μm). A significant improvement has been observed for the lead grade when the grind size was reduced. At 65% Pb recovery, which is typical in the Century lead circuit, the lead grade was improved from 54% to 60%. At 80% Pb recovery, which represents most of the flotation time in the test, the lead grade was improved from 32% to 40%.

Figure 4.10 Lead Grade–Recovery Curves for Flotation Tests Investigating the Effect of Primary Grind Size

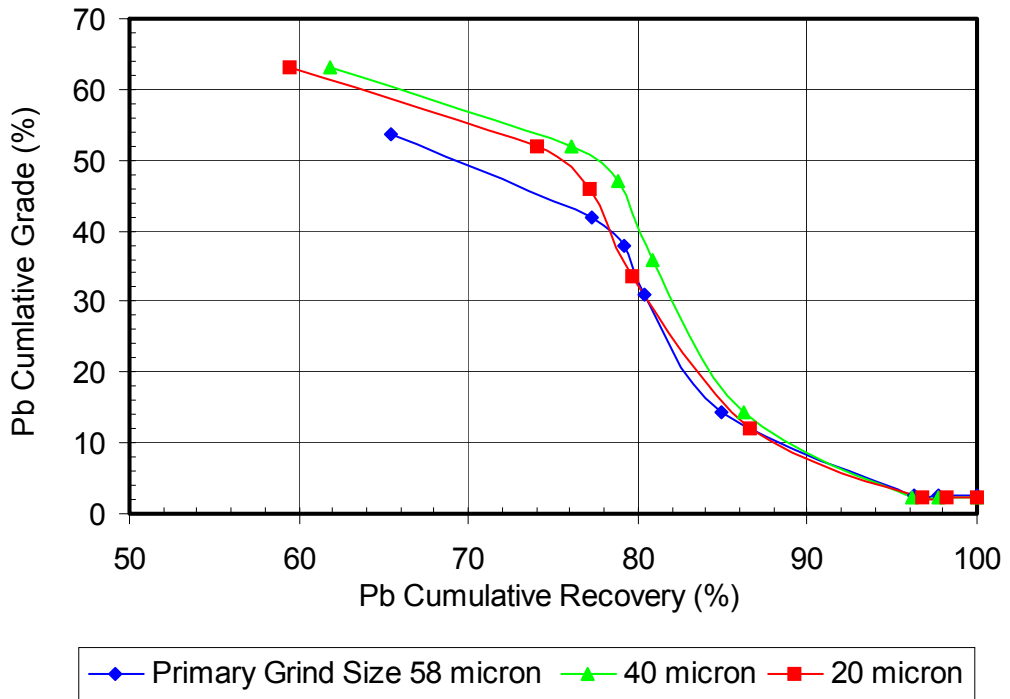
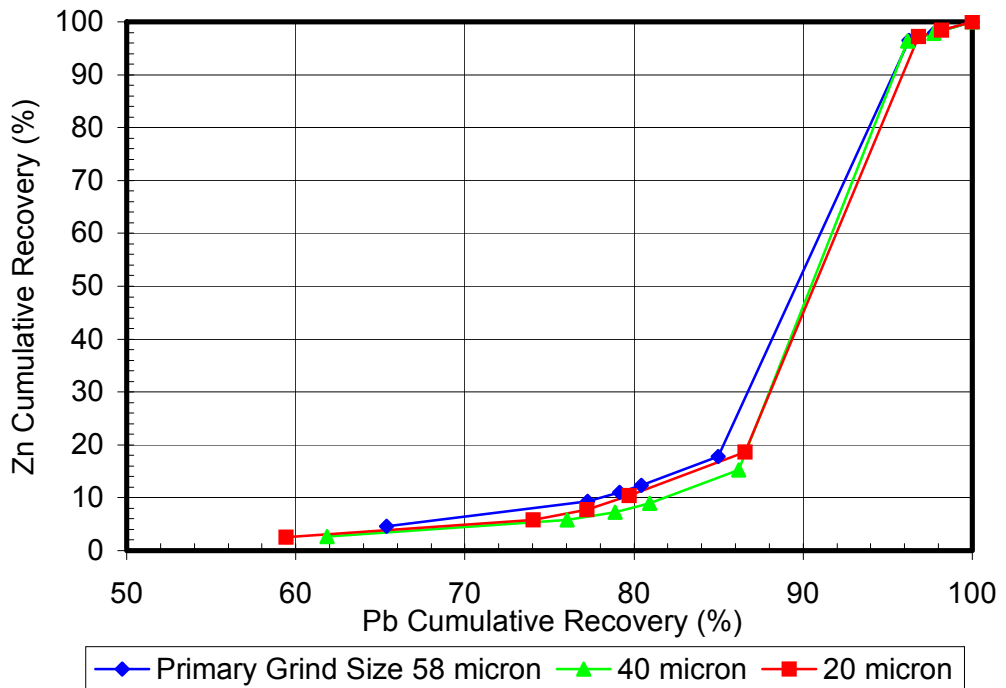


Figure 4.11 Zinc Selectivity Curves for Flotation Tests Investigating the Effect of Primary Grind Size



The lead recovery for 20- μm grind tests is shown to have decreased slightly compared to the 40- μm grind test. More xanthate could have been added in this case to improve galena recovery as no reagent additions were changed from the flotation test procedures when, clearly, the surface areas would have increased with decreasing particle size. Increasing the collector requires a careful control, as significant increases can result in poor selectivity. This effect of insufficient collector addition on lead recovery is negligible for the 40- μm grind compared to the baseline, where a significant improvement on zinc selectivity was observed.

The zinc recovery during pre-flotation does not change significantly between the baseline flotation test and the tests at reduced grind sizes. Only a marginal reduction of zinc recovery ($< 1\%$) was observed for the 20- μm grind test. These findings suggest that the recovery of intermediate sized sphalerite particles during pre-flotation was due to graphitic inclusions in the sphalerite lattice rather than composite particles with carbon or other minerals. Composite particle would be expected to be liberated at a significantly reduced grind size, say 20 μm . However, fine graphitic inclusions less than 1 μm in size would be more difficult to cleave from the sphalerite lattice.

The zinc recovery during lead flotation was reduced to nearly 2% for the 40- μm grind and this was comparable with the typical recovery at plant scale of 1% (Table 4.7). The reduction of the primary grind size to 80% passing 40 μm has reduced the zinc recovery during lead flotation, whilst the recoveries of other gangue mineral have been maintained at very low levels. Less zinc dilution of the final lead concentrate has resulted in an increased lead grade of the lead concentrate. The improved lead grade and better zinc selectivity with decreasing grind size to 80%

passing 40 μm shows that improvement to sphalerite liberation was achieved. This supports the findings in Section 4.3.3, where composite particles were identified as the main mechanism for sphalerite recovery during lead flotation in the laboratory scale tests.

4.4.2 The Effect of Varying Primary Grind Size on Primary Zinc Flotation

The lead circuit tailings from the laboratory scale batch flotation tests were used in primary zinc flotation testwork carried out following the procedure in Section 3.4.4. No adjustments were made to reagent additions in the standard laboratory flotation process flowsheet. The cumulative grade and cumulative recoveries were calculated from the product weights and assay results and are shown in Appendix 4.12. The zinc grade–recovery and iron selectivity curves for various grind sizes are plotted in Figures 4.12 and 4.13. They show that changes in 80% passing grind size from 58 μm to 40 μm had no effect on recovery during primary zinc flotation. The iron selectivity, which is important to the zinc flotation flowsheet, did not change significantly over this size range either. This indicates that reducing the primary grind size from 40 μm to 20 μm has no benefit towards reducing the ultra-fine grinding required in the zinc cleaner flotation circuit. The use of copper sulfate and xanthate was clearly sufficient for the flotation as no effect was observed with the increased mineral surface area at 40 μm .

Figure 4.12 Zinc Grade–Recovery Curves for Flotation Tests

Investigating the Effect of Primary Grind Size on Zinc Flotation

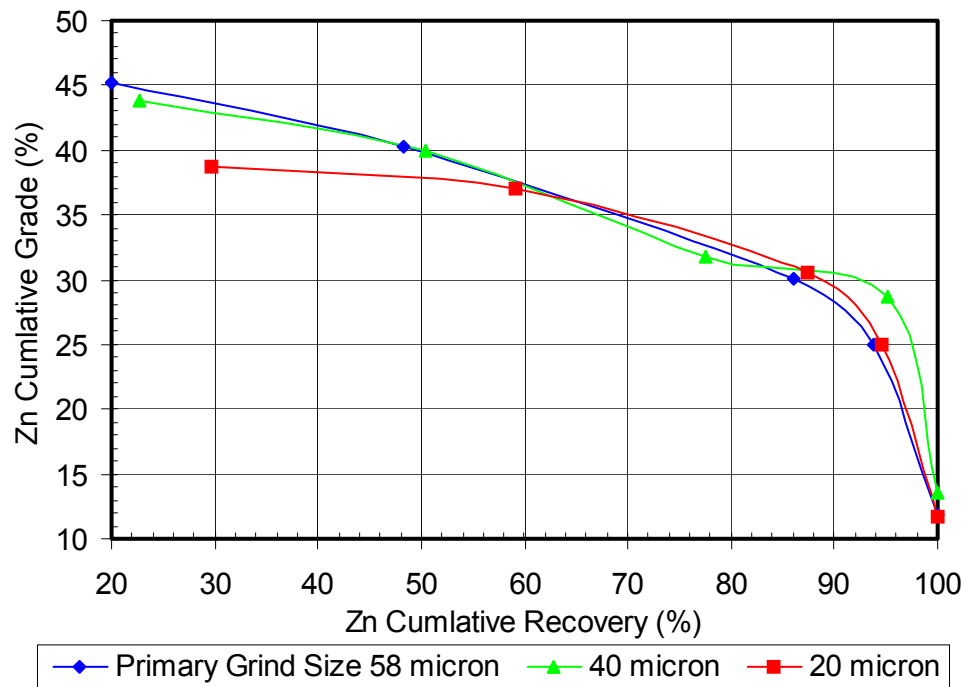
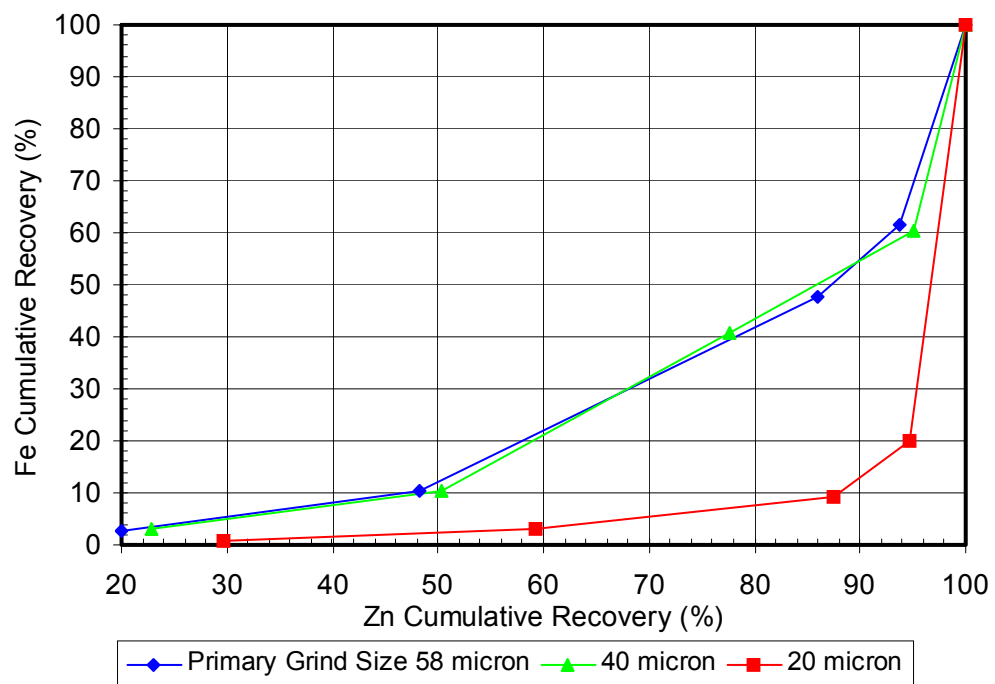


Figure 4.13 Iron Selectivity Curves for Flotation Tests Investigating the

Effect of Primary Grind Size on Zinc Flotation



The 20- μm test showed a significant improvement in selectivity between zinc and iron recovery (Figure 4.13). Figure 4.9 clearly showed that of the total pyrite present in the flotation feed, 51% was recovered in the lead circuit tailing as intermediate or coarse pyrite particles (+C3 or +17 μm). The lead circuit tailing is the feed to the zinc circuit and the observed improvement in iron selectivity during primary zinc flotation was due a reduction of these intermediate and coarse pyrite particles, which were most likely to be present as composite particles with other minerals. Grinding at or below 20 μm in the Century Mine concentrator primary grind circuit whilst maintaining tonnages would be difficult to achieve and grinding below 40 μm has not been found in the current study to improve flotation in the pre-flotation and lead flotation circuits. If it were practical to conduct primary zinc flotation at 20 μm through regrinding, an improved zinc recovery might be possible considering that approximately 10% less sphalerite is lost to the gangue in the zinc scavenger tail. The Century concentrator, however, has a significant capacity in the primary zinc circuits to control losses to the zinc scavenger tailing and ultra fine media (UFM) grinding is used to liberate iron in the primary zinc flotation product prior to the zinc cleaner flotation process.

4.4.3 The Effect of Varying the Pulp Density of the Flotation Feed

Primary cyclone overflow samples were used in flotation tests to examine the effect of varying the pulp density of the flotation feed on selectivity during pre-flotation. The sample was collected from the Century Mine concentrator following the procedure in Section 3.1.4. The sample was filtered as described in Section 3.1.5, but not dried. The moist filter cake was then sub-sampled to produce six test portions of various weights, so that the required pulp density (as % solids) would be obtained

when the sample was diluted in the flotation cell with tap water. Laboratory scale batch pre-flotation rougher tests were carried out following the procedure in Section 3.4.2. The amount of reagents required to make 320 g/t frother (MIBC) and 180 g/t sodium cyanide during conditioning was calculated based on the approximate dry mass of solids in the pulp.

The carbon grade–recovery and zinc selectivity curves for flotation tests at pulp densities of between 15% and 40% solids have been plotted in Figures 4.14 and 4.15. The supporting data are shown in Appendices 4.13 and 4.14. The curves clearly show that as the pulp density decreases, carbon grade and zinc selectivity improves. Plots of lead, iron and silica selectivity curves are at Appendix 4.15 and show similar trends to Figure 4.15. All of these selectivity curves show a nearly linear relationship and coincidentally the mineral recovery is closely related to mass recovery during pre-flotation. A plot of zinc recovery versus mass recovery for all of the flotation tests is shown in Figure 4.16 and the results confirm that zinc recovery is directly proportional to mass recovery.

Figure 4.14 Carbon Grade–Recovery Curves for Flotation Tests Investigating the Effect of Pulp Density

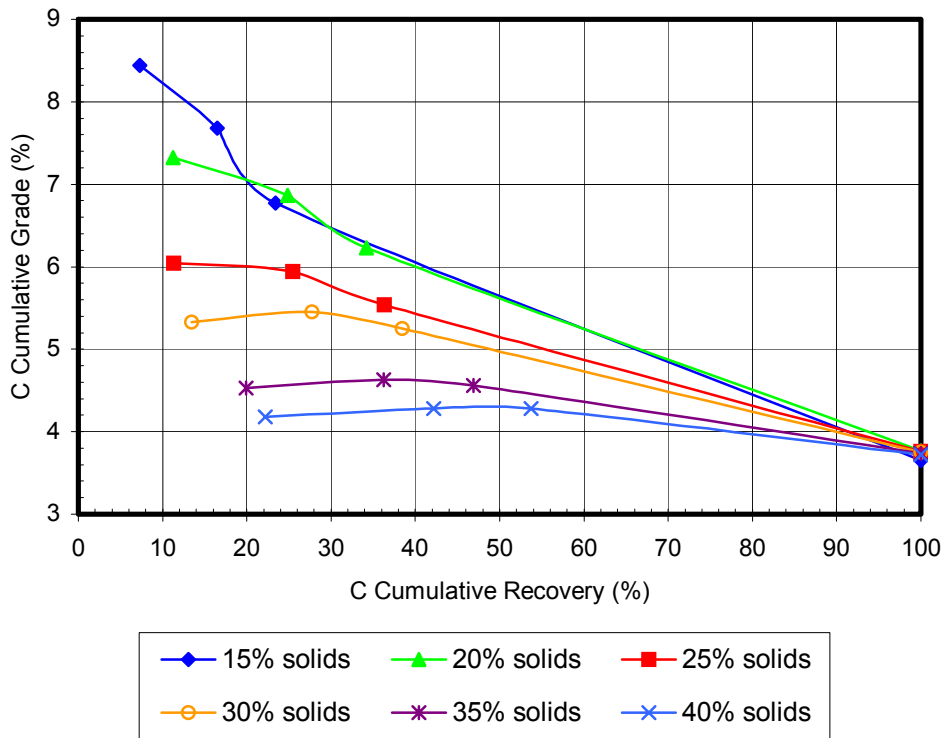
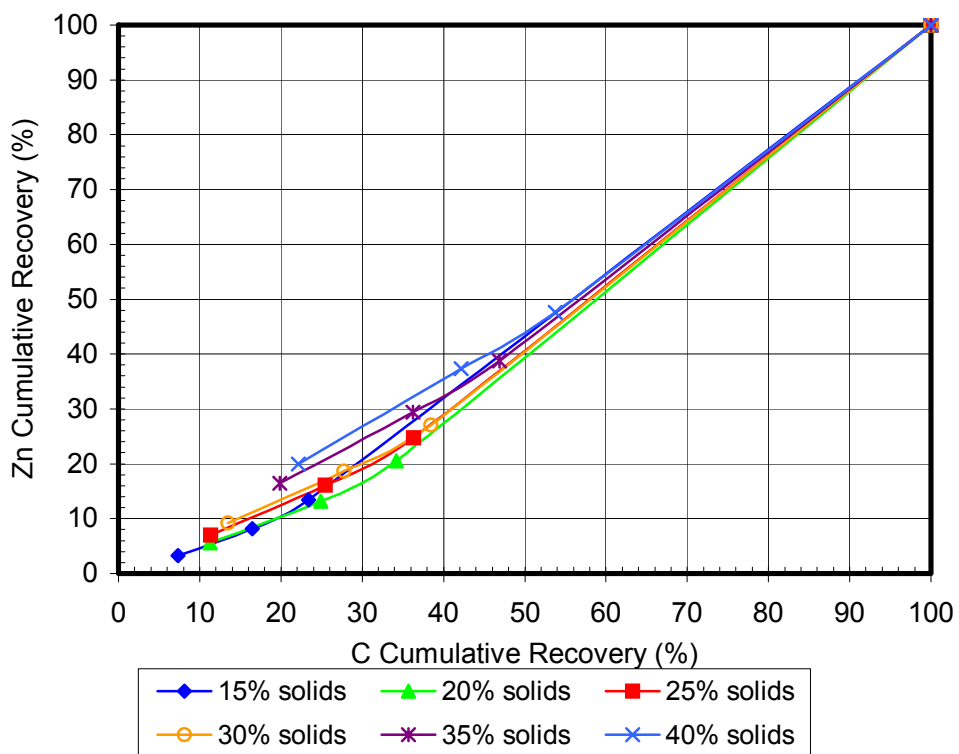


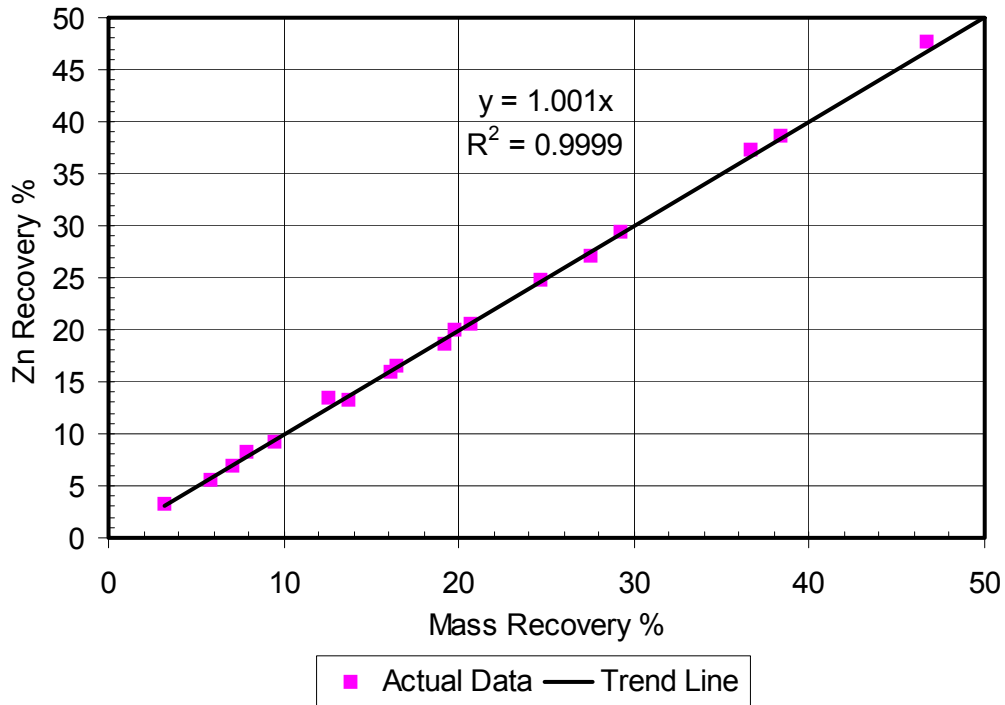
Figure 4.15 Zinc Selectivity Curves for Flotation Tests Investigating the Effect of Pulp Density



The pre-flotation circuit at Century was originally designed as shown in the flowsheet in Appendix 1.7 to produce a concentrate at 15% C grade, 25% C recovery and 3% Zn recovery (loss). The original flowsheet was only operated for a short period during commissioning when the concentrator feed tonnages were at half of the targeted processing capacity. Now at full production the current flowsheet shown in Appendix 1.8, is typically operated at 30% solids. It produces a concentrate at 8% C grade, 15% C recovery and 4.5% Zn recovery. The present results from laboratory flotation tests show that the optimum pulp density was 15–20% solids.

