

## CHAPTER 1

### INTRODUCTION

#### 1.1 Historical background

Peter van den Krogt (2003) reports that centuries before zinc was recognised as a distinct element, zinc ores were used for making brass. Tubal-Cain, seven generations after Adam, is mentioned as being an "instructor of every artificer in brass and iron."

Habashi (2000) mentions that in the latter part of the thirteenth century, Marco Polo described the manufacture of zinc oxide in Persia and how the Persians prepared tutia (a solution of zinc vitriol) for healing sore eyes.

Habashi (2000) reports that the Roman writer Strabo (66 B.C. - 24 A.D.) mentioned in his writings that only the Cyprian ore contained "the cadmian stones, copper vitriol, and tutty," that is to say, the constituents from which brass can be made. It is believed that the Romans first made brass in the time of Augustus (20 B.C. to 14 A.D.) by heating a mixture of powdered calamine, charcoal and granules of copper. Roman writers observed that coins made from orichalcum were indistinguishable from gold.

Gowland (1912) reported that pure zinc was not known until quite modern times, the ore employed being calamine, which is an impure zinc carbonate rich in silica. Mixing ground calamine ore with copper and heating the mixture in a crucible produced the earliest brass. The heat applied was sufficient to reduce the zinc to the metallic state, but

not to melt the copper. They knew it as 'oreichalcos', a brilliant and white copper, which was made by mixing tin and copper with a special earth called "calmia" that came originally from the shores of the Black Sea. The vapour from the zinc, however, permeated the copper and formed brass, which was then melted. The Romans were the first to use brass on any significant scale, although the Greeks were well acquainted with it in Aristotle's time (c. 330 B.C.).

The first smelting and extraction of the impure metal was carried out in China and India, around 1000 A.D. The first slab zinc or spelter was imported from the East in the early seventeenth century, late when compared with iron, copper or lead. The metal did not even have a universally accepted name at this time, being known as tutanego, Indian tin, calamine or spiauter. The term "zink" was first used by Löhneyes in 1697. The commercial designation for zinc from a distillation process is still referred to as spelter. Figurines, candlesticks and other pieces were made of spelter and given a bronze or painted finish. The metal has been used since about the 1860s to make statues, tableware and lamps that resemble bronze. Spelter is soft and breaks easily.

RXN Communications (2002) reports that the commercial production of zinc did not start in Europe until the middle of the 18th century and in the United States until 1860. Zinc is used for galvanising (coating) iron and steel to protect against rust in large-scale construction projects, in motor vehicle bodies and roof sheeting.

Figure 1: Structure of sphalerite (Bragg et al. 1935)

## 1.2 Mineral forms of zinc

Amethyst Galleries (1996) declare that sphalerite is undoubtedly the most important ore of zinc, an industrially and at times strategically important metal.

The mineral Galena (1996) describes the appearance of Zinc sulfide, which gives it a dark colour giving it the popular name "blackjack". It also occurs in red, yellow or brown.

Other zinc ores include hemimorphite, smithsonite, willemite, franklinite and zincite. The Minerals Council of Australia (2002) provides the following description of the natural occurrence of zinc. The mineral sphalerite ( $\text{Zn,FeS}$ ), contains up to 67% zinc when pure. Smithsonite ( $\text{ZnCO}_3$ , 52% zinc), willemite ( $(\text{Zn,Mn})_2\text{SiO}_2$ , 59% Zn) and hemimorphite ( $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ , 54% Zn) may occur in the near-surface weathered or oxidised zone of an ore body. Trinity Minerals Company (2002) reports that zincite has the chemical formula  $(\text{Zn,Mn})\text{O}$  and in its pure form can consist of up to 80.34 % Zn.

Bragg *et al* (1965) report that the zinc atoms are arranged in a face-centred cubic lattice and that the sulphur atoms are arranged in a similar lattice, arranged in such a way as to ensure coordination between four zinc atoms. Figure 1 gives a schematic representation of the sphalerite crystal.

