

# The environmental impact of metalliferous mining: Korea, Chile and Zimbabwe case studies

Pollution, Waste Management and Extractive Industries Impacts Programme

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#### BRITISH GEOLOGICAL, SURVEY

#### COMMISSIONED REPORT CR/02/190N

# The environmental impact of metalliferous mining: Korea, Chile and Zimbabwe case studies

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*Frontispiece* 

Contaminated village water supply well adjacent to tailings from gold mine, central Chile.

*Key words* 

Mining; acid mine drainage; groundwater; contamination.

*Bibliographical reference* 

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## Foreword

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# Summary

This report provides some of the conceptual background to the MINDEC model, which was developed as part of DHD research project R7118: Cost effective evaluation of hazards from mine waste. The report is structured along the lines of the risk assessment paradigm of source - pathway - receptor. Reference is made to examples of sources, pathways and receptors studied during field visits to Chile and Zimbabwe and a risk assessment methodology is demonstrated using a Korean case study of abandoned gold mine tailings.

## <span id="page-7-0"></span>1 Introduction

Environmental degradation due to abandoned mining activities is not just a developing world phenomenon and one does not have to look very far in Europe to see that the legacy of abandoned mining is also a major problem there. In the United Kingdom for instance the legacy of metalliferous mining goes back to pre-Roman times and the mining of metal ores and their processing has inevitably caused pollution of the environment. Even now, there is no national inventory of waste products or national understanding of possible environmental impacts. The main environmental health hazards deriving from mines and mine tailings arise from the discharge of acid mine drainage (AMD) to surface and groundwater, and the contamination of soils through associated industrial activity. Discharges can contain very high concentrations of toxic heavy metals derived from sulphide ores and associated gangue minerals; and the concentration of toxic heavy metals in soils can also pose a serious health risk. Abandoned mines, tailings piles and associated, untreated, acid mine drainage constitute an important source of heavy metal contamination to the biosphere. Mine wastes are a threat to the quality of life of local inhabitants, affecting their health, and inhibiting the development of affected areas.

It is only when major disasters occur that mining-related hazards are highlighted by the media and brought to public attention. Perhaps the most recently publicised, high profile event was the Aznacollar tailings dam failure in Spain which threatened the entire ecosystem of the Dofiana National Park (EFE, 1998). According to Arenas et al. (2001) the failure of the Aznacollar mine settling pond on April  $25<sup>th</sup>$ , 1998, was responsible for releasing 6hm<sup>3</sup> of sludge and acidic water with a pH of  $\sim$ 5.5 and high concentrations of heavy metals. An area of approximately 4630ha was affected and 62km of river bank was contaminated to an average width of 500m reaching the north-west limits of the Dofiana National Park. This event constituted an environmental catastrophe on a scale never before seen in Europe.

More recently in Romania the failure of the Baia Mare tailings dam on  $30<sup>th</sup>$  January, 1999, released 100,000  $m<sup>3</sup>$  of tailings water containing heavy metals and cyanide. This flowed into the Lipus River and the upper Tisa river system occasioning significant fish kills. Hungarian authorities reported that 1240 tonnes of fish were killed as a result of the spill. The Baia Mare incident was followed in March of the same year by a second dam failure on the Ukranian border at Baia Borsa that released 20,000 tonnes of tailings into the Novat River before flowing into Hungary. The medium term impacts of this spill are of more concern because of the amount of heavy metals released, which have the potential to bioaccumulate in aquatic organisms. The findings of an independent

**1** 

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investigation (Garvey et al., 2000) were that tailings management facility designs were not appropriate, that there was inadequate monitoring of construction and operation of the dams, and that failure was triggered by severe, but not exceptional weather.

A compilation of contamination incidents associated with the discharge of mine tailings into the environment through the collapse of tailings dams is given in Appendix B.

In developing countries, the hazards posed by both active mine wastes and residues at abandoned mine sites are especially acute as regulatory controls and environmental legislation may not be in place. The possibility of contaminant transport from mine wastes to the local population via a number of different pathways forms the basis of the work described in this report.