The current study used 1-kg test samples and a 2.5-L flotation cell in the pre-flotation stage. Consequently the pulp density in these tests was 40% solids and this resulted in the high mass recovery and poor selectivity observed in Figures 4.14 and 4.15. A single cleaner stage was used in the laboratory flotation flowsheet to produce a concentrate that represents the mass, grades and recoveries observed in pre-flotation rougher concentrate produced in the plant (Table 4.10). The results indicate that by decreasing the pulp density and installing a larger test cell in the flotation machine, the laboratory scale flotation test may be able to reproduce the conditions in the plant and remove the need for the cleaner flotation stage. However, the mass of the test sample would not be significantly reduced as an alternative approach to reducing the % solids in the pulp, as a 1-kg sample is required to produce sufficient lead concentrate (> 20 g) for flotation test reproducibility, sample preparation and chemical analysis.

Figure 4.16 Zinc Recovery–Mass Recovery Relationship for Pre-flotation Tests at Different Pulp Densities



The direct relationship ($y = x$) between zinc recovery (y) and mass recovery (x) shown in Figure 4.16, shows that no matter what % solids at which the process is operated, zinc losses during pre-flotation can be minimised by reducing the mass recovery. This is was achieved in laboratory scale tests through the use of a cleaner stage, which has been added to produce a product that represents the rougher concentrate produced in the plant scale. Hence, the addition of a cleaner stage to plant pre-flotation is one way of reducing mass recovery and hence zinc recovery. During the current study, the Century concentrator was examining various cleaner flotation options, including Jameson cell flotation described in Section 2.3.3. The advantages of Jameson flotation or conventional column flotation is the low capital cost of infrastructure required and the ability to employ sufficient froth washing which may reduce the mass recovery and thereby improve zinc selectivity.

4.5 The Effect of Pulp Chemistry and Reagents on Flotation

EDTA extraction tests were conducted to profile the extent of oxidation of the main sulfide minerals in the laboratory baseline flotation test and Century Mine concentrator flowsheet. Flotation tests were carried out to examine the effect of varying pH, frother addition, and depressants such as cyanide and zinc sulfate, on flotation.

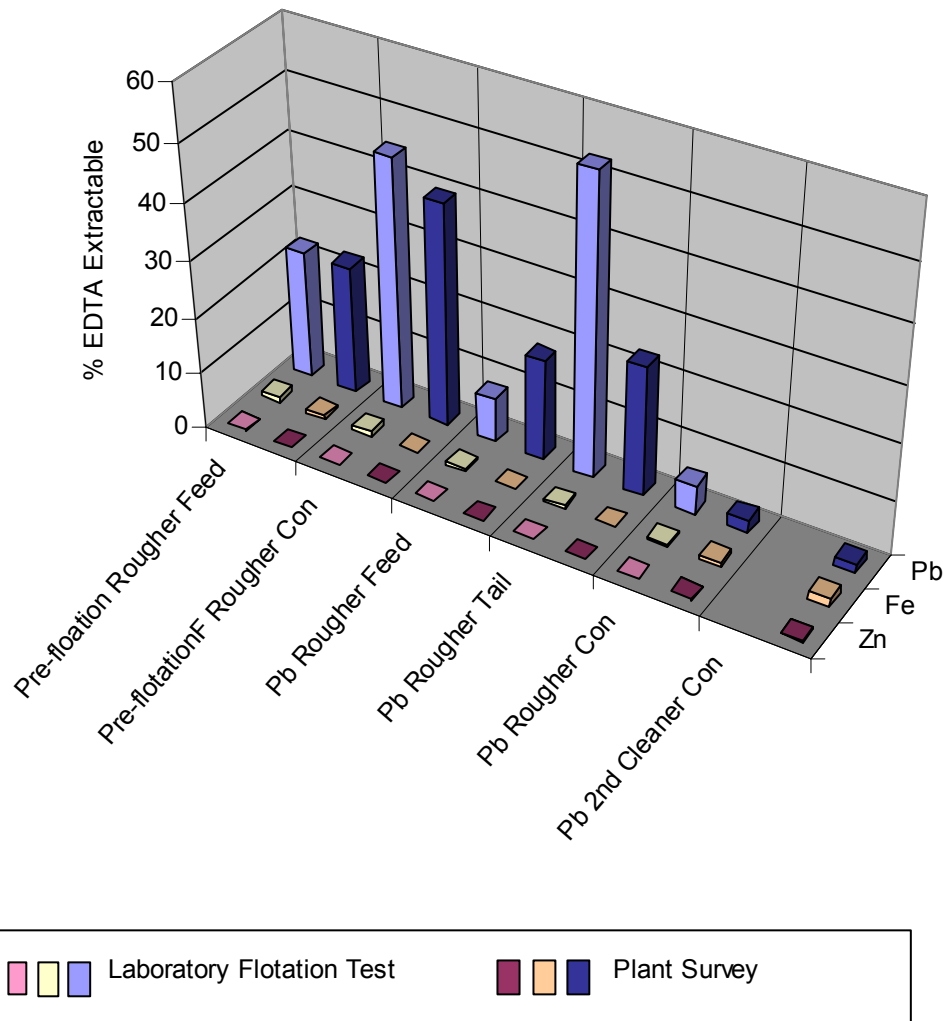
4.5.1 The Effect of Mineral Oxidation on Flotation

The pulp was sampled during the baseline flotation test to determine EDTA extractable metal contents of each stream following the procedure in Section 3.6. The procedure was repeated using plant samples obtained from the Century Mine concentrator as described in Section 3.1.5. The percentage of EDTA extractable metal in each stream provides a profile of mineral oxidation throughout the flowsheet and the results are shown in Figure 4.17. The supporting data are shown in Appendix 4.16.

The results for % EDTA extractable metals in various flotation streams in Figure 4.17 show similar profiles of mineral oxidation between the laboratory flotation test and the plant survey. The most significant deviation between laboratory and plant tests for % EDTA extractable lead was in the lead rougher tailing. This was probably due to sampling and analytical errors, since the sample mass of the lead rougher tail in the flotation test was relatively large (70% of the flotation feed) and the lead assay grade was relatively low (< 1%). An assay error of even 0.1% absolute would amount to more than 10% difference in the % EDTA extractable results. Clearly, the lead mineral galena is the only sulfide mineral that was significantly oxidised in the

flotation of Century Mine ore. The results observed for % EDTA extractable zinc and iron were insignificant.

Figure 4.17 EDTA Extractable Metals in Various Flotation Streams



These results show that galena is oxidised in the pre-flotation rougher feed, lead rougher feed and lead rougher tail and further oxidised during pre-flotation as shown by the relatively significant amount of % EDTA extractable lead in the pre-flotation concentrate. This indicates that the oxidation of galena during grinding and pre-flotation and the subsequent products of hydrolysis could be enhancing hydrophobicity and consequently contributing to the recovery mechanisms for galena

and, possibly, sphalerite, as described in Section 2.1.4. The loss of galena is significantly more so than sphalerite during pre-flotation, with 8% Pb recovery compared with 5% Zn recovery to the pre-flotation concentrate. More than half the galena and sphalerite recovered during pre-flotation was in C7 (approximately 2 μm) size fraction and the recovery of particles in this size range was less than water recovery indicating significant recovery due to entrainment in the froth. According to Johnson (2003, pers. comm., 18 March) approximately 60–75% of this recovery is usually attributed to entrainment in the froth. Fine particles are particularly susceptible to oxidation in any process due to their significant surface area, compared to larger particles. Thus, the oxidation products formed during pre-flotation, including the formation of elemental sulfur or polysulfides on mineral surfaces, may enhance the hydrophobicity of the fine particles and contribute to the remaining 25–40% of the observed recovery.

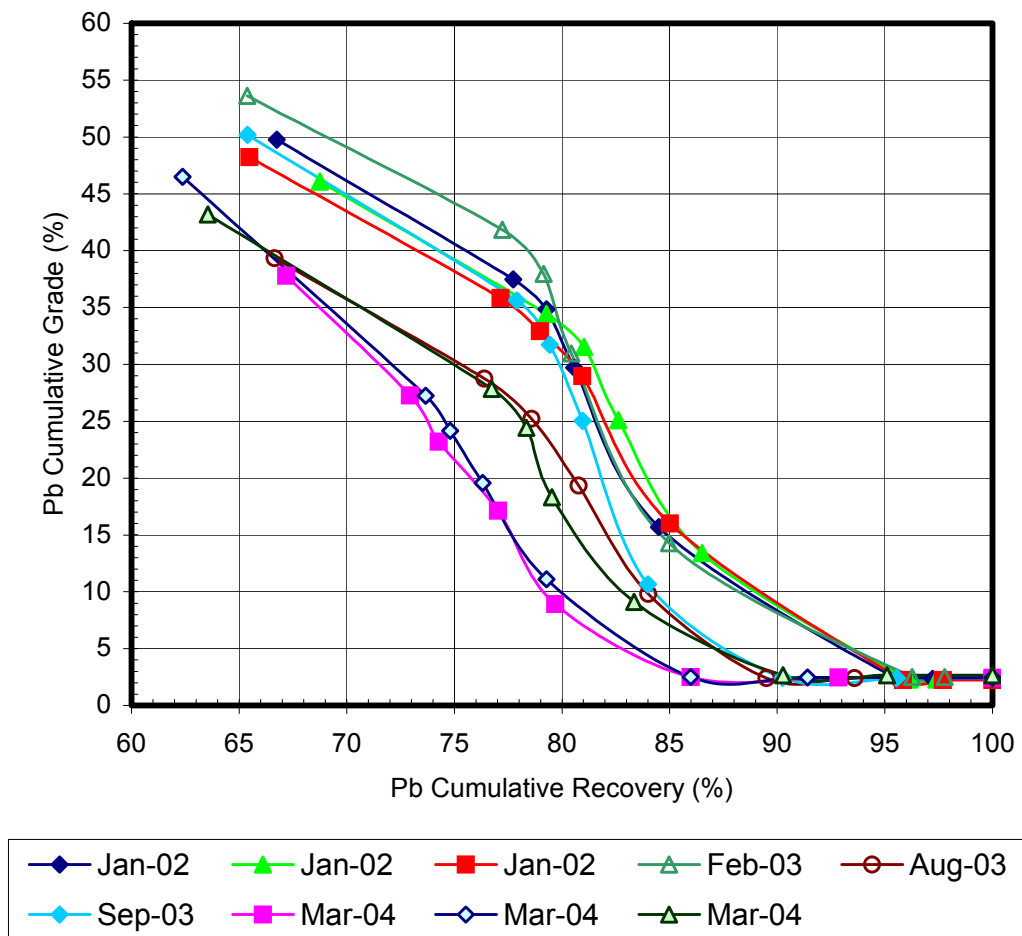
The recovery of a significant amount of oxidised galena to the pre-flotation concentrate, indicates that oxidation products are not introduced as significantly to the lead flotation circuit as they might be in other operations where there is no pre-flotation stage. There was probably a very low availability of oxidation products such as Pb^{2+} , Pb(OH)^+ or Pb(OH)_2 as indicated by the observed recovery during pre-flotation, but also due to the low lead grade in Century Mine ore (2.4%) compared to other mines (varying around approximately 5% Pb). Thus, activation of sphalerite during lead flotation and any subsequent interaction with the collector was not likely to have a significant role at Century as it might have in other plants.

It has been shown in Section 4.3.3 that as much as 15% of all fine sphalerite particles (approximately 2 μm size) in the laboratory test flotation feed were recovered during

lead flotation, which is significantly above the water recovery level and contributes nearly 1% of the total sphalerite recovery. The intermediate sized particles are more likely to be recovered as composite particles. Hence, the recovery of these fine particles was probably the most significant contribution that surface activation mechanism of recovery has on sphalerite recovery during lead flotation. The concentrator had one-fifth of the sphalerite recovery of the laboratory scale lead flotation. This was probably due to the differences between the two processes (Section 4.3.1).

A baseline test was carried out for each set of laboratory scale flotation tests as a reference. Purging with nitrogen and refrigeration preserved the 1-kg test portions used in the flotation testwork as described in Section 3.1.1. However, it appeared that oxidation occurred as indicated by the change over time of the baseline curve. The effect of mineral surface oxidation on flotation performance over a 2-year storage period is shown in the lead grade–recovery curves in Figure 4.18. The main effect of oxidation of the sample over time, as observed during pre-flotation and lead rougher flotation, is indicated in Figure 4.18. This is shown by the significant deviation of the curve (33% to 8% Pb grade) during these stages at 80–95% Pb recovery. In addition to this deviation, the remainder of the flotation test was affected such that the final lead grade is reduced by up to 10% Pb. The selectivity curves for other analytes, such as zinc, iron, silica and carbon, show that there was no individual decrease in selectivity and the dilution of the lead grade was due to a slight increase in the recovery of all minerals.

**Figure 4.18 Lead Grade–Recovery Curves for Baseline Flotation Tests
Conducted over the Course of the Study**



In the current study, the baseline flotation test was repeated for every set of tests, on the same day of the testwork, to allow a comparison under the same experimental conditions such as sample oxidation, temperature, pressure and any other environmental factors. Most of the flotation tests using the same ore sample were completed within 12 months of sample preparation. Samples collected from the Century Mine concentrator were used to carry out further tests specific to either the pre-flotation or the lead flotation circuit. Thus, it appeared that oxidation of the sample had not affected the outcome of any of the tests of the current study.

4.5.2 The Effect of Varying Pulp pH on Flotation

Laboratory scale batch flotation tests were carried out following the procedure in Section 3.4 except that different pH values were used. Three tests were carried out with their pH of the pulp at natural levels (pH 6.1–8.2), pH 8.5 and pH 9.5. The cumulative grade and cumulative recoveries were calculated from the product weights and assay results. The data are shown in Appendix 4.17. The lead grade–recovery and the zinc and iron selectivity curves for flotation tests at various pulp pH are plotted in Figures 4.19, 4.20 and 4.21.

Figure 4.19 Lead Grade–Recovery Curves for Flotation Tests Investigating the Effect of pH

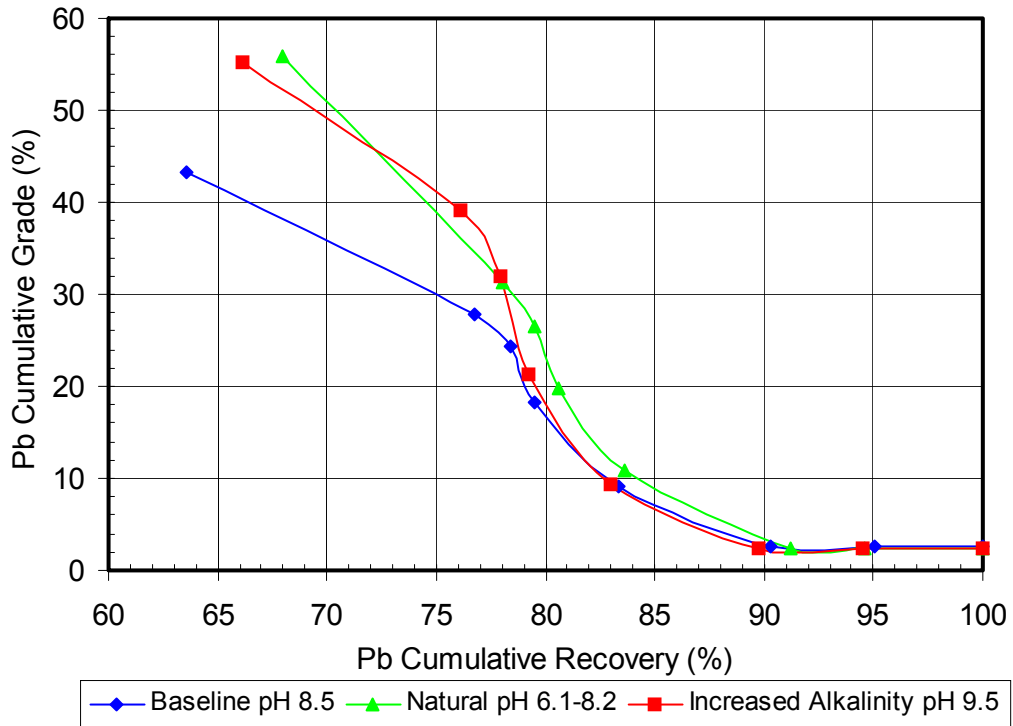


Figure 4.20 Zinc Selectivity Curves for Flotation Tests Investigating the Effect of pH

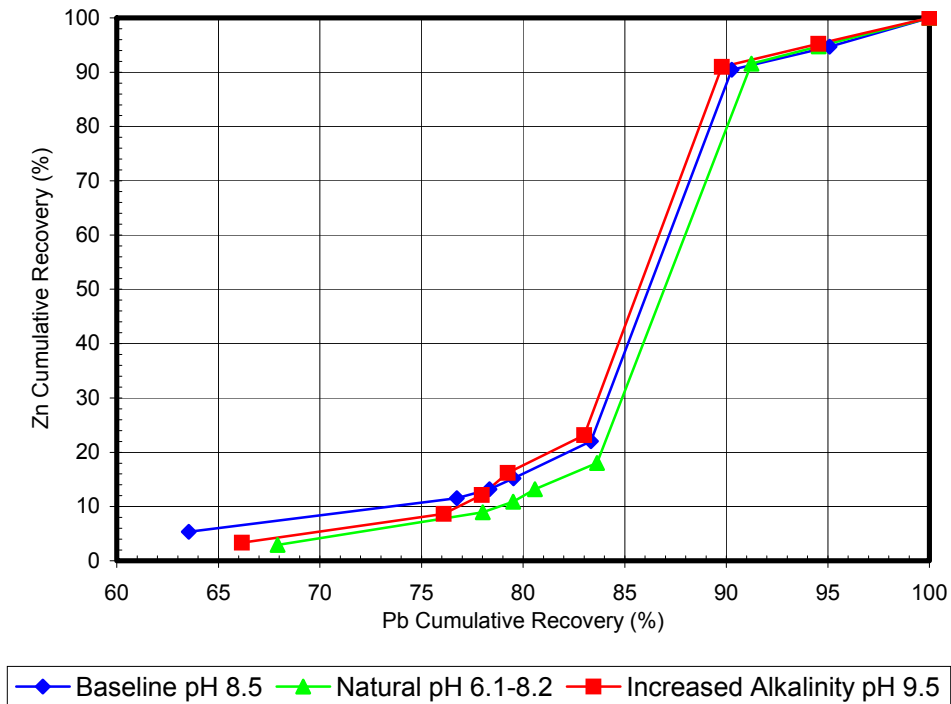


Figure 4.21 Iron Selectivity Curves for Flotation Tests Investigating the Effect of pH

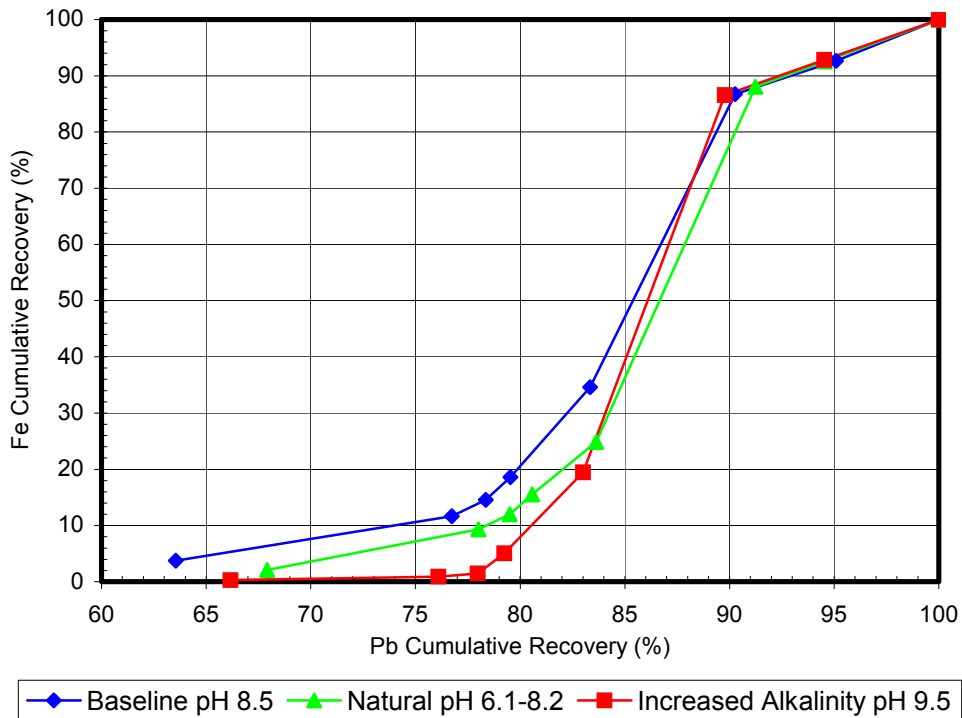


Figure 4.19 clearly shows that varying the pH from the baseline conditions which was at pH 8.5 resulted in improved lead grade and recovery for the second lead cleaner concentrates. Flotation at natural pH (pH 6.1–8.2) and much higher alkalinity (pH 9.5) resulted in a comparable lead grade–recovery trend. Figures 4.20 and 4.21 show that lead flotation was improved in terms of zinc and iron selectivity, but this was dependant on how the pH was changed. A decrease in pulp pH was particularly more selective against zinc recovery and, to a lesser extent, iron recovery compared to the baseline conditions. An increase pulp pH had little effect on the recovery during pre-flotation. However, during lead flotation, the selectivity against iron was improved to nearly zero recovery, whilst some improvement to zinc selectivity was also observed.