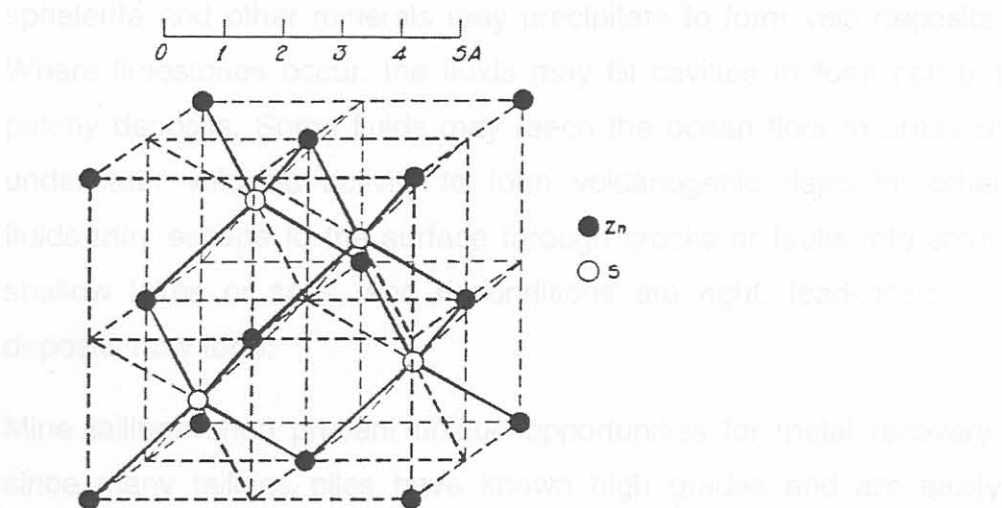


Figure 1: Structure of sphalerite (Bragg *et al.* 1965)

The Amethyst Galleries (1996) describes the appearance of  $\text{ZnS}$  as adamantine or resinous or submetallic to earthy in massive forms. It has a resinous lustre, exists in massive or crystalline form and usually contains iron sulphide, which gives it a dark colour, giving rise to the popular name "blackjack". It also occurs in red, yellow or green;



because of these variations and its resemblance to other minerals, it is difficult to identify. Table 1 lists general information on sphalerite.

Table 1: General information on sphalerite	
Chemical formula:	(Zn,Fe)S
Composition:	Molecular mass: 97.46 g/mol
	Sulphur: 32.90 % S
	Zinc: 67.10 % Zn

According to The Minerals Council of Australia (2002), deposits contain zinc from hot (hydrothermal) fluids generated within the earth. These fluids may be trapped below the surface in cracks where sphalerite and other minerals may precipitate to form vein deposits. Where limestones occur, the fluids may fill cavities to form rich but patchy deposits. Some fluids may reach the ocean floor in areas of underwater volcanic activity to form volcanogenic deposits; other fluids may escape to the surface through cracks or faults into small shallow lakes or seas, and if conditions are right, lead-zinc-silver deposits may form.

Mine tailings often present unique opportunities for metal recovery, since many tailings piles have known high grades and are easily accessible. The opportunity is often offset, however, by the coincidence of other mill or process by-products such as sulphides, which carry certain environmental liabilities.

### 1.3 Chemistry of zinc

Deer *et al* (1966) report that sphalerite is rarely found as pure ZnS; part of the Zn is practically always isomorphously substituted by Fe, often by Mn and Cd, and to a minor extent by Ba, In, Tl and Hg. They mention that the highest iron content reported is 26% Fe by weight, which corresponds to 45 mol per cent FeS. Experimental studies give about 40 mol per cent FeS in (Zn,Fe)S at 900°C and a pressure of 1 atmosphere as an upper limit. Some of the iron reported in natural specimens may be present as pyrrhotite. In natural sphalerites as much as 4 to 5% Cd and Mn has been reported. Minor and trace concentrations of other elements, e.g. Ga, Ge, In, Co and Hg may occur as well as Fe, Mn and Cd, substituting for Zn in sphalerite. Copper, silver and tin are also often recorded in sphalerite analyses, but some of these elements may be present in small inclusions of other minerals. Blebs of chalcopyrite, for example, are often found in sphalerite, and are attributed to exsolution (i.e. minerals segregate into discrete phases ) on cooling from a higher temperature ZnS-CuFeS<sub>2</sub> solid solution. Antimony and bismuth as well as lead, when reported, are probably present as galena. Some of the physical properties of sphalerite are represented in Table 2.

Table 2: Physical properties of sphalerite (John Betts, 2002)	
Cleavage:	[110] Perfect, [110] Perfect, [110] Perfect
Colour:	Brown, yellow, red, green, or black.
Density:	3.9 - 4.2, average = 4.05 g/cm <sup>3</sup>
Diaphaneity:	Translucent to transparent
Habits:	Euhedral crystals – occurs as well-formed crystals showing good external form
	Granular – generally occurs as anhedral to



Table 2: Physical properties of sphalerite (John Betts, 2002)

	subhedral crystals in matrix
	Colloform – formed from a gel or colloidal mass
Hardness:	Moh scale 3.5 - 4
Luminescence:	Fluorescent and triboluminescent.
Lustre:	Resinous – Greasy
Streak:	Brownish white

Ramdohr (1980) is of the opinion that the other elements found in sphalerite analyses are due to accidental or perhaps genetically important (as in the case of Cu and Sn) contamination.