#### $1.1$ TECHNOLOGICAL HAZARDS AND THE SOURCE-PATHWAY-RECEPTOR PARADIGM OF RISK ASSESSMENT

Within the context of mine waste contamination, risk assessment provides a formalised framework that describes the relationship between the exposure / concentration of a given substance and the adverse effects on a given receptor. Risk can be defined as the likelihood that one or more adverse effects will occur in response to a hazardous situation.

Figure 1.1 illustrates a generic risk assessment framework, which can be applied to mining impact studies.



The central element of the scheme is the risk assessment (RA) and the classical approach for conducting this is to identify sources of hazard, the pathways of exposure and receptor exposure factors in order to calculate a dose (exposure assessment). The risk assessment usually involves a comparison of the calculated dose with a trigger value in the case of contaminated soils, an environmental quality standard in the case of surface waters or maximum allowable concentration or tolerable daily intake in the case of human ingestion.

In order to assess mining related hazards it is normal practice to establish a conceptual model of how a particular site is behaving in relation to potential receptors. Figure 1.2 illustrates the source-pathway-receptor model for a mine site. Table 1.1 categorises the elements of the model, which constitute sources, pathways, and events, which might occur as a result of exposure or which might lead to exposure. The site prioritisation software MINDEC (Klinck et al., 2001) focuses specifically on tailings as the source of contamination and water as the transport medium. From the simple model presented it is evident that some features can be both sources and receptors. It is very important to clearly establish the linkages between the features of the model (F), the events (E) that precipitate a hazard and the processes (P) involved in the resulting impact. Such a structured FEP approach is used routinely in conceptualising the impact of radioactive waste disposal.



Table 1.1 Source - Pathway - Receptor Analysis of Simple Conceptual Model

In the following account the risk assessment paradigm is examined and relevant FEPs are explored in the context of site specific studies which have been carried out in Chile,

 $\overline{a}$ 

 $\bar{z}$ 

Korea and Zimbabwe. Where a particular feature is poorly represented, reference will be made to the published literature to provide further examples. The final section of the report illustrates the approach to assessing mining impact using a case study from Korea.

*A* 



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Environmental impact of mining

# <span id="page-12-0"></span>2 Sources

The most common sources of contamination related to mining and mineral processing are mine wastes in the form of waste rock, tailings or process water. Additionally some mineral processing operations can give rise to gaseous and particulate emissions through, for example, grinding and ore roasting. At abandoned mine sites, acid mine drainage and acid rock drainage that develops as a consequence of the weathering of sulphide rich wastes may represent the principal contaminant source.

### 2.1 TAILINGS AND TAILINGS DAMS

The first stage of mineral processing involves reducing the ore grain size so that mineral grains are no longer locked in a rigid aggregate of gangue. The second stage involves the separation of the mineral grains from the gangue, which may proceed via physical, surface chemical or bulk chemical means. Physical and surface chemical treatments are the most widely used processes as they are generally the least expensive to operate. The waste products from these operations are piped to a tailings dam facility as a paste. **At**  the tailings dam gravity separation of the solid material leaves a supernatant liquid that may either be recycled to the plant, allowed to evaporate or in some cases discharged to a surface water body.

The erosion or catastrophic collapse of tailings dams may result in the rapid movement of contaminated residues downstream and this may have both immediate and long-term consequences for wildlife and any human population in the vicinity. For example, in 1995, 2.9 million cubic metres of cyanide-contaminated tailings escaped into the Omani River in Guyana causing 346 fish deaths. Da Rosa (1997) on the other hand, suggests that as many as 11,000 fish died. A public enquiry concluded that the incident occurred as a result of dam core failure due to faulty construction (George et al., 1996).

Less catastrophic or smaller-scale events are often not reported. For example the collapse of the Maiten tailings dam in Chile, which fell into the Rio Illapel (Figure 2.1), or the case of the Puerto Cristal tailings dam which is being gradually eroded into Lago General Carrera in Patagonia have apparently gone unnoticed. [Table 2.1](#page-14-0) provides an example of the composition of the Puerto Cristal tailings that were derived as a by-product of processing a polymetallic type deposit.