Flotation at pH less than 7 is known to result in an increased risk of corrosion of the infrastructure. Whilst the natural pH of the pulp in flotation began at around pH 6.1, the concentrator feeds at the Century Mine typically produce pulps of around pH 7 without the addition of lime or any other pH regulator during grinding. Often, pre-flotation at Century is carried out at natural pH, unless the ore is oxidised in which case, a significant amount of lime is added. The oxidation of the ore samples used in the current study was probably responsible for the low pH of the flotation feed, as oxidised sulfide minerals are known to produce acidic conditions.

Flotation at pH 9.5 has shown a particularly good selectivity against iron during lead flotation and this was probably due to the depressing effect of lime on pyrite as discussed in Section 2.3.4. Although the depression of iron is not a significant issue for lead flotation at Century, flotation at pH 9.5 has also shown an improvement in zinc selectivity and together with improved iron selectivity, adds to improving both the grade and recovery during lead flotation. Clearly the results suggest that pre-flotation is best operated at natural or near neutral-pH and the lead flotation is best operated at alkaline conditions close to pH 9.5.

4.5.3 The Effect of Varying the Pre-flotation Frother Addition

Primary cyclone overflow samples were collected from the plant and used in flotation tests to examine the effect of frother (MIBC) addition to the flotation feed on zinc selectivity during pre-flotation. Twelve samples were collected from the Century Mine concentrator following the procedure in Section 3.1.4.

The pulp density was determined as described in Section 3.1.5. The remaining samples were used in laboratory scale batch pre-flotation rougher tests, which were

carried out following the procedure in Section 3.4.2. The frother (MIBC) was added to the pulp during conditioning in various amounts from 100–400 g/t. The amounts were calculated based on the approximate pulp density. The carbon grade–recovery and zinc selectivity curves for flotation tests with MIBC additions of between 100–300 g/t and conditioning times between 0–12 minutes are shown in Figure 4.22 and 4.23. The supporting data are shown in Appendix 4.18.

Figure 4.22 Carbon Grade–Recovery Curves for Flotation Tests Investigating the Effect of MIBC

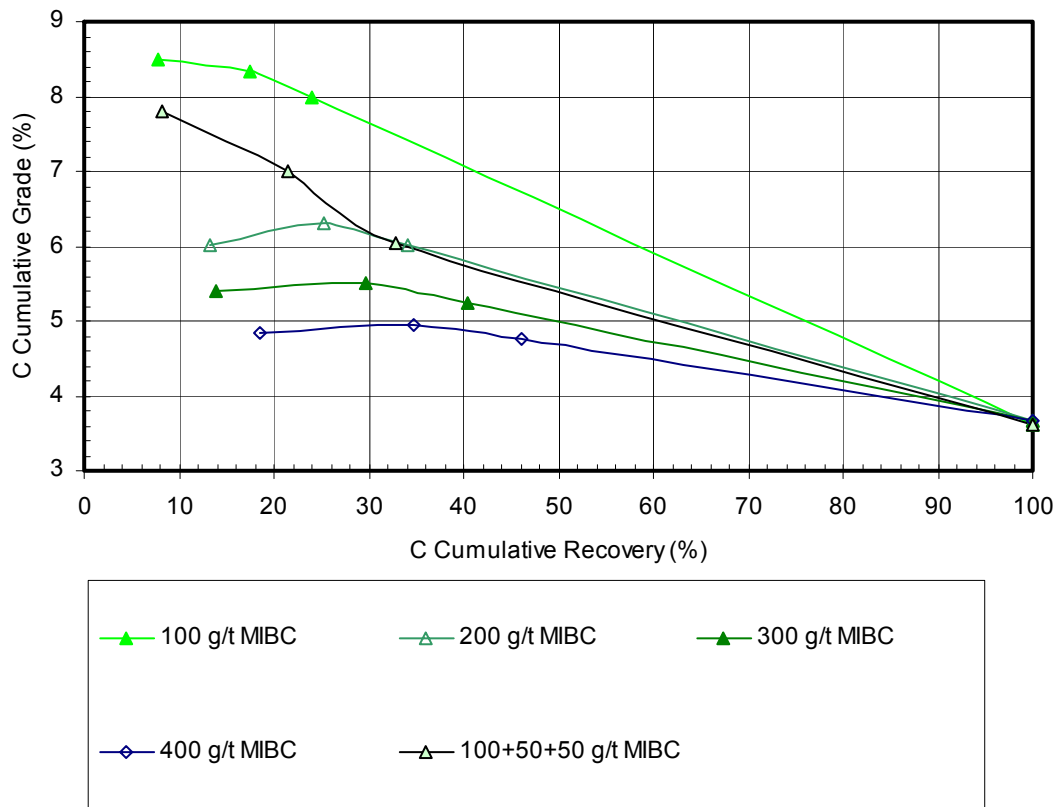
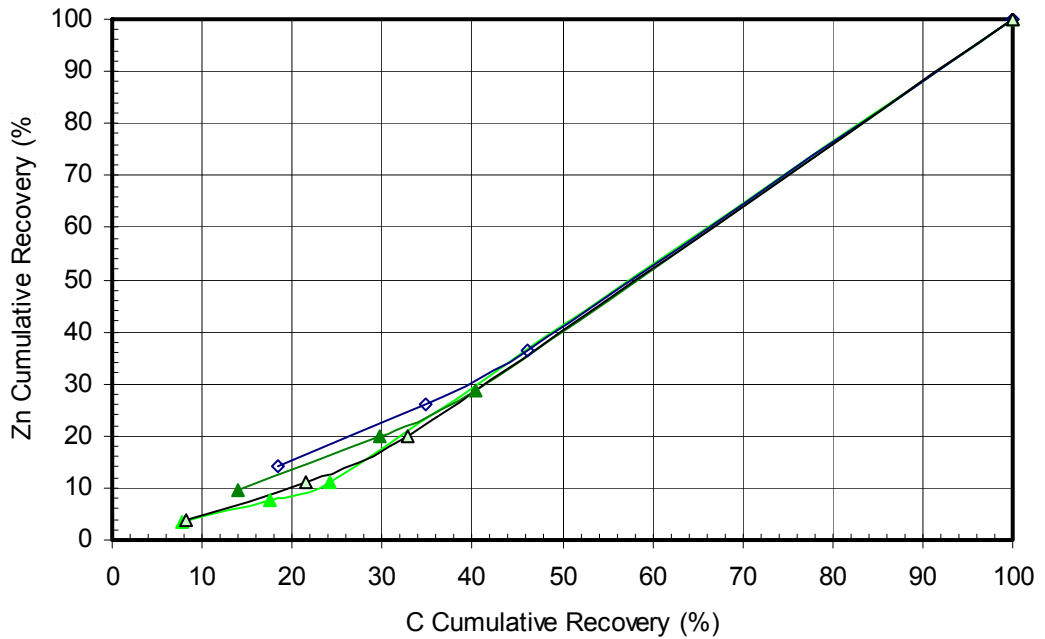


Figure 4.23 Zinc Selectivity Curves for Flotation Tests Investigating the Effect of MIBC*



**Refer to Figure 4.22 for Legend*

Figure 4.22 clearly shows that by decreasing the amount of MIBC added, resulted in higher carbon grades without any significant change in carbon recovery. The zinc selectivity curve shown in Figure 4.23, has similar profile to the lead, iron and silica selectivity curves (Appendix 4.19) and shows a consistent improvement in flotation with decreases in MIBC addition. This significant improvement clearly shows that the amount of MIBC (approximately 300 g/t) was excessively added to the pre-flotation stage in the flotation test and possibly the plant. The consistency among the selectivity curves for each analyte suggests that excess use of MIBC results in bulk flotation of all minerals and that MIBC addition is proportional to total mass recovery. This compares well with the results of Section 4.4.3 where at 300-g/t MIBC, flotation was improved by simply reducing % solids in the pulp and hence the mass available for flotation. The results in this section clearly showed that for sphalerite in particular, the recovery was directly proportional to mass recovery in

flotation tests with pulps varying from 15% to 40% solids. Thus, mass recovery needs to be reduced to improve selectivity and a reduction in the use of MIBC is shown here to achieve this improvement.

A considerable amount of frother is added to the flotation feed at Century Mine compared to other mining process flowsheets. As much as 300 g/t of MIBC is used at Century because it is believed that this amount of MIBC is necessary during the process and consumed, possibly by adsorption on to the carbonaceous minerals during the pre-flotation process (Bode, P.C. 2003, pers. comm., 11 Sep). The results in Figure 4.22 show that this does not seem to occur at lower MIBC concentrations. It appeared that a MIBC addition of 100 g/t is sufficient as shown by the fact that there was no significant difference between the carbon grade–recovery curves for the various conditioning times (Appendix 4.20) and an adequate froth was observed to form in the flotation test. However, flotation tests using 200 g/t and 300 g/t of MIBC do show an improvement in carbon grade and recovery when the conditioning time is increased to 12 minutes. Figure 4.22 shows that when the MIBC addition was reduced to 100 g/t, both the carbon grade and recovery improved. Therefore, the improvement observed for 200-g/t and 300-g/t MIBC tests with an increased conditioning time may be consistent with a decrease in MIBC concentration due to absorption on to the carbonaceous minerals. It is also possible that MIBC losses are due to evaporation in a pulp at a temperature of approximately 35 °C. This may be more pronounced at plant scale at Century Mine where the pulp temperature can be from 40–60 °C due to grinding and also the climatic conditions.

The conditioning time is not significant in the plant where MIBC is added at the first flotation cell in the pre-flotation circuit, and hence adsorption should not have a

significant opportunity to occur other than during flotation in the pre-flotation roughing cells. To reduce the amount MIBC used during pre-flotation in the plant, there may be potential benefits in adopting a staged addition of MIBC, where 50 g/t is added initially to the flotation feed, followed by the addition of another 50 g/t down the bank.

4.5.4 The Effect of Zinc Sulfate and Iron Sulfate on Flotation Selectivity

Laboratory scale batch flotation tests were carried out following the procedures in Section 3.4 with various amounts of cyanide, zinc sulfate and iron sulfate as depressants (Table 4.11). The lead grade–recovery, zinc selectivity, and iron selectivity curves for flotation tests that investigated the use of cyanide are plotted in Figures 4.24, 4.25 and 4.26. These curves have been plotted for flotation tests investigating the use of zinc sulfate and iron sulfate in Figures 4.27, 4.28 and 4.29. The supporting data are shown in Appendices 4.21 and 4.22.

Table 4.11 Scheme of Depressants for Flotation Tests Investigating the Effect of Zinc Sulfate and Iron Sulfate as Depressants

Test Description	Test Stage			
	Primary Grind	Pb Rougher	Pb 1 st Cleaner	Pb 2 nd Cleaner
1. Baseline	300 g/t NaCN	–	80 g/t NaCN	–
2. Baseline with increased cyanide	400 g/t NaCN	100 g/t NaCN	100 g/t NaCN	50 g/t NaCN
3. Zn(II) without cyanide	1000 g/t ZnSO ₄	300 g/t ZnSO ₄	100 g/t ZnSO ₄	50 g/t ZnSO ₄
4. Zn(II) with reduced cyanide	200 g/t NaCN	200 g/t ZnSO ₄	40 g/t NaCN	–
	500 g/t ZnSO ₄		100 g/t ZnSO ₄	
5. Zn(II) with standard cyanide	300 g/t NaCN	150 g/t ZnSO ₄	80 g/t NaCN	–
	250 g/t ZnSO ₄		80 g/t ZnSO ₄	
6. Fe(II) with reduced cyanide	200 g/t NaCN	200 g/t FeSO ₄	40 g/t NaCN	–
	500 g/t FeSO ₄		100 g/t FeSO ₄	
7. Zn(II), Fe(II) and reduced cyanide	150 g/t NaCN	200 g/t ZnSO ₄	40 g/t NaCN	–
	300 g/t ZnSO ₄		100 g/t ZnSO ₄	
	300 g/t FeSO ₄		100 g/t FeSO ₄	
8. Zn(II), Fe(II) and standard cyanide	300 g/t NaCN	150 g/t ZnSO ₄	80 g/t NaCN	–
	250 g/t ZnSO ₄		80 g/t ZnSO ₄	
	250 g/t FeSO ₄		80 g/t FeSO ₄	

It appeared that by increasing the cyanide additions to the process flowsheet, the zinc selectivity did not improve and the lead recovery was observed to be slightly lower. The iron selectivity was maintained at very low levels of recovery. However this was already the case with standard cyanide additions in baseline test. Clearly, the amount of cyanide added in the baseline flowsheet is sufficient and thus, increasing the added cyanide only adds excess cyanide to the pulp. Flotation tests were attempted without the addition of cyanide during grinding, but very low lead grades and recoveries were observed during lead flotation due to significant losses in the pre-flotation stage. Tests with no cyanide added until the conditioning of the pre-flotation rougher feed and the lead rougher feed resulted in lead concentrate with less than 30% Pb grade at 65% Pb recovery.

In the laboratory flotation test, the addition of cyanide as a depressant needs to be made at the grinding stage to allow sufficient conditioning for the subsequent reaction. This is in contrast to the plant, where cyanide is being added either during and after grinding with no reported changes to selectivity between the two different addition points. The ores used in the laboratory flotation tests are slightly more oxidised than those in the plant owing to storage and thus, the significantly long and thorough conditioning time during grinding may be necessary for cyanide to react with the mineral oxidation products which would otherwise enhance galena or sphalerite hydrophobicity during pre-flotation.

Figure 4.24 Lead Grade–Recovery Curves for Flotation Tests

Investigating the Use of Cyanide

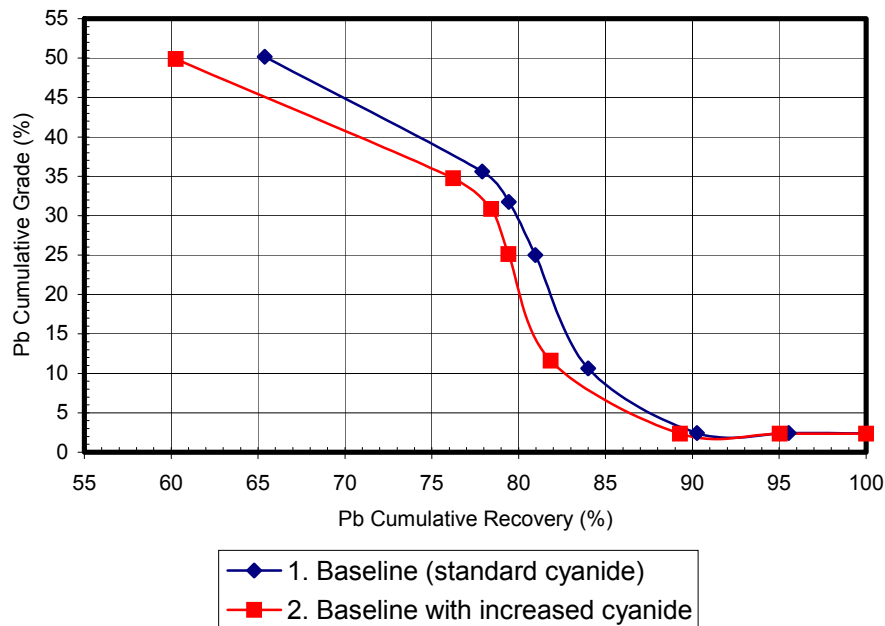


Figure 4.25 Zinc Selectivity Curves for Flotation Tests Investigating the Use of Cyanide*

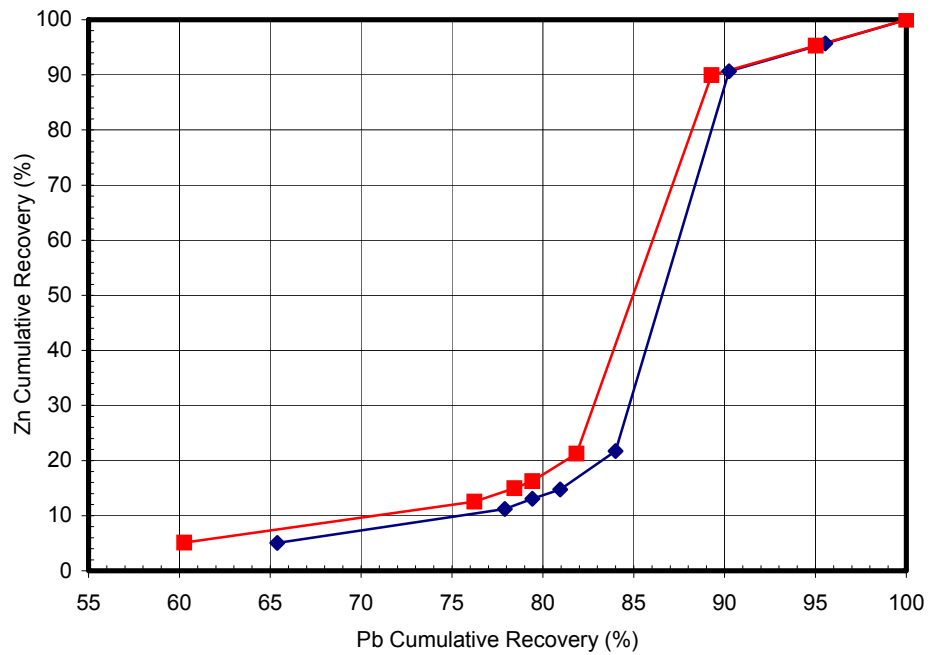
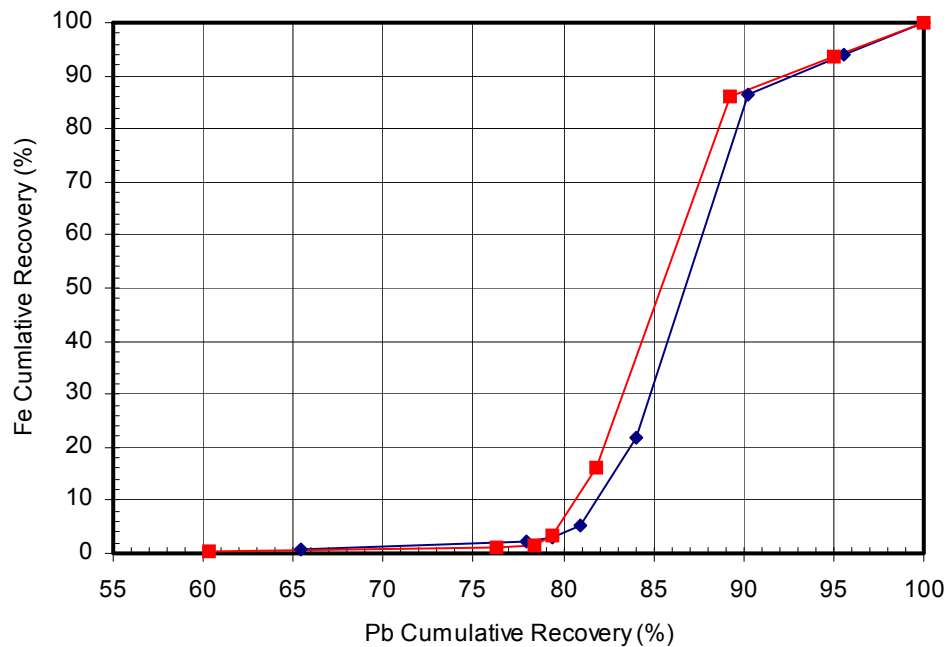


Figure 4.26 Iron Selectivity Curves for Flotation Tests Investigating the Effect of Zinc Sulfate and Iron Sulfate as Depressants*



* Refer to Figure 4.24 for Legend

The depression of sphalerite without the use of cyanide has only been successful in laboratory tests when zinc sulfate has been added but, even then, selectivity has only improved during lead flotation with losses during pre-flotation affecting lead recovery. In the flotation test using zinc sulfate (or zinc (II) depressant) without cyanide, zinc selectivity improved but iron selectivity decreased. This clearly shows that cyanide was essential in the depression of pyrite, the only iron sulfide in Century ore, and that cyanide addition was most critical prior to pre-flotation.