#### 1.4 Mintek study of Rosh Pinah tailings dump samples

##### 1.4.1 Background

Fierce competition, the increasing necessity to use lower-grade ores, stringent environmental demands and other financial issues are necessitating the reduction of the costs of recovering metal from the ore.

Chemical simulations exist that could be employed to predict extraction phenomena such as kinetics, rates and extraction feasibility. Most recovery processes entail upgrading (beneficiation), product recovery and purification. This study covers the middle part of a typical metal-from-mineral recovery process, which requires the dissolution of the beneficiated mineral from the tailings dam before the metal can be recovered from the solution.

Rosh Pinah, a zinc/lead/silver mine in Namibia, is the owner of a tailings dump that contains recoverable grades of valuable metals, such as Zn. In 1999 Rosh Pinah requested Mintek to conduct flotation

tests on Rosh Pinah tailings dump samples with the objective of determining whether a saleable zinc concentrate at a grade of 50 % Zn could be produced from this type of material. A weathered sample from the old part of the dump ("dump") and a fresh tailings sample from the plant ("stream") were evaluated. Two reports were presented.

Froth flotation is used in mineral beneficiation to produce a concentrate from the metal-bearing mineral in the ore. Run-of-mine ore is ground to a fine powder, usually in a ball mill, and introduced into a flotation cell where it is mixed with water, frothing reagents and collecting reagents. Air is forced into the system, creating a large number of microbubbles. The hydrophobic particles (in the case of sphalerite flotation, the sulphide) attach to the bubbles, which rise to form a froth on the surface. The waste material (gangue), which is hydrophilic, is removed from the bottom of the flotation cell. The froth is skimmed off and the water removed by belt or pressure filtration, leaving a clean concentrate to be dispatched to the smelter. The process is used for the beneficiation of a number of minerals; in the case of Rosh Pinah, zinc.

Mintek was appointed by Rosh Pinah to investigate the recovery of pyrite from both current and dump tails at the Rosh Pinah lead-zinc concentrator.

#### **1.4.2 Conclusions from Report 1 (Mintek)**

Flotation tests on the dump sample indicate that only around 10% of the zinc is recoverable by standard flotation procedures as a high-grade concentrate. Scouting tests to evaluate other flotation procedures indicated that these have a low chance of success.

The bulk of the zinc of the stream sample, even though at a grade lower than typically produced, could be recovered as a rougher concentrate at a recovery of 67.1 % and at a grade of 10.7 % Zn. Further upgrading is possible through the use of a regrinding stage of the rougher and cleaner concentrate and two stages of cleaning. A recovery of 33.9 % was obtained at a grade of 25 % Zn.

#### **1.4.3 Conclusions from Report 2 (Mintek)**

Mintek also investigated the recovery of pyrite from both current and dump tails at the Rosh Pinah lead-zinc concentrator.

The possible development of zinc deposits close to Rosh Pinah would require a supply of sulphuric acid. To this end, Rosh Pinah requested Mintek to investigate the recovery of pyrite from Rosh Pinah tailings (both current arisings and dump).

Flotation and gravity separation of pyrite was investigated. Flotation was conducted using a collector and frother only.

It appears that a sulphur grade of greater than 40% will be difficult to achieve in closed circuit with two stages of cleaning. If higher grades are desired, the options are:

- 1) The use of gangue depressant in final cleaner stage,

- 2) Additional cleaner stage(s),

- 3) Discarding either cleaner tails or cleaner tails and recleaner tailings.

Options 1) and 2) will increase capital and operating costs through additional reagent mixing facilities, additional flotation cells, pumps etc. Option 3) will reduce sulphur recovery.

The locked cycle tests show that sulphur recovery is unlikely to exceed 70% (plant tails) and 45% (dump tails) if the simple reagent



scheme reported here is employed. If higher recoveries are desired, two options could be considered:

Activate the pyrite (by copper sulphate)

Use some of the sulphuric acid produced from the pyrite concentrate to reduce the flotation pH to 4 or 5.

Either option would incur additional operating costs and, in the case of option 2), significant capital costs (rubber-lined equipment, corrosion-proofed structures and floors etc.).