For comparison the composition of a tailings sample from the Rancagua area of central Chile is provided. In this example the discharge was directly from the Minas del Prado

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processing plant to a settlement area with overflow into a nearby stream. In both cases the mercury content is considered to be high, approaching the Dutch intervention value of 10mg/kg at Minas del Prado and in both cases is in excess of the 0.3 mg/kg target value. In the Puerto Cristal example the lead and arsenic contents are both of concern, exceeding relevant intervention limits significantly. One of the problems in taking account of total heavy metal contents in assessing risk is that not all of the metal present may be bioaccessible and this is explored further in the Korean case study.

An article in the magazine *Induambiente* (Anon, 1999a) titled 'No basta decir Adios' (It's not enough to say goodbye) mentions the fact that there are more than 800 abandoned tailings facilities in Chile incorrectly closed down. Juanita Conzalez, Asesora Externa de Conama is quoted as saying: "Alguien tiene que hacerse cargo de ellos y de determinar si existe un riesgo real" (Someone has to take charge of them and determine if there is a real risk).



Figure 2.1 Tailings dam collapse at El Maiten, Chile



<span id="page-14-0"></span>Table 2.1 Trace element content of two tailings samples discharging to surface water  $(Concentrations in mg/kg)$ 

### 2.2 ACID ROCK DRAINAGE

One of the most common waste by-products of metalliferous mining is pyrite, a sulphide of iron. Its presence in the wastes from ore treatment constitutes a major source of acid rock drainage (ARD) and in flooded abandoned mine workings, acid mine drainage (AMD). Large volumes of freshly broken and crushed sulphide-bearing rock are discarded as waste at metalliferous mine sites, commonly giving rise to contamination of surface and groundwater with high concentrations of metals and other harmful elements. Oxidation is the process responsible for the release of AMD and occurs where mining activities open voids in the rock mass, or expose waste rock and process tailings to the atmosphere. The oxidation and dissolution of minerals also releases potentially toxic heavy metals and metalloids (e.g. As, Cd, Zn, Cu and Pb), which are soluble in acidic solutions. The acid and heavy metal load represents a serious hazard for communities living downstream from a mine. Watercourses contaminated by mine water may be used for irrigation or drinking water purposes possibly leading to community ill health.

Micro-organisms play a key role in the formation of AMD. The bacterium *Thiobacillus thiooxidans* oxidises sulphide minerals, whilst *Thiobacillus ferrooxidans* oxidises ferrous iron. It has been suggested that the action of bacteria increases the rate of AMD

*0* 

production by a factor of **1** million. Chemical oxidation of ferrous iron occurs rapidly at near neutral pH. When pyrite is first exposed to oxygen and water, the reaction described in Equation **1** proceeds via a chemical only pathway. The reaction produces acidic conditions under which ferrous iron is kinetically stable. *T.ferrooxidans* then catalyses the oxidation of ferrous to ferric iron. Ferric iron, which has **a** higher solubility in water than oxygen, reacts with pyrite (as an oxidant) to produce more ferrous and sulphate ions. This is known as the propagation cycle, equations 1-3 in Figure 2.2, and is the root cause of acid mine drainage. Expression by a factor of 1 million. Chemical oxidation of ferrous iron occurs rapidly at<br>
near neutral pH. When pyrite is first exposed to oxygen and water, the reaction described<br>
in Equation 1 proceeds via a chemical o



Figure 2.2 The oxidation of pyrite to form acid mine drainage

Processes can also occur that reduce acidity and the heavy metal loading of mine waters. Buffering minerals such as calcite and dolomite may be present in the rock matrix. These carbonates rapidly undergo dissolution in acidic solutions (Equations **4** and 5), consuming protons and thereby raising the pH.

$$
CaCO3 + 2H+ \rightarrow Ca2+ + H2CO3
$$
 (4)

(Calcite dissolution)

$$
CaMg(CO3)2 + 4H+ \to Ca2+ + Mg2+ + 2H2CO3
$$
 (5)

(Dolomite dissolution)

However, some carbonate minerals (e.g. siderite) have no buffering effect. Ferrous iron released during siderite dissolution oxidises to ferric iron, and precipitates as iron oxy-

hydroxide. The number of protons released during precipitation is equal to that consumed by the initial dissolution of siderite.