Figure 4.27 Lead Grade–Recovery Curves for Flotation Tests

Investigating the Effect of Zinc Sulfate and Iron Sulfate as Depressants

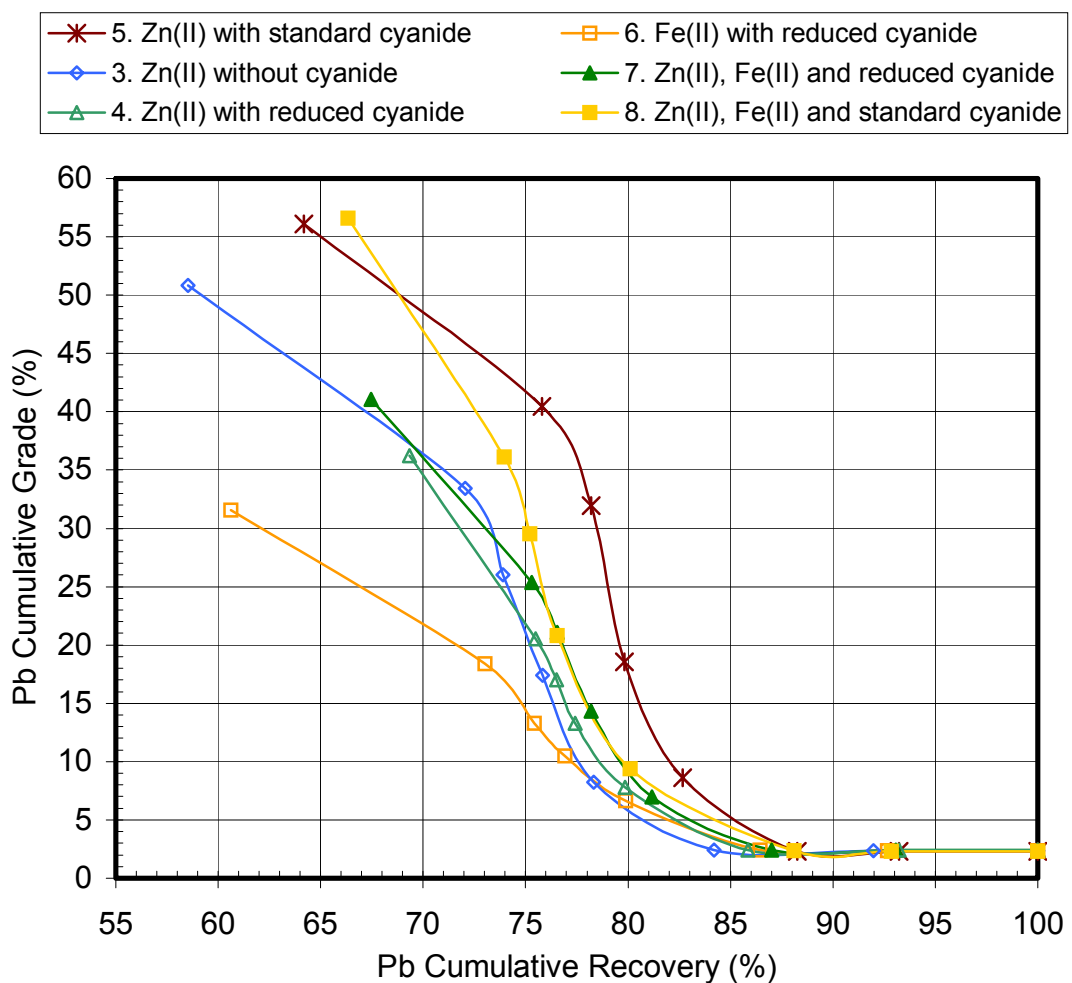


Figure 4.28 Zinc Selectivity Curves for Flotation Tests Investigating the Effect of Zinc Sulfate and Iron Sulfate as Depressants*

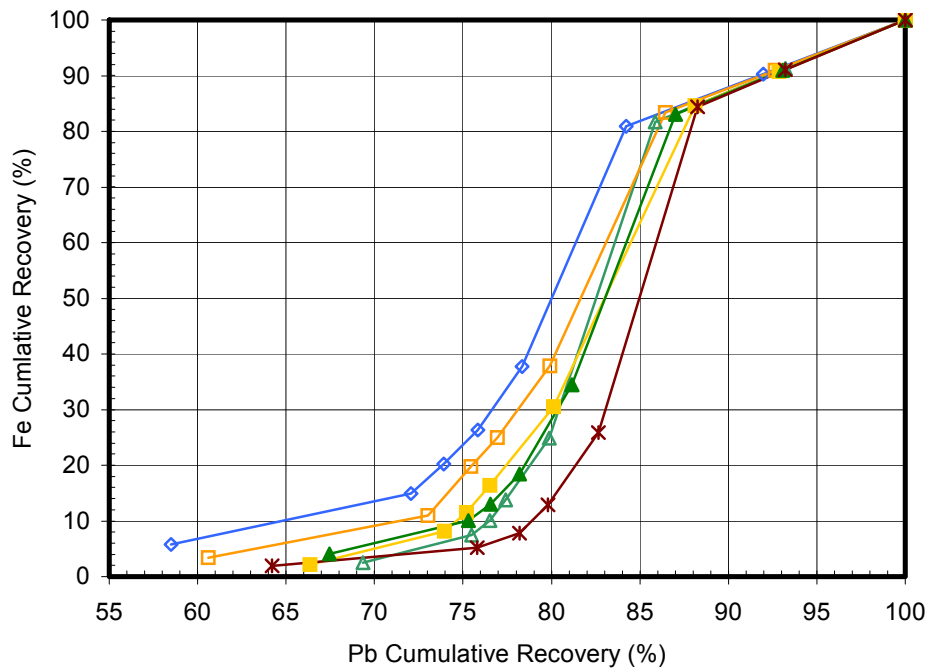
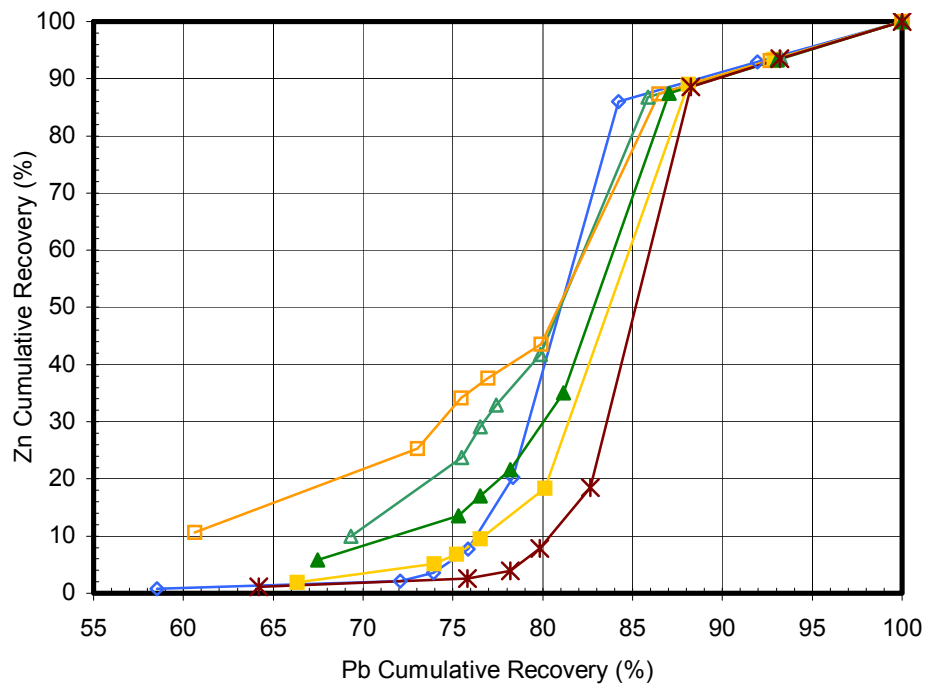


Figure 4.29 Iron Selectivity Curves for Flotation Tests Investigating the Effect of Zinc Sulfate and Iron Sulfate as Depressants*



* Refer to Figure 4.27 for Legend

Flotation tests to explore the use of zinc sulfate or zinc sulfate–iron sulfate with standard cyanide additions were successful in improving zinc selectivity, whilst maintaining iron selectivity at a reasonable level. In all cases where zinc (II) ions were added to the pulp, selectivity has only improved during the lead flotation process. Flotation tests attempting to reduce cyanide use by supplementing it with zinc sulfate or a combination of zinc sulfate–iron sulfate were not successful with poorer selectivity observed for both zinc and iron. It is possible that when zinc (II) or iron (II) ions are added to the pulp as zinc sulfate and iron sulfate with a reduced amount of cyanide, the cyanide salts that form between the two reagents result in an insufficient amount of these depressants in the pulp for sphalerite or pyrite depression. An attempt to supplement cyanide with iron sulfate alone resulted in very poor selectivity for both zinc and iron, showing that whilst zinc (II) ions added to the pulp as zinc sulfate can improve the depression of sphalerite (ZnS), iron (II) ions added as iron sulfate showed no similar improvement in the depression of pyrite (FeS₂).

4.5.5 The Effect of Zinc Sulfate during Lead Flotation

Lead circuit flotation feed samples were collected from the Century Mine concentrator and used in laboratory flotation tests to examine the effect of the addition zinc sulfate on selectivity during lead flotation. The samples were collected following the procedures in Section 3.1.4.

The laboratory scale batch flotation tests were carried out following the procedures in Section 3.4.3, except that 0, 20, 30 and 50 g/t of zinc sulfate were used as the depressant. The flotation test using 30-g/t of zinc sulfate was conducted so that the

zinc sulfate was added in stages with 20 g/t added during the lead rougher conditioning stage and 10 g/t added during the first lead cleaner conditioning stage. The lead grade–recovery and zinc selectivity curves for the flotation tests are plotted in Figures 4.30 and 4.31. The supporting data are shown in Appendix 4.23.

Figure 4.30 Lead Grade–Recovery Curves for Lead Circuit Flotation
Tests to Test the Effect of Zinc Sulfate

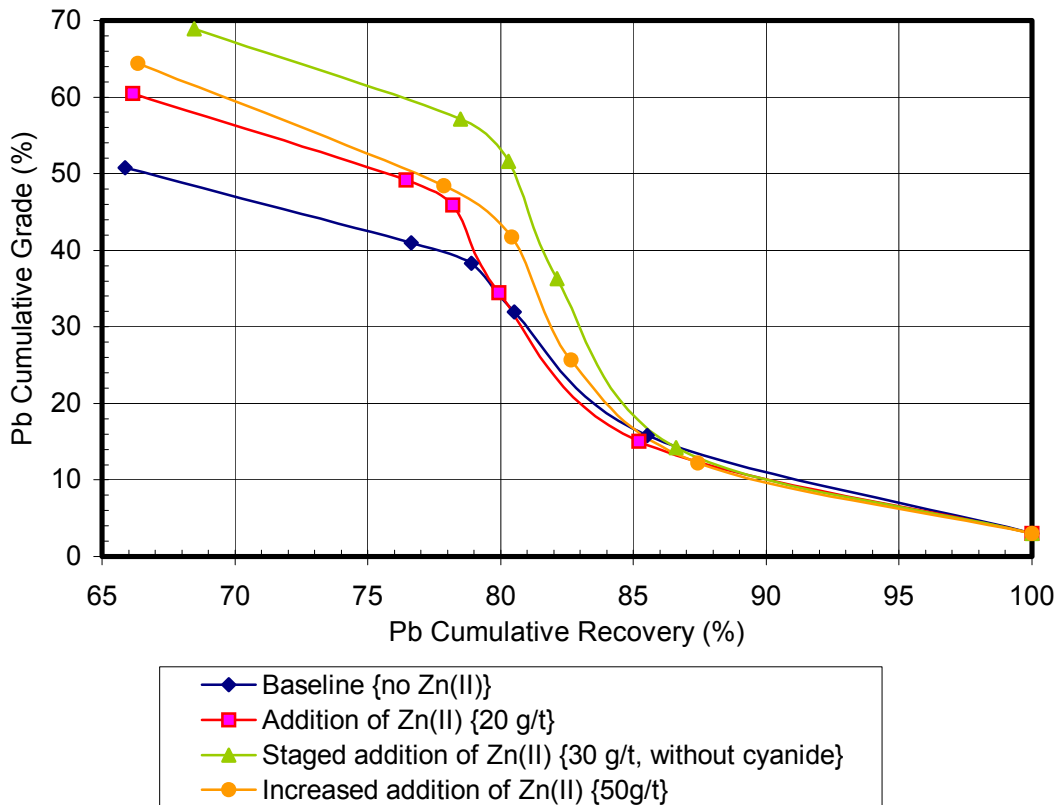
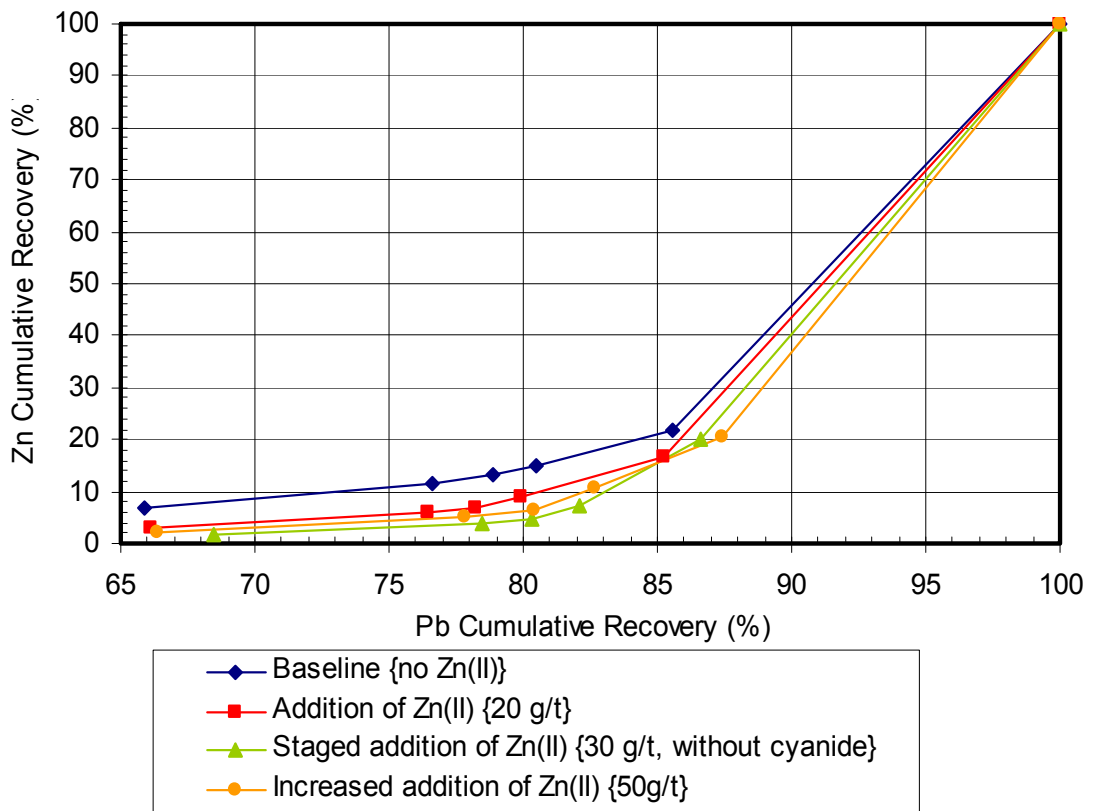


Figure 4.31 Zinc Selectivity Curves for Lead Circuit Flotation Tests to Test the Effect of Zinc Sulfate



The lead grade–recovery curves and zinc selectivity curves clearly show that the use of zinc sulfate was more effective than cyanide in the depression of sphalerite in the lead circuit of the laboratory flotation test. The selectivity curves for iron, silica and carbon are shown in Appendix 4.24. These did not change between the various tests indicating that the depressive action of zinc sulfate is specific to sphalerite. The staged addition of 30 g/t of zinc sulfate without cyanide was the most effective among all the tests, including the addition of 50 g/t of zinc sulfate in a single stage before commencing lead flotation, showing that staged additions can reduce reagent use. These results suggest that a long conditioning or residence time in the pulp is not critical for the depressive effect of zinc sulfate and that excess reagent added to the lead circuit feed is probably lost to the lead rougher tailing.

The significant improvements to lead flotation in the laboratory test through the use of zinc sulfate may be achieved at plant scale by another means since zinc sulfate has not been used as a depressant in the Century Mine concentrator since the first year of production. The main differences between the process flowsheets for the laboratory tests and plant scale lead flotation are the inclusion of froth washing in the first lead cleaner stage and the recirculation of the lead cleaner tailings to the head of the previous stage. The laboratory scale flotation test is a batch flotation process in which these techniques could not be reproduced. Froth washing is effectively a means of secondary concentration and it is possible that the depressing action of zinc (II) was related to the advantages that froth washing offers towards improving selectivity in the plant.

Zinc sulfate can bring about coagulation by precipitating zinc hydroxide at pH 10.5. This is used to separate soluble organic matter in analytical chemistry procedures, such as biodegradable soluble COD (Mamais et al. 1993). The destabilisation of suspensions by the addition of electrolytes and hydrolysable metal ions which bring about coagulation has also been described by the American Cyanamid Company (Mining Chemicals Handbook 1986, p. 118). The pulp in lead flotation is alkaline and it is possible that zinc hydroxide specifically coagulates inorganic compounds such as zinc sulfide that are present as finely sized sphalerite. These coagulated sphalerite particles are less likely to be entrained in the froth owing to their increased size and the mechanism of depression may be therefore similar to secondary concentration by froth washing. This action of zinc sulfate is likely to be specific to sphalerite as the selectivity of other inorganic minerals such as pyrite was not observed to change with increasing zinc (II) concentration.

The recovery of sphalerite as fine particles (approximately 2 μm) in the baseline flotation test is shown in Section 4.3.3 to be only about 1–2% of all sphalerite in the flotation feed. Figure 4.7 shows that another 6% of all the sphalerite was recovered during lead flotation as intermediate particles of approximately 10–30 μm in size (C4–C2 fractions). The use of zinc sulfate led to an improvement in selectivity that was much greater than what could be achieved by reducing the recovery of fine sphalerite particles. The zinc recovery decreased by as much as 6% (absolute) with the effective use of zinc sulfate when compared with the baseline flotation test. Clearly, the depressing effect of zinc sulfate includes the depression of intermediately sized sphalerite particles that were possibly present as complex composites including galena, pyrite and silica.

Intermediate particles, most of which are present as mineral composites, are less likely to react with the collector (xanthate) as only parts of the surface would be amenable to forming stable mineral–xanthate bonds. Any surface covered with zinc hydroxide precipitate would further inhibit any strong bond between the mineral particle and collector to result in the flotation of the particle. Thus, the precipitation of zinc hydroxide on the surface of sphalerite particles by the addition of zinc sulfate to an alkaline pulp must result in depression in two possible ways: (a) the coagulation of fine sphalerite particles which decreases the efficiency of transport into the froth, and (b) precipitation that results in coating of the sites on the surface of composite galena–sphalerite particles so that collector adsorption is insufficient for flotation to occur. The depression of sphalerite in the concentrator, where only froth washing is used, may still be consistent with these mechanisms of depression for intermediate particles by the addition of zinc sulfate, as it is possible that froth

washing may also further reduce the recovery of particles where the mineral–collector interaction is not very strong.