There is every likelihood that the lower recovery achieved from dump tails is due to sulphur being present in other forms than sulphide, i.e. over the years oxidation into sulphate and other sulphony compounds has occurred.

#### *1.4.3.1 Flotation*

According to the locked cycle tests, there are definite advantages in terms of concentrate sulphur grade and recovery. The decision to be made is whether a concentrate grade of 35-37% S is acceptable. Desliming appears to be ineffective in increasing concentrate sulphur grade.

#### *1.4.3.2 Gravity concentration*

According to the limited data generated by this work, gravity concentration of pyrite (especially of the dump tails) is definitely worth considering, provided that -

a concentrate grade of 40% sulphur is acceptable,

45% sulphur recovery is acceptable (this is as high as has been achieved by flotation so far).

The advantages would be a simple plant and reagents configuration. The plant would consist of screening (to remove debris and accreted lumps), desliming at about 25 microns, spirals for concentration and dewatering equipment.

### 1.5 Mineralogy

A mineralogical investigation was performed by Reyneke (2000) on the tailings dump samples from Rosh Pinah which originated during the test work.

According to XRD analyses, the concentrate sample consists mainly of sphalerite with minor amounts of pyrite, dolomite and quartz. The mineralogical compositions of the scavenger and cleaner tailings samples are similar in that both consist mainly of dolomite and quartz. However, the cleaner tailings sample may contain relatively more sphalerite compared with the scavenger sample. Quartz is the main mineral present in the tailings sample, with lesser dolomite present.

Particle counts reveal that the scavenger and cleaner tailings samples are very similar with reference to the textural properties of the minerals. The tailings sample appears to contain appreciably fewer liberated sulphide minerals (specifically pyrite) and more gangue particles without associated sulphide minerals.

A single zincite ( $\text{ZnO}$ ) particle was observed in the scavenger sample and is the only indication of Zn occurring in minerals other than sulphides or carbonates (discussed below).

The formula of dolomite can generally be expressed as  $\text{CaMg}(\text{CO}_3)_2$ , where Fe and Mn may replace Mg in many dolomites. Zincian dolomite has been described and is termed "minrecondorite". Microanalyses reveal that trace amounts of Zn may be present in many of the dolomites. Dolomites in the scavenger sample exhibit

compositions close to those of published data. Dolomites in the cleaner tailings and tailings samples appear to exhibit lower CaO and higher MgO contents, suggesting the occurrence of the magnesite-siderite series in association with the dolomite-ankerite series. Backscattered electron images reveal lighter and darker areas in some dolomite particles that can generally be correlated with variation in chemical composition. For these types of particles occurring in the scavenger sample, the lighter areas exhibit appreciably higher Zn-contents (for example 7.00 % ZnO) and may then be approaching minrecdorite in composition. In the dolomites analysed in the cleaner tailings and tailings samples, the variation in chemical composition between lighter and darker areas is not as pronounced as in the scavenger sample, or not noticeable at all.

## **1.6 Aim of this study**

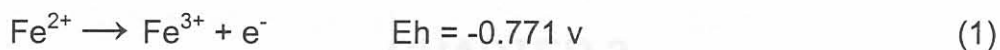
The aim of this study was to perform leaching tests after completion of a literature survey of the beneficiation, extraction and processing of zinc from the mineral sphalerite. The study and test work focus on the ferric chloride leaching of concentrate recovered from the Rosh Pinah tailings and on updating the existing technological knowledge of zinc processing, with the necessary consultation of knowledgeable persons.

The study will also address the leaching kinetics of an upgraded Rosh Pinah tailings dam concentrate as well as a synthetic zinc sulphide in a ferric chloride medium

### **1.6.1 Why ferric chloride?**

Peters (1970) has summarised many of the important reactions occurring during the dissolution of sulphides in various media, including ferric-ion.





He gives the following equation for the oxidising potential of the ferrous/ferric couple (equation 1) at 25°C:

$$E = 0.771 + 0.0591 \log \frac{\text{Fe}^{3+}}{\text{Fe}^{2+}} \quad (2)$$

This equation indicates that solutions containing even one part  $\text{Fe}^{3+}$  per million parts  $\text{Fe}^{2+}$  have an oxidising potential higher than +0.4 V and could, consequently, attack most base metal sulphides.

This specific route was chosen to prove the sustainability of a process that could be less capital intensive than the more established processes discussed in chapter 3.



Figure 2: Different processing routes for zinc recovery (Yazawa, 1985)