4.6 Summary of the Chapter

A test sample was prepared to closely represent the chemical and mineral content of a typical concentrator head grade at Century Mine, which was then appropriately divided into portions for the flotation tests. Further test samples were collected from the concentrator pre-flotation and lead circuits. The most significant results from the tests conducted with the test sample and samples collected from the concentrator are as follows:

- a low lead grade and trace amounts (< 100 g/t) of impurity metals including copper, cadmium and bismuth, indicate that sphalerite activation by lead (II) and other 2+ metal ions is probably less significant than for other ores;
- mineral distributions were determined to be roughly even across the size fractions in the grind product with slightly increased amounts of each mineral in the fine (C7) and intermediate ($-53\mu\text{m} +\text{C1}$) size fractions;
- QEM–SCAN was used to determine the average grain sizes and mineral associations for the main components of the ore. Galena was found to exist as coarse (87 μm) grains, while sphalerite, pyrite and quartz were much finer (16–42 μm). The sphalerite associations with other minerals were more significant, with other minerals than that with galena due the latter’s low concentration in Century Mine ore. Galena on the other hand was found to have a relatively significant association with sphalerite as well as the gangue minerals;

- the reproducibility of the results of the baseline flotation tests was very good and the concentrates and tailings were chemically similar to those in the concentrator, except that a higher sphalerite recovery was observed during lead flotation in the laboratory test;
- chemical–size distribution analyses of the pre-flotation concentrate showed that sphalerite recovery increases almost linearly with decreases in particle size. The recoveries of the other main mineral components were similar for the laboratory test and the plant, except for pyrite, which had a significant intermediate-size particle recovery. The sphalerite recovery was observed to be typically less than water recovery indicating that entrainment in the froth is the most significant mechanism for the recovery of sphalerite. The remainder of the recovery was found to be most likely due to hydrophobicity enhanced by mineral oxidation and the formation of elemental sulfur or polysulfides on the sphalerite surface, and possibly of graphitic inclusions in the sphalerite particles;
- chemical–size distribution analyses of the lead concentrate showed that the sphalerite recovery was most significant for intermediate particles (approximately 14–26 μm). An increase in galena recovery was observed in this size range, whilst gangue minerals recovery was at or below water recovery. This indicates that the sphalerite was predominantly recovered during lead flotation due to composite particle flotation with galena. To a lesser extent, some fine (approximately 2–6 μm) sphalerite particle flotation was observed to be higher than water recovery, indicating the possibility of surface activation and subsequent interaction with the collector, or hydrophobicity due to surface oxidation, on sphalerite particles which were probably liberated;

- flotation tests to determine the effect of the primary grind size of the flotation feed indicated that the optimum grind size was 80% passing 40 μm . With this grind size, both the lead grade–recovery and zinc selectivity were improved, most probably due to liberation of some of the sphalerite–galena composite particles;
- flotation tests with different pulp densities during the pre-flotation rougher stage indicated that as the pulp density decreases the carbon grade and zinc, lead, iron and silica selectivity improved and the optimum pulp density was found to be 20% solids. A plot of zinc recovery versus mass recovery for all of the flotation tests confirmed that zinc recovery during pre-flotation was directly proportional to mass recovery and implies that sphalerite recovery is significantly due to entrainment in the froth;
- EDTA extraction tests to determine the extent of mineral oxidation in both laboratory and concentrator streams indicated that galena is the only main sulfide mineral that is significantly oxidized during flotation. The oxidation of galena mainly occurred in the pre-flotation rougher feed, lead rougher feed, and lead rougher tail with further oxidation during pre-flotation, which is the first flotation stage. The significant amount of oxidized galena in the pre-flotation concentrate indicated that this may be responsible for the galena and sphalerite recovery not accounted for by entrainment in the froth;
- results of the flotation tests with various pulp pH values showed that lead flotation improved due to better zinc and iron selectivity when the pH were either higher or lower than the baseline conditions. An increased alkalinity was particularly selective against pyrite flotation and it was determined that the pre-

flotation circuit is better operated at natural pH (pH 6.1–8.2) and the lead circuit is better operated with an increased alkalinity (pH 9.5);

- flotation tests with lower addition of frother (MIBC) indicated that excessive amounts of MIBC are being added to the standard laboratory test and possibly the plant, with an improvement in carbon grade–recovery and zinc, lead, iron and silica selectivity observed as MIBC additions were reduced to 100 g/t. The results suggested that excessive MIBC use results in bulk flotation and that the reagent addition is proportional to total mass recovery;
- flotation tests to test the use of cyanide as a depressant found that it is sufficiently added in the baseline flotation test and that any increase in cyanide addition was observed to slightly decrease lead recovery with no improvement of zinc selectivity. Cyanide was identified as a critical depressant because without using it the flotation test results were poor, except when replaced by zinc sulfate;
- flotation tests examining the effect of zinc sulfate as a depressant indicated that zinc sulfate alone depresses sphalerite particularly during lead flotation, where an optimum amount of 30 g/t was found to be effective. However, the best results were achieved when it is used in combination with cyanide, which is essential for pyrite depression;
- flotation tests examining the effect of iron sulfate as a depressant either alone or in combination with cyanide and zinc sulfate were not successful in improving either sphalerite or pyrite selectivity; and
- the findings that zinc sulfate is a suitable depressant during lead flotation at laboratory scale was confirmed using plant samples collected from the lead circuit feed. Composite particles consisting galena and sphalerite are the main cause of sphalerite recovery in the baseline test and in these tests they have

clearly been depressed. The flotation test results indicated that the depressing action of zinc sulfate is specific to sphalerite and that this action is possibly comparable to the depression of entrained sphalerite by froth washing in the plant, the only difference between the laboratory test and plant flowsheets. It has been suggested that zinc sulfate may also bring about the coagulation of fine sphalerite particles, which may be sufficient to decrease the probability of sphalerite particle entrainment in the same way as froth washing.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The depression of sphalerite during carbon pre-flotation and lead flotation at the Century Mine Concentrator was investigated. The aim of this study was to gain a better understanding of the selectivity in lead-zinc flotation in general and at this operation in particular. Specifically, it was aimed to (a) review studies related to selectivity in lead-zinc flotation, (b) identify the mechanisms involved in sphalerite recovery during pre-flotation and lead flotation, (c) determine the variables that affect the flotation of sphalerite during pre-flotation and lead flotation, (d) identify depressants for sphalerite that offer better selectivity during pre-flotation and lead flotation, (e) generate data that are directly relevant to the Century Mine concentrator, and (f) contribute to the knowledge and understanding of the effect of depressants on the recovery of sphalerite during pre-flotation and lead flotation.

The experimental results of the present study indicate that:

- the activation of sphalerite by lead (II) and other 2+ metal ions was less significant at the Century Mine concentrator than those of other lead-zinc ores due to the relatively low Pb grade and the low abundance of minerals containing 2+ metal ions such as copper, cadmium, bismuth and mercury that are known to activate sphalerite;
- the recovery of sphalerite to the pre-flotation concentrate, as shown by the mineral-size distribution results, increased almost linearly with decreases in

particle size and it was typically less than water recovery for all particles sizes indicating that entrainment in the froth was the most significant mechanism for the recovery of sphalerite;

- any sphalerite recovery during pre-flotation not attributed to entrainment in the froth was found to be most likely due to hydrophobicity enhanced by the presence of graphitic inclusions or the formation of elemental sulfur or polysulfides on the sphalerite surface;
- the recovery of the other main mineral components during pre-flotation was similar to sphalerite, except pyrite for which there was a significant intermediate-size particle recovery;
- the recovery of sphalerite to the lead concentrate, as shown by the mineral–size distribution results, was significant for intermediate particles (approximately 14–26 μm). An increase in galena recovery in this size range whilst gangue minerals recovery was at or below water recovery indicated that sphalerite was predominantly recovered due to composite particle flotation with galena. Other results that support these findings include:
 - (a) QEM–SCAN analyses showed that galena grains in the ore have a significant association with sphalerite and the gangue minerals, and despite the relatively low abundance of galena in Century ore, the presence of galena–sphalerite composite particles during lead flotation remains significant as only a small amount of galena in these particles would be required to react sufficiently with the collector for recovery.
 - (b) the mineral distributions in the sample after grinding ($P_{80} = 58 \mu\text{m}$) were slightly increased for intermediately size particles (10–20%).

- (c) the optimum grind size for the ore sample was 80% passing 40 μm and the improvement in both lead grade–recovery and zinc selectivity were due to the liberation of some of the sphalerite–galena composite particles, which were primarily responsible for sphalerite recovery during lead flotation;
- to a lesser extent, some fine (approximately 2–6 μm) sphalerite particle recovery during lead flotation was observed above water recovery, indicating the possibility of surface activation and subsequent interaction with the collector, or hydrophobicity due to surface oxidation on sphalerite particles which were probably liberated;
 - the extent of mineral oxidation in both the laboratory and concentrator flotation processes was only significant for galena, particularly during pre-flotation. The mineral oxidation may be responsible for recovery of liberated galena and sphalerite not accounted for by entrainment in the froth;
 - decreasing the pulp density during pre-flotation coincided with an improvement in the carbon grade and zinc, lead, iron and silica selectivity. The zinc recovery was directly proportional to mass recovery indicating that a bulk recovery effect was occurring;
 - the bulk recovery of minerals occurred as excessive amounts of MIBC were being added to the pre-flotation stage of the standard laboratory test and possibly the plant, with an improvement in carbon grade-recovery and zinc, lead, iron and silica selectivity observed as MIBC additions were reduced to 100 g/t;
 - variations to pulp pH showed that both an increase or decrease in pulp pH improved the zinc and iron selectivity and it was shown that the pre-flotation circuit was best operated at natural pH (pH 6.1–8.2) and the lead circuit operated at elevated alkalinity (pH 9.5);

- the addition of cyanide as a depressant was found to be sufficient and any increase was observed to slightly decrease lead recovery with no improvement of zinc selectivity. However, any decrease in cyanide resulted in decreased selectivity, except when replaced by zinc sulfate;
- the use of zinc sulfate as a depressant indicated that zinc sulfate alone depresses sphalerite particularly during lead flotation, however, the best results were achieved when it was used in combination with cyanide which was essential for pyrite depression;
- the use of iron sulfate as a depressant either alone or in combination with cyanide and zinc sulfate was not successful in improving either sphalerite or pyrite selectivity in the flotation of Century ore; and
- it is well known that in an alkaline pulp, zinc sulfate dissociates to form zinc hydroxide precipitates, which can adsorb onto the sphalerite surface. The results of the present study indicate that this adsorbed species may also coagulate fine sphalerite particles leading to a decrease in the probability of entrainment in the froth similar to froth washing.

5.2 Recommendations and Future Research

Whilst the aims of the present study were achieved, the study led to a number of questions, the study of which would lead to a better understanding of flotation of lead-zinc ores. The following suggestions are made:

- an investigation to determine the best approach of reducing sphalerite recovery during pre-flotation by: (a) reducing MIBC additions, (b) a trial of other frothers which may further improve selectivity, (c) careful control of aeration down the bank of flotation cells, including air starvation in the early cells, and (d) further

examine the requirement for a cleaner flotation stage using techniques such as column flotation and froth washing;

- an investigation on the use of zinc sulfate in sphalerite depression during lead flotation to reduce the Century concentrator's process flowsheet to a single cleaning stage, as practised at other processes such as Teck-Cominco's Red Dog, whilst maintaining a low-level of sphalerite recovery; and
- an investigation to determine whether the use of sodium sulfite or metabisulfite combined with either zinc sulfate or cyanide are suitable as sphalerite depressants at Century Mine. Sodium metabisulfite has been successfully used in combination with zinc sulfate during a talc pre-flotation stage at BHP-Billiton's Cannington Mine and other operations have used it in combination with cyanide.

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Appendix 1.1 Aerial Photograph of the Century Mine Pit



Appendix 1.2 Aerial Photograph of the Century Mine Concentrator Area



Appendix 1.3 Photograph of the Grinding Area



Appendix 1.4 Photograph of the Northern Side of the Concentrator



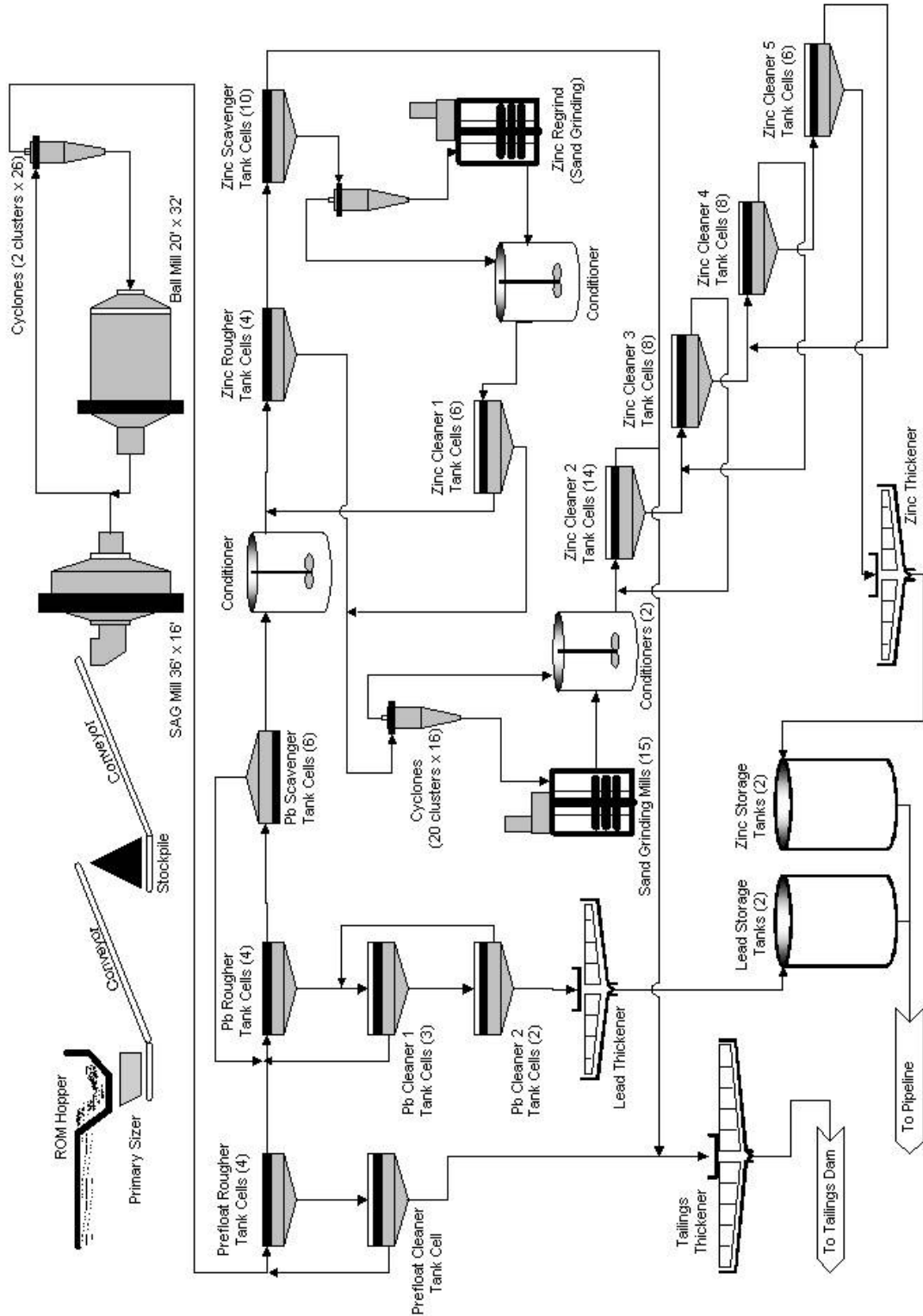
Appendix 1.5 Photograph of the Southern Side of the Concentrator



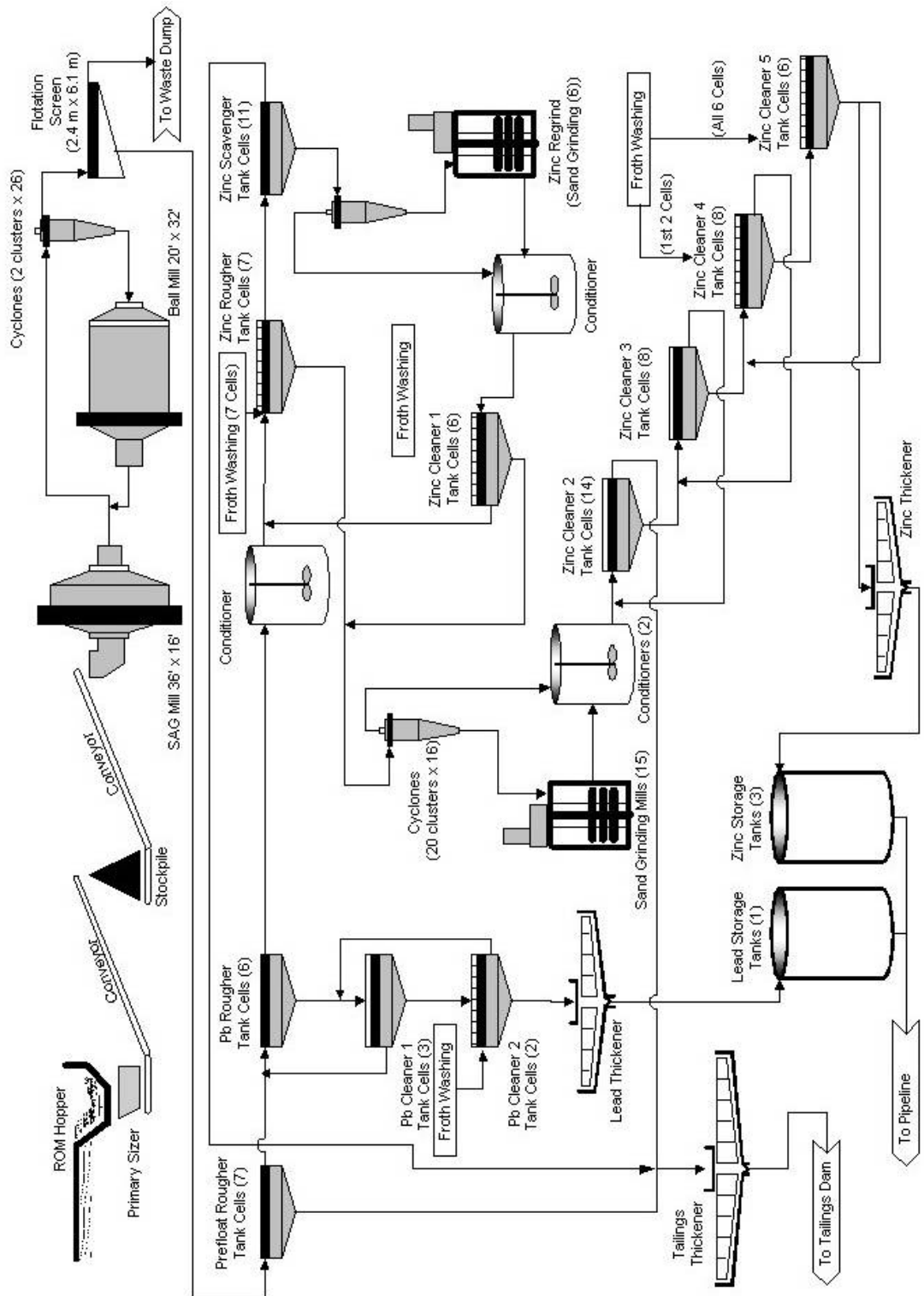
Appendix 1.6 Photograph of Outokumpu® OK-200 Flotation Cell



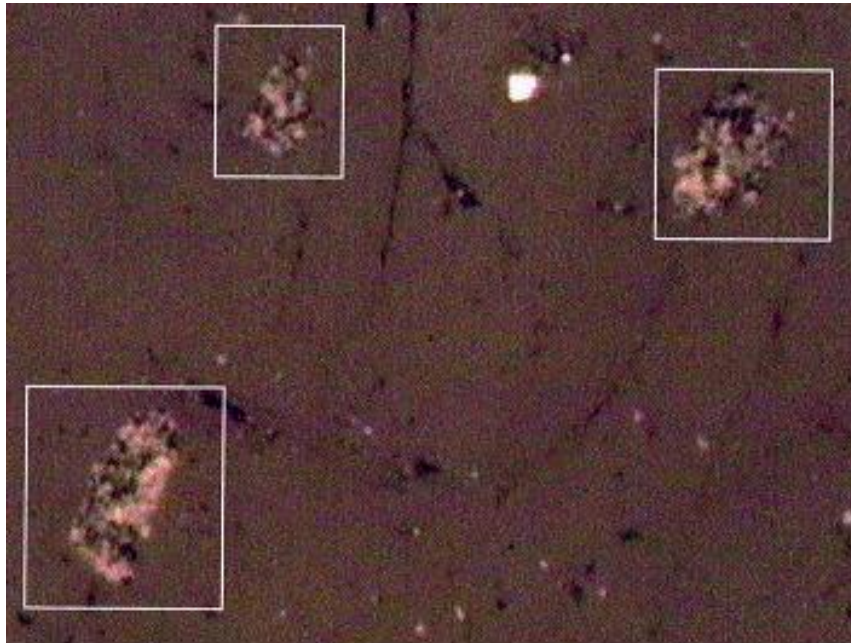
Appendix 1.7 The 1999 Concentrator Process Flowsheet (Commencement of Operations)



Appendix 1.8 The Current (2003) Process Flowsheet (at Full Production)

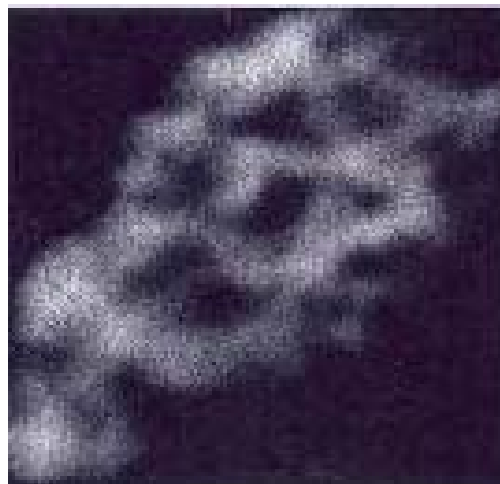


Appendix 2.1 Photomicrograph of Sphalerite Particles with Graphitic Inclusions* (Butcher and Gottlieb 1999a)



** The brownish grey–grey black phases on the sphalerite particles (approximately +7–12 microns) have been identified as graphite. The bright phases are pyrite.*

Appendix 2.2 Back Scattered Electron Micrograph of a Sphalerite Particle with Graphitic Inclusions* (Butcher and Gottlieb 1999a)



** The bright areas in the image are sphalerite and the dark areas mainly consist of graphite.*

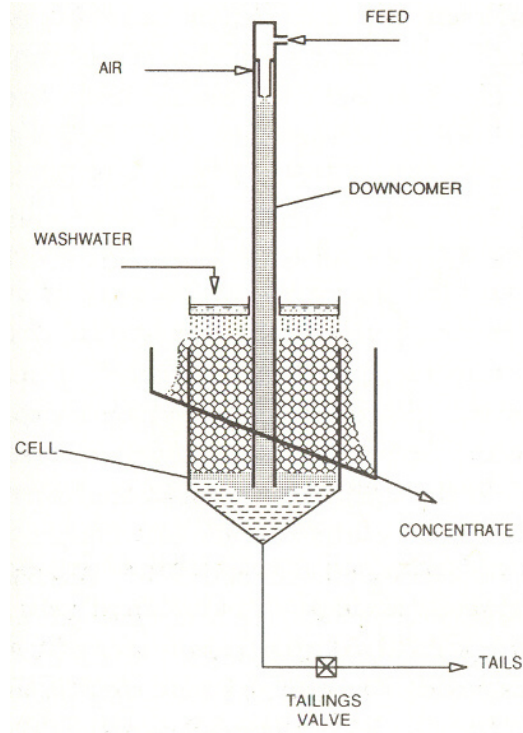
Appendix 2.3 Photograph of Froth Washing Trays



Appendix 2.4 Photograph of the Water Supply System in Froth Washing



**Appendix 2.5 Schematic Drawing of the Jameson Flotation Cell (Wills
1992, p 561)**



Appendix 3.1 Photograph of the Century Mine ROM Pad



Appendix 3.2 Photograph of the Sampling Apparatus for Primary Cyclone Overflow Sampling



Appendix 3.3 Photograph of the MSA Sampling Points



Appendix 3.4 Photograph of the Sampling Apparatus for MSA Sampling



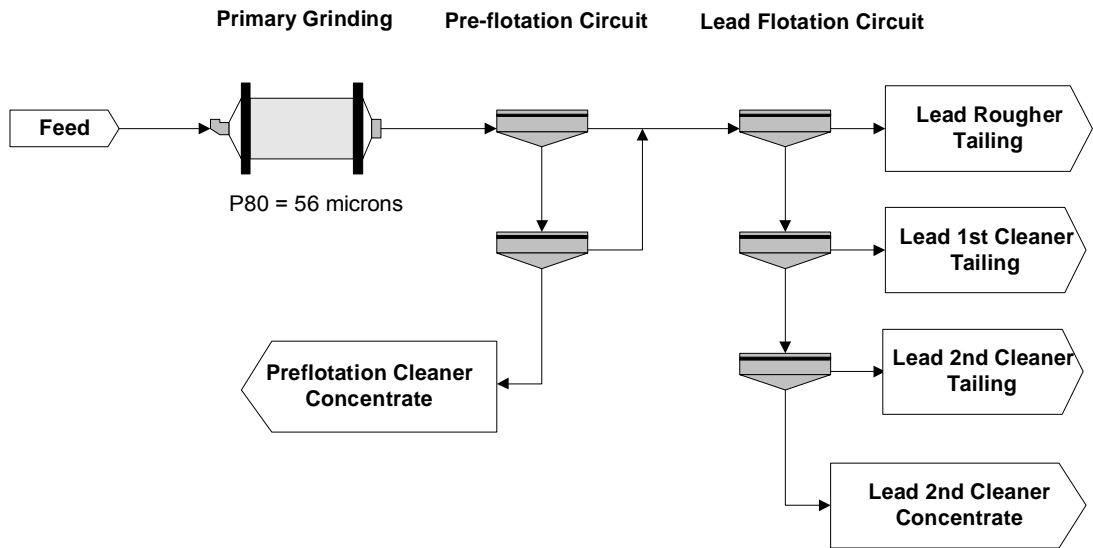
Appendix 3.5 Lead, Zinc, Iron and Copper Contents* of Century

Laboratory Tap Water

Pb (mg/L)	Zn (mg/L)	Fe (mg/L)	Cu (mg/L)
0.03	0.10	0.03	< 0.03

* Assays were performed by Atomic Absorption Spectrometry (AAS) at Redland Water and Waste Laboratory, Water Treatment Plant, Willowie Crescent, Capalaba QLD 4157

Appendix 3.6 The Process Flowsheet for the Laboratory Flotation Tests



Appendix 3.7 Photograph of the Laboratory Flotation Machine and Cells



Appendix 3.8 Photograph of the Pre-cyclone, Cyclosizer and Centrifuge



Appendix 3.9 Procedure for X-Ray Fluorescence (XRF) Spectrometry

The test sample was prepared for analysis by fusion of the sample to produce a borosilicate glass bead. A test portion of 0.30 g was added to 7.80 g of 12:22 Norish flux (5% sodium nitrate, 35.3% lithium tetraborate, lithium metaborate) in a platinum crucible. All weights were determined using a 4-place analytical balance (Mettler Toledo[®]). The combined sample and flux was mixed using a glass rod and the crucible placed in a muffle furnace (700 °C) for 25 minutes. The crucible was transferred to an automated fusion machine (Automated Fusion Technologies Phoenix 6000[®]) shown in Figure 1 using platinum tipped tongs.

The automated fusion machine was fitted with platinum-gold alloy moulds (95% Pt, 5% Au). The instrument pre-melt stage was set at 3 minutes and the swirling stage

was set at 6 minutes. The sample was then fused in a reducing oxygen-propane flame (1050 °C, Mikron[®] M90 Portable Infra-Red Thermometer). A 20-mg ammonium iodide pellet (Ammonium iodide pressed with a starch binary, Automated Fusion Technologies[®]) was added to the melt at the start of the swirling cycle. At the end of the swirling cycle the melt was poured into the platinum-gold alloy mould preheated to 1050 °C. The mould was cooled by a rapid stream of compressed air (0.65 MPa) for 1 minute and then allowed to cool at room temperature until cool enough to touch.

The borosilicate bead produced was removed from the mould, labelled and transferred to the automated loader racks on top of an XRF Spectrometer (Phillips 2404[®] Sequential XRF Spectrometer controlled with Phillips SuperQ[®] software on an external PC) shown in Figure 2. The surface of the bead in contact with the mould was used as the analytical surface during the analysis. The flux and sample weights were transferred to the SuperQ[®] software prior to the commencement of the analysis. After the analysis, all beads were stacked and sealed in specimen sample jars, such that any analytical surface was in contact with the analytical surface of another bead. If the bead was required to be analysed again, the analytical surface was cleaned with absolute ethanol (BDH AnalaR[®]) using Kimwipe[®] tissue paper.

Appendix 3.10 Procedure for Atomic Absorbance Spectrometry (AAS)

Solid samples were prepared for analysis by dissolution using in concentrated hydrochloric and nitric acids, and hydrogen peroxide solution. Aqueous samples were acidified using concentrated nitric acid. A microwave accelerated reaction

system (CEM MARS-5[®]) was used to digest samples. All analyses were carried out following standard Pasmenco Century Mine Laboratory Procedures (1999).

All solutions were prepared following standard procedures (Pasmenco Century Mine Laboratory Manual 1999).

Dilute hydrogen peroxide solution (15% w/v) was prepared by adding 500 mL of hydrogen peroxide solution (30% w/v, AJAX) to 500 mL of deionised water in a 1-L Pyrex[®] glass bottle.

Dilute hydrochloric acid (16% w/v) was prepared by adding 500 mL of hydrochloric acid (32% w/v, BDH AnalaR[®]) to 500 mL of deionised water in 1-L Pyrex[®] glass bottle.

Standard solutions for Atomic Absorption Spectrometry (AAS) were prepared from 1000-mg/L standard solutions (Australian Chemical Reagents[®]) for all elements except iron. A 10000-mg/L standard solution (Australian Chemical Reagents[®]) was used for iron standard preparation. A 100-mg/L standard solution was prepared for each element from these reagents. All standard solutions used in the calibration of the AAS were then prepared from the 100-mg/L standard solutions. These solutions prepared were stored and used for 6 months. Any solution remaining was then discarded and a new standard prepared.

All calibrations standards were aspirated by the Varian SpectrAA 50[®] AAS and the absorbance checked against standards previously used by the laboratory.

The test portion taken from solid samples was 0.50 g weighed using a three-place analytical balance (Ohaus Explorer[®]). The test portion was transferred to a teflon

reaction vessel (CEM HP500 plus[®]). An 10-mL aliquot of hydrochloric acid (32% w/w BDH AnalaR[®]) was added to the sample followed by an 10-mL aliquot of nitric acid (68% w/w BDH AnalaR[®]) and 2-mL aliquot of hydrogen peroxide solution (15% w/v) with swirling between reagent additions. Once the evolution of brown fumes had ceased, the vessel was fitted with a lid containing a new CEM rupture disk. The vessels were fitted in support modules with Kevlar collars and positioned on the instrument carousel. The control vessel was fitted with the fiber optic temperature probe and the carousel placed in the instrument cavity. The samples were digested for 12 minutes at full power (1200 W) to ramp the reaction temperature to 200 °C with a further 12 minutes holding at 200 °C and a 5-minute cooling stage.

The test portion taken for the preparation of aqueous solution samples was 50 mL measured accurately using a 50-mL pipette (Emil[®] A grade). The test portion was transferred to a teflon vessel (CEM HP500 plus[®]). A 5-mL aliquot of nitric acid, 68% w/v (BDH AnalaR[®]) was added to the sample. The vessels were assembled on the carousel and placed in the instrument as described previously for the microwave digestion of solid samples. The samples were digested in the microwave with 10 minutes at full power (1200 W) to ramp the reaction temperature to 170 °C with a further 10 minutes holding at 170 °C and a 5-minute cooling stage.

After the completion of the microwave digestion program, the vessels were removed from the microwave and cooled to room temperature inside a fume cupboard. The vessels were vented and removed from the support modules and Kevlar collars. The lids were removed from each vessel and the underside rinsed with deionised water back into the vessel. Approximately 50 mL of deionised water was added to each

vessel. All test solutions were quantitatively transferred to 100-mL volumetric flasks (Emil[®] A grade) and diluted to 100 mL with deionised water. A portion of the test solution was transferred to a test tube and sealed with a plastic stopper until ready for analysis.

A Varian SpectrAA 50[®] Atomic Absorption Spectrometer, equipped with Varian software and a Varian SPS-5[®] auto-sampler, was used to analyse test solutions and determine the metal concentration in the sample. The instrument parameters for all of the analysed elements are detailed in Table 1.

Table 1 Instrument Parameters for AAS Analysis

Element	Ag	Zn	Pb	Fe
Wavelength (nm)	328.1	213.9	283.3	372.0
Lamp Current (mA)	4	5	5	5
Slit Width (nm)	0.5	1.0	0.5	0.2
Flame Stoichiometry	Air-C ₂ H ₄	Air-C ₂ H ₄	Air-C ₂ H ₄	N ₂ O-C ₂ H ₄
Background Correction	On	On	Off	Off

The instrument pre-read delay was set to 10 seconds and the measurement time was 3 seconds. A Varian deuterium lamp was used in conjunction with hollow cathode lamp when background correction was required. The instrument was optimised and calibrated using aqueous standard solutions with a hydrochloric acid 10% w/v matrix. The standard solutions were prepared using standard Pasmenco Century Mine Laboratory Procedures (1999). A calibration re-slope was carried out after the analysis of every 10 test solutions. The instrument was recalibrated during large runs after 60 analyses.

Appendix 3.11 Procedure Complete Combustion–Infra Red (IR)

Absorption Analysis

Solid samples were analysed for carbon and total organic and elemental carbon (TOEC) contents by complete combustion–Infra Red Absorption Spectrometry using a Leco SC-444DR[®] Carbon-Sulfur Analyser. The sample was completely combusted in an electric furnace purged with industrial grade oxygen gas (98% purity, BOC Gases[®]) and the generated carbon dioxide and sulfur dioxide gas concentrations were analysed in a series of Infra Red absorption cells. In the current study the instrument was only used to measure carbon dioxide concentrations.

A 0.35 g test portion was weighed accurately for all analyses using a 4-place analytical balance (Sartorius[®]). The test portion was weighed directly into a ceramic boat.

If TOEC analysis was required, a second test portion was weighed into a ceramic boat lined with nickel foil. A 2-mL aliquot of hydrochloric acid 16% w/v was added and the boat was heated on a hotplate (100 °C) until the liquor was reduced to dryness.

All boats were loaded into the Leco furnace using a Leco autoloader. The principle instrument settings used are detailed in Table 1.

Table 1 Instrument Parameters for the Leco Carbon Sulfur Analyser

Furnace temperature (°C)	1350
Maximum analysis time (s)	180
Oxygen lance delay (s)	20
Oxygen lance flow (psi)	0.2
Oxygen purge flow (psi)	4.8
Analyse flow (psi)	3.7

The instrument was calibrated using various test portions of calcium carbonate (Leco[®] part number 501-034, 12.00% carbon).

Magnesium perchlorate (Leco[®]) was used as a drying agent in the furnace reagent tubes. Halogen scrubber (Leco[®]) was used to replace half of the magnesium perchlorate in the first reagent tube during TOEC analysis.

Appendix 3.12 Total Uncertainty (U₉₅)* of Century Laboratory Assays

Analyte	Ore (head grade) U ₉₅	Ore/Tailings (low grade) U ₉₅	Pb Concentrate U ₉₅
Pb	0.09	0.05	1.89
Zn	0.30	0.20	0.12
Fe	0.11	0.10	0.09
SiO ₂	0.85	0.79	0.79
S	0.28	0.14	0.39
Ag	17	14	15
C	0.10	0.04	0.09

* All calculated uncertainty data are ± % (absolute) except Ag which is ± g/t

Appendix 4.1 Preparation of Century Mine Ore Weighted Composite

Lot ^{1,2}	Available Mass (kg)	Composite Mass (g)	Zn (%)	Pb (%)	Fe (%)	SiO ₂ (%)	Ag (g/t)	C (%)
1	9.8	2004	7.05	10.10	1.71	66.6	128	3.40
2	13.0	999	28.64	5.81	1.66	36.5	55	5.00
3	10.1	2005	6.52	6.32	1.52	67.7	157	1.81
4	9.3	3503	7.55	3.52	1.47	68.7	168	1.78
5	9.2	9205	0.76	0.48	10.90	62.1	7	2.88
6	10.7	10767	7.62	2.68	3.99	63.8	154	3.38
7	11.3	11037	0.90	0.007	2.74	70.2	< 5	1.84
8	11.3	11286	18.06	1.34	3.15	52.9	271	2.96
9	12.0	11883	8.21	9.37	3.49	60.1	97	3.12
10	11.0	10994	17.29	0.36	7.38	40.9	< 5	3.43
11	11.3	8504	25.48	0.23	5.80	34.6	< 5	4.33
12	13.1	3002	32.06	0.60	5.48	27.4	7	4.12
13	11.1	6007	27.37	0.30	5.01	32.1	< 5	4.69
14	12.4	2500	35.45	0.46	3.78	27.6	117	3.66
15	9.5	6333	0.57	0.95	19.30	40.3	< 5	4.00
16	9.8	2801	10.19	1.78	12.60	37.0	< 5	4.00
Total/Weighted Average		102831	12.43	2.22	5.94	52.20	75	3.29
Excess +1.7 mm ³		-578	2.04	0.95	11.10	63.0	< 5	4.00
Net Weighted Average		102253	12.42	2.22	5.88	51.9	73	3.26

Notes: 1. Lots 1–7 were grab sampled from the upper zone ore stockpiles on the ROM pad and lots 8-17 were sourced from lower zone ore stockpiles. The composite therefore contains 38.4% upper zone ore and 61.6% lower zone ore and closely represents the concentrator feed (37.5% upper zone ore and 62.5% lower zone ore).

2. Lots 5, 7 and 16 contain minimal zinc or lead mineralisation and represent 25% of the composite sample. This is typical of Century ore where approximately 20% of the material in each zone is barren siltstone, containing little or no zinc or lead mineralisation.

3. Excess +1.7 mm represents a small amount of material (578 g), which was not amenable jaw crushing to a particle size –1.7 mm and was excluded from the composite. Plant grinding produces a similar waste product known as scats.

Appendix 4.2 Head Grade Assay Results

TEST	Ag (g/t)	Zn (%)	Pb (%)	Fe (%)	SiO ₂ (%)	S (%)	TOEC* (%)	C _{TOTAL} (%)
1	72	12.54	2.35	5.94	52.1	11.1	2.87	3.39
2	75	12.59	2.50	5.96	51.0	11.2	2.90	3.35
3	71	12.16	2.24	5.86	51.9	10.8	2.85	3.33
4	69	12.09	2.41	5.83	52.4	10.6	2.80	3.33
5	71	12.58	2.38	5.89	52.4	11.1	2.86	3.36
6	71	12.09	2.24	5.74	51.4	10.7	2.86	3.33
7	74	12.20	2.40	5.75	50.5	10.8	2.83	3.38
8	71	12.14	2.25	5.75	51.5	10.7	2.82	3.35
9	71	12.29	2.51	5.89	50.4	11.0	2.90	3.41
10	76	12.46	2.22	5.77	51.6	10.7	2.86	3.40
MEAN	72	12.31	2.35	5.84	51.5	10.9	2.86	3.36
STD DEV	2.2	0.21	0.11	0.08	0.7	0.2	0.03	0.03

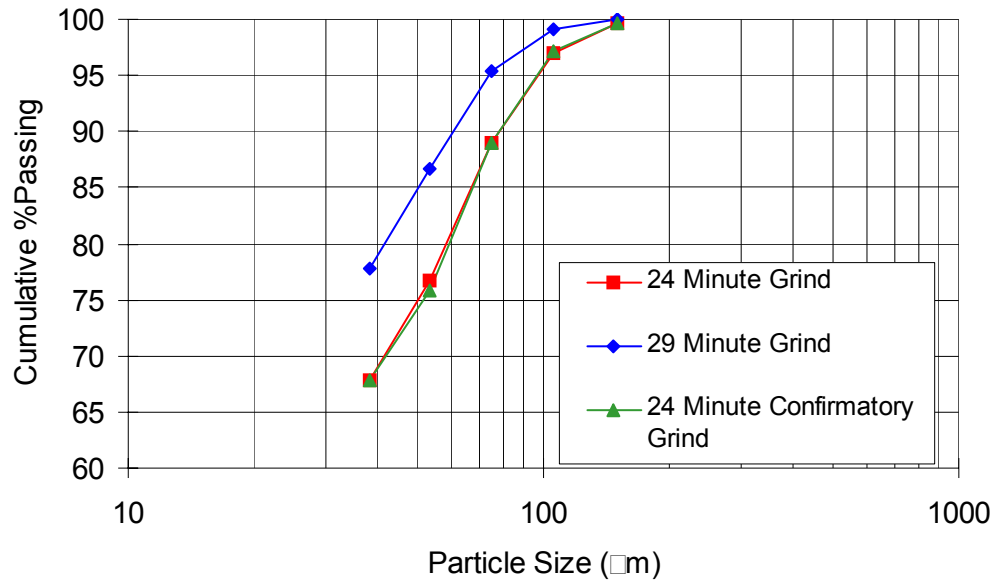
* TOEC represents Total Organic and Elemental Carbon.

Appendix 4.3 Size Distribution Data for the Grinding Calibration*

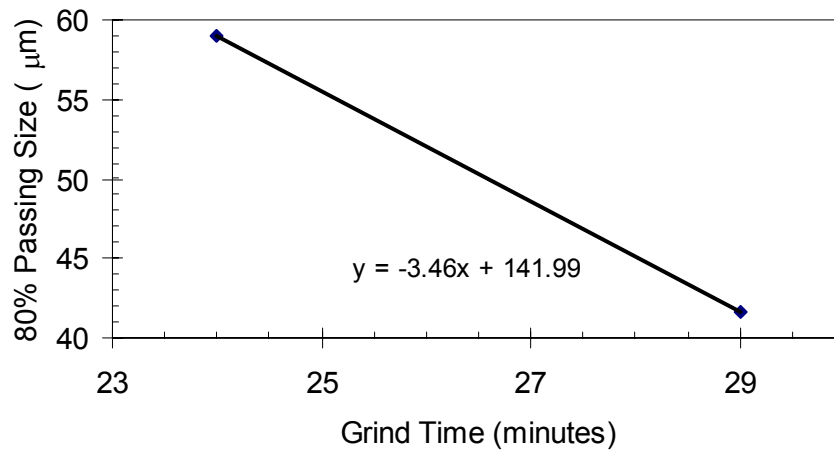
Size (µm)	Weight (g)			Nominal Aperture Size (µm)	Cumulative % Passing		
	Test 1	Test 2	Test 3		Test 1	Test 2	Test 3
-212+150	0.63	0.04	1.16	150	99.58	99.97	99.62
-150+106	3.88	1.04	7.38	106	96.96	99.08	97.20
-106+75	11.81	4.37	24.84	75	88.99	95.36	89.04
-75+53	18.28	10.20	40.33	53	76.66	86.67	75.80
-53+38	13.17	10.35	24.17	38	67.78	77.85	67.86
-38	100.49	91.39	206.70				
Total	148.26	117.39	304.58				
Calculated 80% Passing Size (µm)					58.95	41.66	59.98

*The calibration involved three tests, namely Test 1, Test 2 and Test 3, which represent the 24-minute, 29-minute, and the duplicate 24-minute grinding times, respectively.

Appendix 4.4 Size Distribution Curves for the Grinding Calibration



Appendix 4.5 80% Passing Size versus Grind Time



Appendix 4.6 Size, Weight, Grade and Mineral Distribution in the Flotation Test Feed

Fraction (µm)	%Weight	Grade (%)							Mineral Distribution* (%)						
		Ag	Pb	Zn	Fe	SiO ₂	S	C	Ag ₂ S	PbS	ZnS	FeS ₂	SiO ₂	FeCO ₃	Bitumen
+150	0.38	128	0.94	13.58	3.62	58.9	8.51	2.54	0.6	0.1	0.4	0.2	0.4	0.2	0.29
-150+106	2.42	97	1.39	14.56	3.99	55.1	9.86	3.14	2.8	1.3	2.8	1.5	2.6	1.5	2.28
-106+75	8.16	81	1.61	14.42	4.56	53.6	10.27	3.17	7.8	5.2	9.5	5.9	8.6	5.9	7.76
-75+53	13.24	93	1.79	14.49	5.20	52.8	11.05	3.17	14.6	9.3	15.5	10.9	13.8	10.9	12.60
-53+38	7.94	92	2.02	14.01	5.41	52.0	11.02	3.20	8.6	6.3	9.0	6.8	8.1	6.8	7.62
C1	5.73	191	9.14	25.26	9.89	22.8	21.79	3.09	12.9	20.6	11.7	9.0	2.6	9.0	5.3
C2	7.64	146	2.57	13.62	4.91	52.9	10.28	3.10	13.2	7.7	8.4	5.9	8.0	5.9	7.11
C3	9.06	81	2.28	11.66	4.80	55.7	9.12	3.06	8.7	8.1	8.5	6.9	10.0	6.9	8.32
C4	8.82	67	2.31	10.21	8.18	51.2	12.46	2.85	7.0	8.0	7.3	11.4	8.9	11.4	7.55
C5	4.68	57	2.12	8.41	12.20	45.6	16.21	2.51	3.2	3.9	3.2	9.0	4.2	9.0	3.53
C6	15.69	55	3.43	9.23	10.20	46.7	14.18	3.05	10.2	21.2	11.7	25.3	14.5	25.3	14.37
C7	16.24	55	1.30	9.35	2.84	57.0	5.46	4.77	10.6	8.3	12.2	7.3	18.3	7.3	23.25
Total	100.0	85	2.54	12.42	6.33	50.68	11.28	3.33	100.0	100.0	100.0	100.0	100.0	100.0	100.0

* Sample Calculations for Mineral Grade and Distribution are shown in Appendix 4.25

Appendix 4.7 Mineral Associations for the Main Gangue Minerals

Mineral	Pyrite Association (%)	Quartz Association (%)	Feldspar Association (%)
Background	16.4	16.3	19.5
Sphalerite	15.3	13.2	7.7
Galena	0.2	0.8	0.4
Pyrite	—	14.3	5.8
Pyrrhotite	0.1	Not detected	Not detected
Chalcopyrite	Not detected	Not detected	Not detected
Arsenopyrite	Not detected	Not detected	Not detected
Other Sulfides	4.4	4.7	4.1
Quartz	25.0	—	10.0
Feldspars	25.5	24.8	—
Other NSG	13.1	25.9	52.4

Appendix 4.8 Baseline Flotation Tests–Cumulative Data*

Stream	Cumulative Weight (%)			Cumulative Pb Grade (%)			Cumulative Zn Grade (%)			Cumulative Pb Recovery (%)			Cumulative Zn Recovery (%)		
	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3	Test 1	Test 2	Test 3
Pb 2 nd Cleaner Concentrate 1	3.15	3.38	3.05	49.75	46.06	48.24	22.71	22.23	21.88	66.75	68.75	65.48	5.73	6.44	5.45
Pb 2 nd Cleaner Concentrate 2	4.86	5.21	4.84	37.49	34.44	35.84	29.28	28.98	29.10	77.73	79.28	77.15	11.43	12.95	11.50
Pb 2 nd Cleaner Concentrate 3	5.33	5.82	5.39	34.86	31.55	32.92	29.83	29.72	30.13	79.28	81.02	78.98	12.77	14.81	13.28
Pb 2 nd Cleaner Tail	6.36	7.46	6.28	29.71	25.08	28.98	26.81	25.98	28.00	80.57	82.61	80.94	13.68	16.61	14.37
Pb 1 st Cleaner Tail	12.62	14.59	11.95	15.70	13.43	16.00	17.63	17.48	18.70	84.50	86.51	85.01	17.85	21.85	18.25
Pb Rougher–Scavenger Tail	95.08	95.75	95.59	2.36	2.27	2.25	12.56	11.73	12.33	95.54	96.14	95.85	95.82	96.25	96.29
P/F Cleaner Concentrate 1	96.94	97.13	97.57	2.35	2.27	2.25	12.51	11.71	12.29	97.21	97.38	97.69	97.37	97.43	97.93
P/F Cleaner Concentrate 2	100.0	100.0	100.0	2.34	2.26	2.25	12.46	11.67	12.24	100.0	100.0	100.0	100.0	100.0	100.0

** Sample Calculations for Cumulative Weight, Grade and Recovery are shown in Appendix 4.25*

Appendix 4.9 Recovery–by Size* for Pre-flotation and Lead Concentrate Size Fractions

Fraction Size	Pre-flotation Concentrate–Flotation Feed					Lead Concentrate–Flotation Feed				Lead Concentrate–Circuit Feed					
	C %	Ga %	Sp %	IS %	NSG %	Ga %	Sp %	IS %	NSG %	C %	Ga %	Sp %	IS %	NSG %	C %
+53 µm	0.43	0.03	0.10	0.03	0.17	58.94	0.85	0.09	0.49	0.84	58.96	0.85	0.09	0.49	0.84
-53 µm +C1	0.48	0.17	0.08	0.19	0.21	21.30	0.86	0.02	0.12	0.27	21.34	0.86	0.02	0.12	0.27
C2	0.98	2.10	0.81	2.30	0.31	79.63	16.71	0.50	0.83	3.38	81.33	16.84	0.51	0.83	3.41
C3	3.57	2.47	2.54	1.41	2.36	43.84	13.04	0.07	1.04	3.18	44.95	13.38	0.08	1.06	3.29
C4	9.32	9.10	8.60	15.23	4.39	70.20	10.15	0.19	0.37	1.98	77.23	11.10	0.22	0.39	2.18
C5	14.65	8.68	9.53	22.53	5.83	67.37	6.29	0.07	0.19	1.24	73.77	6.95	0.09	0.20	1.46
C6	18.63	10.47	12.58	13.56	9.02	54.71	3.67	0.04	0.21	1.03	61.11	4.20	0.04	0.23	1.27
C7	31.90	6.70	10.49	1.38	12.75	73.37	4.84	0.13	0.89	0.86	78.64	5.40	0.13	1.02	1.26
Total	13.42	4.27	3.85	4.62	4.77	59.23	5.53	0.10	0.59	1.30	61.87	5.75	0.11	0.62	1.50

* Sample Calculations for Recovery–by Size are shown in Appendix 4.24

Appendix 4.10 Recovery–Total* for Pre-flotation and Lead Concentrate Size Fractions

Fraction Size	Pre-flotation Concentrate–Flotation Feed					Lead Concentrate–Flotation Feed				Lead Circuit Tailing–Flotation Feed					
	C %	Ga %	Sp %	IS %	NSG %	Ga %	Sp %	IS %	NSG %	C %	Ga %	Sp %	IS %	NSG %	C %
+53 µm	0.10	0.01	0.03	<0.01	0.05	9.88	0.22	0.01	0.13	0.19	6.88	25.79	12.62	26.64	22.31
-53 µm +C1	0.05	0.02	0.02	0.02	0.02	2.19	0.17	0.00	0.01	0.03	8.06	19.05	12.14	9.95	11.14
C2	0.09	0.21	0.08	0.10	0.04	8.00	1.72	0.02	0.10	0.31	1.84	8.50	4.31	11.34	8.84
C3	0.28	0.43	0.28	0.31	0.14	7.64	1.42	0.02	0.06	0.25	9.36	9.17	21.71	5.75	7.43
C4	0.62	0.77	0.62	0.84	0.41	5.94	0.74	0.01	0.03	0.13	1.75	5.89	4.65	8.87	5.90
C5	0.47	0.34	0.30	1.43	0.27	2.66	0.20	0.00	0.01	0.04	0.94	2.69	4.90	4.32	2.72
C6	0.93	0.76	0.56	1.57	0.52	3.97	0.16	0.00	0.01	0.05	2.52	3.72	9.98	5.25	3.99
C7	10.88	1.73	1.96	0.35	3.33	18.97	0.90	0.03	0.23	0.29	5.15	15.81	24.97	22.52	22.93
Total	13.42	4.27	3.85	4.62	4.77	59.23	5.53	0.10	0.59	1.30	36.50	90.63	95.28	94.64	85.28

** Sample Calculations for Recovery–Total are shown in Appendix 4.25*

Appendix 4.11 Flotation Tests with Various Primary Grind Sizes–Cumulative Data*

Stream	Cumulative Weight (%)			Cumulative Pb Grade (%)			Cumulative Zn Grade (%)			Cumulative Pb Recovery (%)			Cumulative Zn Recovery (%)		
	58 µm	40 µm	20 µm	58 µm	40 µm	20 µm	58 µm	40 µm	20 µm	58 µm	40 µm	20 µm	58 µm	40 µm	20 µm
Pb 2 nd Cleaner Concentrate 1	3.05	2.33	2.25	53.63	63.25	63.07	19.65	13.36	13.52	65.37	61.83	59.43	4.65	2.61	2.53
Pb 2 nd Cleaner Concentrate 2	4.61	3.49	3.41	41.85	51.83	51.82	25.87	19.85	20.24	77.24	76.02	74.04	9.27	5.82	5.75
Pb 2 nd Cleaner Concentrate 3	5.21	3.99	4.01	37.96	47.08	45.95	27.15	21.64	23.15	79.15	78.89	77.20	10.99	7.25	7.73
Pb 2 nd Cleaner Tail	6.49	5.36	5.68	30.97	35.92	33.47	24.40	19.76	22.04	80.43	80.92	79.72	12.30	8.90	10.43
Pb 1 st Cleaner Tail	14.89	14.34	17.33	14.27	14.31	11.92	15.34	12.66	12.88	84.97	86.19	86.54	17.74	15.25	18.60
Pb Rougher–Scavenger Tail	95.81	95.92	96.72	2.51	2.39	2.39	12.98	11.96	12.06	96.27	96.16	96.83	96.52	96.38	97.22
P/F Cleaner Concentrate 1	97.52	97.65	98.14	2.51	2.38	2.39	12.93	11.93	12.03	97.78	97.74	98.18	97.91	97.87	98.42
P/F Cleaner Concentrate 2	100.0	100.0	100.0	2.50	2.38	2.39	12.88	11.91	12.00	100.0	100.0	100.0	100.0	100.0	100.0

* Sample Calculations for Cumulative Weight, Grade and Recovery are shown in Appendix 4.25

Appendix 4.12 Flotation Tests for Primary Zinc Flotation with Various Primary Grind Sizes–Cumulative Data*

Stream	Cumulative Weight (%)			Cumulative Pb Grade (%)			Cumulative Zn Grade (%)			Cumulative Pb Recovery (%)			Cumulative Zn Recovery (%)		
	58 µm	40 µm	20 µm	58 µm	40 µm	20 µm	58 µm	40 µm	20 µm	58 µm	40 µm	20 µm	58 µm	40 µm	20 µm
Zn Rougher Concentrate 1	5.28	7.08	8.99	0.89	0.82	0.86	45.18	43.77	38.68	12.12	14.26	17.94	20.02	22.79	29.63
Zn Rougher Concentrate 2	14.31	17.14	18.73	0.77	0.80	0.87	40.23	39.95	37.09	28.42	33.82	38.04	48.34	50.36	59.22
Zn Scavenger Concentrate 1	34.06	33.24	33.59	0.56	0.63	0.68	30.07	31.75	30.56	49.10	51.12	52.85	85.98	77.59	87.47
Zn Scavenger Concentrate 2	44.69	45.23	44.50	0.53	0.56	0.63	24.99	28.62	24.94	61.68	62.64	65.23	93.72	95.16	94.60
Zn Scavenger Tail	100.0	100.0	100.0	0.39	0.41	0.43	11.91	13.60	11.73	100.0	100.0	100.0	100.0	100.0	100.0

** Sample Calculations for Cumulative Weight, Grade and Recovery are shown in Appendix 4.25*

Appendix 4.13 Pre-Flotation Roughing Tests at Various % Solids–Cumulative Weight, Carbon Grade and Recovery*

Stream	Cumulative Weight (%)						Cumulative C Grade (%)						Cumulative C Recovery (%)					
	15%	20%	25%	30%	35%	40%	15%	20%	25%	30%	35%	40%	15%	20%	25%	30%	35%	40%
Concentrate 1	3.16	5.81	7.07	9.50	16.39	19.74	8.44	7.32	6.04	5.33	4.53	4.18	7.31	11.27	11.36	13.48	19.87	22.18
Concentrate 2	7.83	13.66	16.11	19.13	29.25	36.64	7.68	6.87	5.94	5.45	4.63	4.28	16.49	24.87	25.47	27.76	36.27	42.17
Concentrate 3	12.61	20.72	24.65	27.49	38.39	46.69	6.77	6.23	5.54	5.25	4.56	4.28	23.38	34.21	36.29	38.42	46.89	53.71
Tail	100.0	100.0	100.0	100.0	100.0	100.0	3.65	3.77	3.76	3.76	3.74	3.72	100.0	100.0	100.0	100.0	100.0	100.0

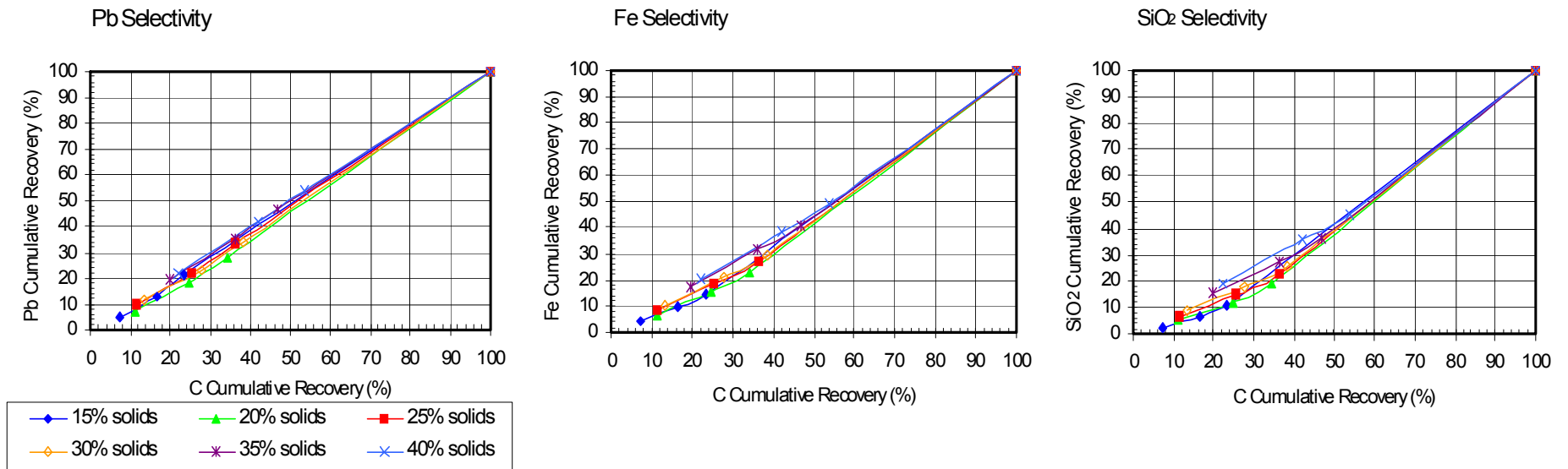
** Sample Calculations for Cumulative Weight, Grade and Recovery are shown in Appendix 4.24*

Appendix 4.14 Pre-Flotation Roughing Tests at Various % Solids–Cumulative Zinc Grade, Zinc and Water Recovery*

Stream	Cumulative Zn Grade (%)						Cumulative Zn Recovery (%)						Cumulative Water Recovery (%)					
	15%	20%	25%	30%	35%	40%	15%	20%	25%	30%	35%	40%	15%	20%	25%	30%	35%	40%
Concentrate 1	10.75	10.47	10.74	10.71	10.96	11.08	3.22	5.55	7.00	9.26	16.47	20.00	7.77	10.50	12.38	15.27	22.58	24.31
Concentrate 2	11.04	10.61	10.81	10.71	10.94	11.14	8.19	13.24	16.06	18.65	29.36	37.34	20.17	24.92	29.43	32.78	43.45	48.53
Concentrate 3	11.28	10.84	10.92	10.83	10.99	11.15	13.47	20.50	24.79	27.11	38.69	47.60	32.94	38.67	46.05	48.11	59.57	64.25
Tail	10.55	10.95	10.85	10.98	10.90	10.94	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

** Sample Calculations for Cumulative Grade and Recovery are shown in Appendix 4.25*

Appendix 4.15 Lead, Iron and Silica Selectivity Curves for Pre-Flotation Roughing Tests at Various % Solids



Appendix 4.16 % EDTA Extractable Metals* in Laboratory and Plant Flotation Streams

Stream	Laboratory			Plant		
	Pb % w/w	Zn % w/w	Fe % w/w	Pb % w/w	Zn % w/w	Fe % w/w
Pre-Flotation Rougher Feed	22.90	0.39	2.81	22.83	0.34	1.99
Pre-Flotation Cleaner Feed	44.94	0.62	3.32	39.68	0.76	0.97
Pb Rougher Feed	8.03	0.29	1.85	17.96	0.17	0.83
Pb Rougher Tail	53.06	0.32	1.52	23.17	0.23	0.55
Pb Ist Cleaner Feed	5.20	0.44	1.62	2.42	0.18	2.22
Pb 2nd Cleaner Concentrate	Insufficient Sample			1.55	0.47	4.16

** Sample Calculations for % EDTA Extractable Metals are shown in Appendix 4.25*

Appendix 4.17 Flotation Tests with Various Pulp pH –Cumulative Data*

Stream	Cumulative Weight (%)			Cumulative Pb Grade (%)			Cumulative Pb Recovery (%)			Cumulative Zn Recovery (%)			Cumulative Fe Recovery (%)		
	pH < 8	pH 8.5	pH 9.5	pH < 8	pH 8.5	pH 9.5	pH < 8	pH 8.5	pH 9.5	pH < 8	pH 8.5	pH 9.5	pH <8	pH 8.5	pH 9.5
Pb 2 nd Cleaner Concentrate 1	2.97	3.90	2.78	55.95	43.18	55.12	67.92	63.54	66.15	2.96	3.37	5.35	2.08	3.78	0.31
Pb 2 nd Cleaner Concentrate 2	6.09	7.30	4.49	31.36	27.86	39.19	78.01	76.74	76.10	8.96	8.68	11.54	9.31	11.68	0.88
Pb 2 nd Cleaner Concentrate 3	7.37	8.50	5.63	26.42	24.43	32.05	79.51	78.35	77.97	10.92	12.12	13.19	12.03	14.59	1.47
Pb 2 nd Cleaner Tail	10.01	11.50	8.65	19.71	18.33	21.22	80.58	79.53	79.25	13.19	16.20	15.22	15.55	18.59	5.08
Pb 1 st Cleaner Tail	18.69	24.20	20.41	10.96	9.13	9.41	83.63	83.34	83.01	18.01	23.18	22.02	24.85	34.60	19.47
Pb Rougher–Scavenger Tail	89.85	89.30	89.72	2.49	2.68	2.32	91.25	90.27	89.78	91.55	91.00	90.48	88.02	86.73	86.55
P/F Cleaner Concentrate 1	93.70	94.10	94.57	2.47	2.68	2.31	94.56	95.09	94.53	94.74	95.20	94.71	92.54	92.63	92.83
P/F Cleaner Concentrate 2	100.0	100.0	100.0	2.45	2.65	2.31	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

* Sample Calculations for Cumulative Weight, Grade and Recovery are shown in Appendix 4.25

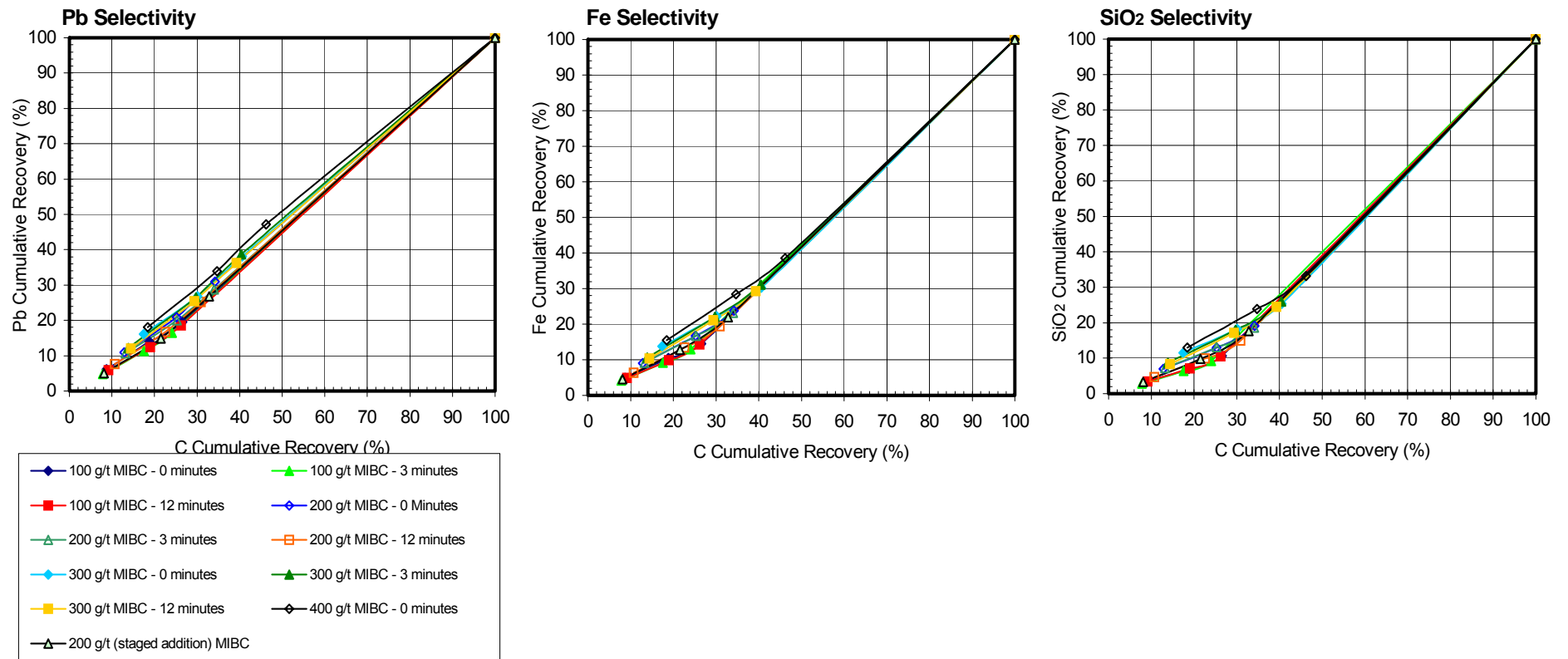
Appendix 4.18 Pre-Flotation Roughing Tests with Varying MIBC–Cumulative Carbon Grade, Carbon Recovery and Zinc

Recovery*

Test MIBC– Conditioning	Cumulative C Grade (%)				Cumulative C Recovery (%)				Cumulative Zn Recovery (%)			
	Con 1	Con 2	Con 3	Tail	Con 1	Con 2	Con 3	Tail	Con 1	Con 2	Con 3	Tail
100 g/t–0 minutes	8.26	8.16	7.53	3.60	8.68	18.83	26.54	100.0	3.95	8.71	12.36	100.0
100 g/t–3 minutes	8.49	8.34	8.00	3.63	7.84	17.55	24.08	100.0	3.33	7.60	10.96	100.0
100 g/t–12 minutes	8.12	8.14	7.72	3.61	9.20	18.98	26.22	100.0	3.99	8.22	12.15	100.0
200 g/t–0 minutes	6.08	6.26	5.87	3.68	12.85	25.24	34.16	100.0	7.88	14.64	21.60	100.0
200 g/t–3 minutes	6.02	6.30	6.00	3.66	13.19	25.34	34.04	100.0	8.16	14.94	21.27	100.0
200 g/t–12 minutes	7.32	7.20	6.64	3.67	10.69	22.63	30.90	100.0	5.31	11.47	17.22	100.0
300 g/t–0 minutes	5.11	5.45	5.29	3.60	17.43	30.16	40.56	100.0	12.57	20.17	28.17	100.0
300 g/t–3 minutes	5.39	5.50	5.23	3.67	13.88	29.72	40.44	100.0	9.54	19.89	28.82	100.0
300 g/t–12 minutes	5.76	5.69	5.37	3.64	14.41	29.37	39.28	100.0	9.15	18.91	27.11	100.0
400 g/t–0 minutes	4.84	4.94	4.76	3.67	18.43	34.72	46.20	100.0	14.26	26.18	36.42	100.0
200 g/t–Added in Stages	7.79	7.00	6.05	3.61	8.12	21.52	32.81	100.0	3.72	11.04	19.80	100.0

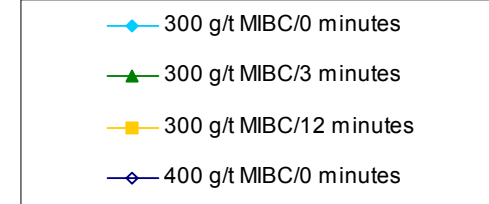
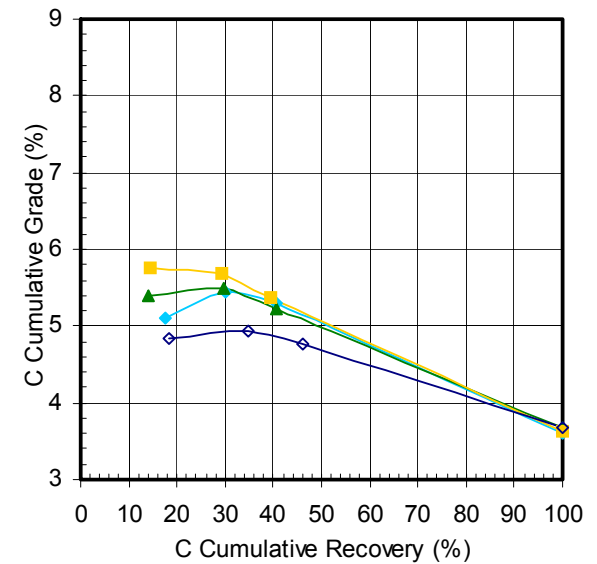
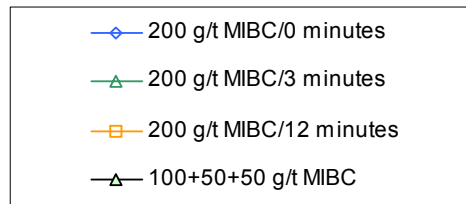
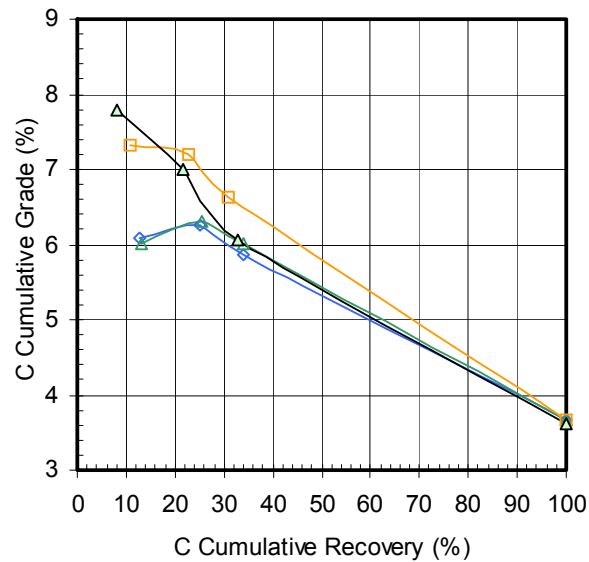
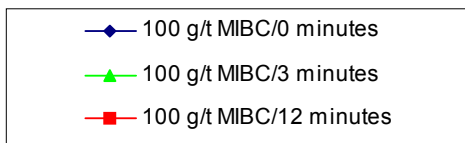
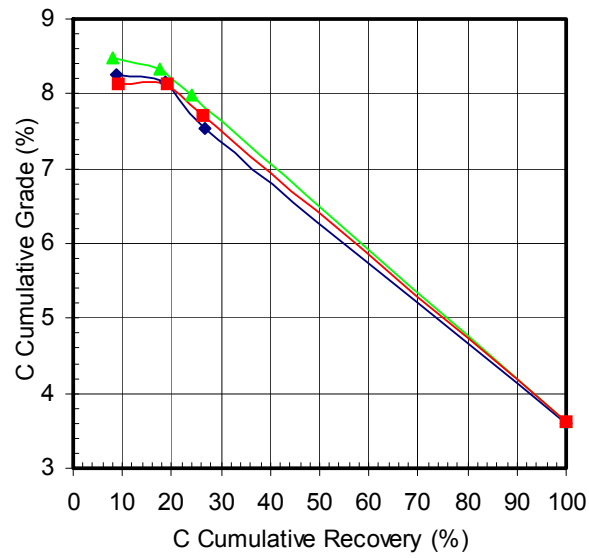
* Sample Calculations for Cumulative Grade and Recovery are shown in Appendix 4.25

Appendix 4.19 Lead, Iron and Silica Selectivity Curves for Pre-Flotation Roughing Tests with Varying MIBC



Appendix 4.20 Carbon Grade–Recovery Curves for Pre-Flotation Roughing Tests with Varying MIBC and Conditioning

Times



**Appendix 4.21 Flotation Tests Testing Zinc Sulfate and Iron Sulfate as Depressants–Calculated Cumulative Lead Grade
and Recovery***

Stream	Cumulative Pb Grade (%)								Cumulative Pb Recovery (%)							
	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
Pb 2 nd Cleaner Concentrate 1	50.17	49.87	50.84	36.23	56.09	31.58	41.04	56.58	65.39	60.27	58.51	69.34	64.19	60.62	67.46	66.34
Pb 2 nd Cleaner Concentrate 2	35.60	34.74	33.46	20.55	40.46	18.39	25.34	36.12	77.90	76.23	72.05	75.50	75.81	73.03	75.31	73.96
Pb 2 nd Cleaner Concentrate 3	31.73	30.84	26.04	17.04	31.94	13.29	21.08	29.55	79.43	78.43	73.90	76.52	78.19	75.44	76.54	75.19
Pb 2 nd Cleaner Tail	25.01	25.12	17.41	13.31	18.54	10.48	14.31	20.81	80.96	79.42	75.83	77.42	79.82	76.93	78.19	76.54
Pb 1 st Cleaner Tail	10.64	11.60	8.22	7.81	8.61	6.67	6.98	9.41	83.99	81.84	78.34	79.87	82.66	79.90	81.16	80.11
Pb Rougher–Scavenger Tail	2.44	2.37	2.39	2.42	2.32	2.39	2.43	2.34	90.25	89.28	84.21	85.87	88.26	86.46	87.01	88.11
P/F Cleaner Concentrate 1	2.42	2.36	2.39	2.40	2.31	2.38	2.41	2.33	95.55	91.52	91.96	93.22	93.21	92.65	93.06	92.86
P/F Cleaner Concentrate 2	2.41	2.35	2.38	2.39	2.30	2.37	2.39	2.32	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

* Sample Calculations for Cumulative Grade and Recovery are shown in Appendix 4.25

Appendix 4.22 Flotation Tests Testing Zinc Sulfate and Iron Sulfate as Depressants–Calculated Cumulative Zinc and Iron

Recovery*

Stream	Cumulative Zn Recovery (%)								Cumulative Fe Recovery (%)							
	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 8
Pb 2 nd Cleaner Concentrate 1	5.04	5.11	0.73	9.96	1.12	10.66	5.79	1.86	0.70	0.32	5.71	2.50	1.88	3.36	4.06	2.11
Pb 2 nd Cleaner Concentrate 2	11.19	12.56	2.13	23.78	2.60	25.34	13.50	5.15	2.21	0.96	14.93	7.47	5.21	10.94	10.07	8.09
Pb 2 nd Cleaner Concentrate 3	13.04	15.00	3.57	29.12	3.97	34.19	17.00	6.88	3.14	1.39	20.24	10.02	7.81	19.73	13.00	11.57
Pb 2 nd Cleaner Tail	14.73	16.29	7.70	32.94	7.83	37.66	21.66	9.55	5.44	3.30	26.35	13.83	12.87	24.97	18.42	16.43
Pb 1 st Cleaner Tail	21.69	21.23	20.27	41.81	18.44	43.52	35.07	18.41	21.76	16.33	37.74	24.89	25.84	37.89	34.42	30.48
Pb Rougher–Scavenger Tail	90.63	89.98	86.04	86.79	88.62	87.37	87.50	88.98	86.61	86.03	80.90	81.73	84.43	83.40	83.04	84.64
P/F Cleaner Concentrate 1	95.73	95.32	92.90	93.68	93.48	93.17	93.32	93.35	93.88	93.43	90.29	91.27	91.06	91.00	90.98	90.74
P/F Cleaner Concentrate 2	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

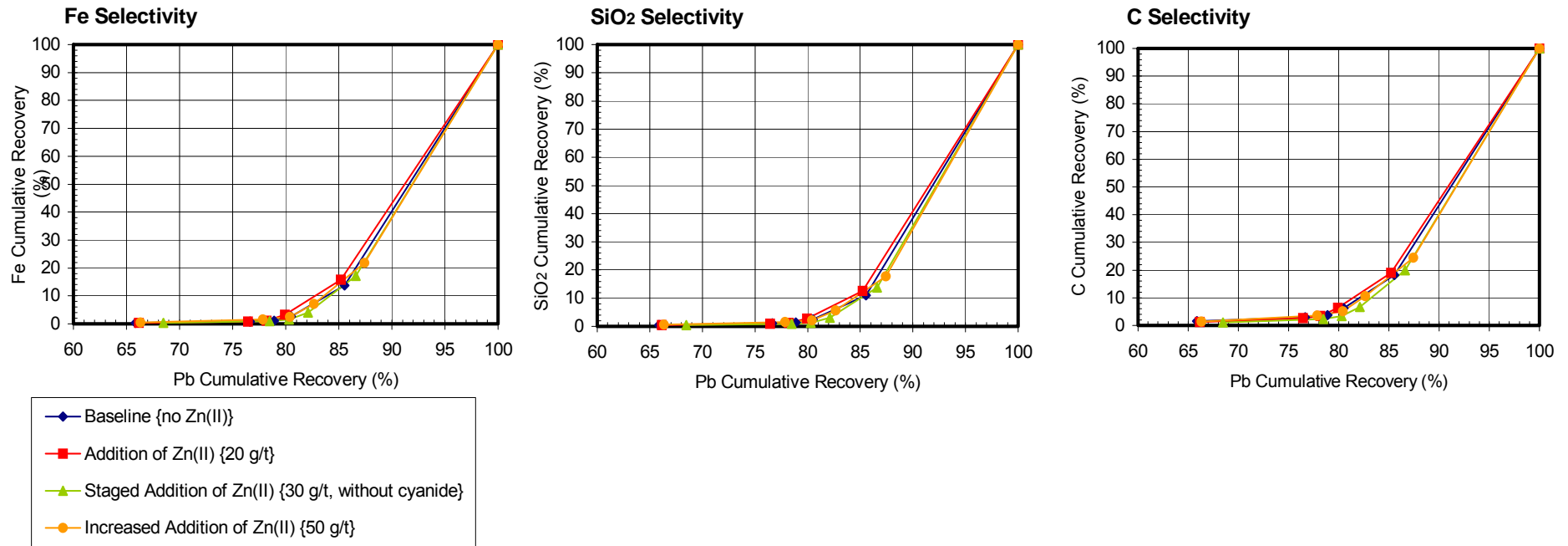
** Sample Calculations for Cumulative Weight, Grade and Recovery are shown in Appendix 4.25*

Appendix 4.23 Flotation Tests Testing Zinc Sulfate during Lead Flotation–Calculated Cumulative Data*

Stream	Cumulative Pb Grade (%)				Cumulative Pb Recovery (%)				Cumulative Zn Recovery (%)			
	Test 1	Test 2	Test 3	Test 4	Test 1	Test 2	Test 3	Test 4	Test 1	Test 2	Test 3	Test 4
Pb 2 nd Cleaner Concentrate 1	50.8	58.8	68.9	64.4	65.87	65.51	68.48	66.34	6.80	2.82	1.70	2.06
Pb 2 nd Cleaner Concentrate 2	41.00	47.95	57.11	48.42	76.63	75.98	78.48	77.86	11.74	5.98	3.77	5.05
Pb 2 nd Cleaner Concentrate 3	38.26	44.82	51.63	41.77	78.89	77.78	80.31	80.41	13.12	6.83	4.74	6.59
Pb 2 nd Cleaner Tail	31.93	33.65	36.28	25.67	80.51	79.54	82.12	82.66	14.91	8.95	7.21	10.63
Pb 1 st Cleaner Tail	15.82	14.75	14.20	12.23	85.53	84.92	86.60	87.44	21.65	16.83	20.14	20.58
Pb Rougher–Scavenger Tail	2.97	2.91	2.97	2.99	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

** Sample Calculations for Cumulative Weight, Grade and Recovery are shown in Appendix 4.25*

Appendix 4.24 Iron, Silica and Carbon Selectivity Curves for Testing Zinc Sulfate during Lead Flotation



Appendix 4.25 Sample Calculations for Data from Grinding, Flotation and Size Distribution Tests

Calculations for Grinding Calibration Test Data:

$$\text{Cumulative \% Passing} = \left(1 - \frac{\text{Weight}}{\text{Total Weight}}\right) \times 100\%$$

$$\text{Calculated 80\% Passing} = (80 - CP_1) \times \frac{(S_2 - S_1)}{(CP_2 - CP_1)} + S_1$$

Where: Cumulative % passing result < 80 % = CP_1 for the nominal aperture size, S_1 ; and

Cumulative % passing result > 80 % = CP_2 for the nominal aperture size, S_2 .

Calculations for Mineral Grade from Assay Results

$$\text{Mineral Grade \%} = \text{Assay Grade \%} \times \frac{\text{MW (Mineral)}}{\text{MW (Analyte)}}$$

Where: MW(Mineral) and MW(Analyte) represent the molecular weights of the mineral and the analyte, respectively, for example: the factor for

galena (PbS) is equivalent $\text{MW(PbS)} \div \text{MW(Pb)} = 1.155$; and

Pyrite (FeS_2) and Siderite (FeCO_3) grades have been calculated for the flotation feed on the basis that 60% of the Fe content is contained as pyrite and 40% contained as siderite.

Calculations for Chemical or Mineral Distribution:

$$\text{Distribution, X \%} = \frac{\text{Weight \%} \times \text{Grade X \%}}{\text{Weighted Average Grade X \%}}$$

Where: X represents the particular chemical or mineral analyte, such as Pb, Zn, and Fe or PbS, ZnS and FeS₂;

Weight % represents the percentage weight for the fraction size; and

Weighted Average Grade X % represents the weighted average grade for the particular analyte.

Calculations for Flotation Test–Cumulative Weight, Grade and Recovery:

$$\text{Cumulative Weight}_{\text{Stream } n} \% = \text{Weight}_{\text{Stream } 1} \% + \text{Weight}_{\text{Stream } 2} \% + \dots + \text{Weight}_{\text{Stream } n} \%$$

$$\text{Cumulative Grade}_{\text{Stream } n} \text{ X \%} = \frac{\text{Weight}_{\text{Stream } 1} \times \text{Grade}_{\text{Stream } 1} \text{ X \%} + \text{Weight}_{\text{Stream } 2} \times \text{Grade}_{\text{Stream } 2} \text{ X \%} + \dots + \text{Weight}_{\text{Stream } n} \times \text{Grade}_{\text{Stream } n} \text{ X \%}}{\text{Cumulative Weight}_{\text{Stream } n}}$$

Where: Cumulative Grade_{Stream n} X % represents the cumulative grade of analyte X (X = Pb, Zn) for the nth stream;

Weight_{Stream 1}, Weight_{Stream 2}, ... Weight_{Stream n} represent the stream weights for streams 1 to n; and

Grade_{Stream 1} X %, Grade_{Stream 2} X %, ... Grade_{Stream n} X % represent the grades for analyte X in each stream.

$$\text{Cumulative Recovery}_{\text{Stream } n} \text{ X \%} = \text{Recovery}_{\text{Stream } 1} \text{ X \%} + \text{Recovery}_{\text{Stream } 2} \text{ X \%} + \dots + \text{Recovery}_{\text{Stream } n} \text{ X \%}$$

Where: Cumulative Recovery_{Stream n} X % represents the cumulative recovery of analyte X (X = Pb, Zn) for the nth stream; and

Recovery_{Stream 1} X %, Recovery_{Stream 2} X %, ... Recovery_{Stream n} X % represent the stream recoveries for streams 1 to n, given by:

$$\text{Recovery}_{\text{Stream } X \%} = \frac{\text{Weight}_{\text{Stream } \%} \times \text{Grade}_{\text{Stream } X \%}}{\text{Grade}_{\text{Flotation Feed } X \%}}$$

Calculations for Recovery with respect to Flotation Feed–by Size:

$$\text{Recovery, X \%} = \frac{(\text{Test Weight}_{\text{stream}} \times \text{Grade X \%}_{\text{stream}})}{(\text{Test Weight}_{\text{flotation feed}} \times \text{Grade X \%}_{\text{flotation feed}})} \times 100\%$$

Where: X represents the particular chemical or mineral analyte, such as Pb, Zn, and Fe or PbS, ZnS and FeS₂;

Test Weight_{stream} and Grade X %_{stream} represent the weight and analyte grade for the particular fraction size; and

Test Weight_{flotation feed} and Grade X %_{flotation feed} represent the weight and analyte grade for the particular fraction size in the flotation feed.

Calculations for Recovery with respect to Flotation Feed–Total:

$$\text{Recovery, X \%} = \frac{(\text{Test Weight}_{\text{stream}} \times \text{Grade X \%}_{\text{stream}})}{(\text{Total Test Weight}_{\text{flotation feed}} \times \text{Weighted Average Grade X \%}_{\text{flotation feed}})} \times 100\%$$

Where: X represents the particular chemical or mineral analyte, such as Pb, Zn, and Fe or PbS, ZnS and FeS₂;

Test Weight_{stream} and Grade X %_{stream} represent the weight and analyte grade for the particular fraction size;

Total Test Weight_{flotation feed} represents the total weight of the flotation feed, equivalent to 1000 g; and

Weighted Average Grade X %_{flotation feed} represents the weighted average grade for the analyte, X in the flotation feed.

Calculations for Recovery with respect to Lead Circuit Feed–Total:

$$\text{Recovery, X \%} = \frac{(\text{Test Weight}_{\text{stream}} \times \text{Grade X \%}_{\text{stream}})}{(\text{Total Test Weight}_{\text{circuit feed}} \times \text{Weighted Average Grade X \%}_{\text{circuit feed}})} \times 100\%$$

Where: X represents the particular analyte, such as Pb, Zn, and Fe;

Test Weight_{stream} and Grade X %_{stream} represent the weight and analyte grade for the particular fraction size;

Total Test Weight_{circuit feed} represents the total weight of the lead circuit feed; and

Weighted Average Grade X %_{circuit feed} represents the weighted average grade for the analyte, X in the circuit feed.

Calculations for % EDTA Extractable Metal:

$$\text{EDTA Soluble Mass} = \text{Concentration (Aqueous Phase)} \times (\text{EDTA Volume} + \text{Total Sample Weight} \times \frac{(100 - \% \text{ Solids})}{100}) - \frac{25}{50} \times \text{Water Soluble Mass}$$

Where: $(\text{Total Sample Weight g} \times (100 \% - \% \text{ Solids}))$ is an approximation of the aqueous phase volume, where 1 g = 1 mL

$(25/50 \times \text{Water Soluble Mass})$ represents the water-soluble metal ions in the aqueous phase, where the EDTA extraction sample was 25 mL and the water extraction sample was 50 mL

$$\% \text{ Solids} = \frac{\text{Solids Weight}}{\text{Total Sample Weight}} \times 100\%$$

$$\text{Water Soluble Mass} = \text{Aqueous Phase Concentration} \times \text{Total Sample Weight} \times \frac{(100 - \% \text{ Solids})}{100}$$

$$\text{Mass in Solid Phase} = \text{Concentration in Solid Phase \%} \times \text{Solids Weight}$$

$$\% \text{ EDTA Extractable Metal} = \frac{\text{EDTA Soluble Mass}}{\text{Mass in Solid Phase}} \times 100\%$$