 $FeCO<sub>3</sub> + 2H<sup>+</sup> \rightarrow Fe<sup>2+</sup> + H<sub>2</sub>CO<sub>3</sub>$  $(6)$ 

(Siderite dissolution, consumes 2 moles of protons)

$$
Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O
$$
 (7)

(Ferrous iron oxidation, consumes 1 mole of protons)

The precipitation of  $Fe(OH)$ <sub>3</sub> (ochre) results in an orange deposit commonly seen coating stream beds in mining-contaminated areas. The coating smothers and kills benthic life, but does provide sites for sorption (see below), which can act to reduce the metal loading of the water.

Aluminosilicate minerals can also act as buffers (though the kinetics of dissolution is slower than for carbonate minerals). The acidic dissolution of albite releases 1 mole of aluminium and removes 4 moles of protons (Equation 9). Subsequent dissolution of gibbsite (often observed as a white precipitate in streams contaminated by AMD), rereleases 3 moles of protons and hence 1 mole of protons is removed overall (Equation 10).

$$
NaAlSi3O8 + 4H+ + 4H2O \rightarrow Na+ + Al3+ + 3H4SiO4
$$
 (8)

(Albite dissolution)

$$
Al^{3+} + 3H_2O \to Al(OH)_3 + 3H^+ \tag{9}
$$

(Gibbsite precipitation)

Figure 2.3 illustrates an example of acid rock drainage discharge from La Cocinera Mine, Chile. The white gibbsite precipitate is clearly evident.



Figure 2.3 Acid rock drainage discharge from La Cocinera Mine, Chile

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#### 2.2.1 Iron Duke Mine, Zimbabwe

Iron Duke Mine is an excellent example of the acute generation of AMD. The mine has been in operation for over 80 years, initially as a gold mine and subsequently exploiting strata-bound massive pyrite deposits. Figure 2.4 illustrates the setting of the mine, which lies in the valley of the Yellow Jacket River.





Figure 2.4 Location of Iron Duke Mine sampling points

<span id="page-19-0"></span>Williams and Smith (1994) described the dump to the east of the workings as showing numerous surface seepages that united and flowed into the Yellow Jacket River with resulting deposition of thick, yellow ochre. When the site was revisited in 2000 the mine dumps had been remediated and surface drainage was controlled via a sump to the Yellow Jacket River. A treatment plant at the mine site dealt with the AMD by liming and the resultant sludges were disposed to settlement lagoons on the north side of the river. Table 2.2 summarises the major element, surface water chemistry of the Yellow Jacket River, observed seepages and pre-treatment *AMD* (full chemical analyses are provided in Appendix **A).** The data are plotted as a Piper Diagram in Figure 2.5 which clearly demonstrates the departure from background concentrations in 212 through a mixing line on which all the other samples plot, to 220, the AMD at the mine site. Of particular interest is the spring sample, 214, which has a pH of 3.25 (well below anything expected from a groundwater) and an arsenic content of 1.4  $\mu$ g/l. The origin of the groundwater acidity and arsenic is tentatively attributed to leakage to groundwater from the treatment sludge lagoons, with final discharge to the Yellow Jacket River. If this interpretation is correct it would suggest that the liming is not neutralising all of the available acid. The interpretation is based on the groundwater data collected from around the lagoons, Table 2.3. Four groundwater samples collected in March 2001 had pH values of much less than 7 and very high arsenic values of between 0.9 and 1.92 mg/l compared with 2.17 mg/l for the waste rock discharge (DW1). The earlier work of Williams and Smith (1994) documents a pH<0.6 and As concentrations of 72mg/l for a February sampling round whereas 1.11 mg/l was the highest recorded value for the AMD in March 2000. The data are quite variable and possibly reflect remediation works and climatic influences on leaching rate and contaminant load concentrations. The impact of the mine is still apparent in samples 218 and Z19 with elevated sulphate and reduced pH over 212 background values. These sample localities are at a distance of approximately four kilometres from the mine workings.

#### Table *2.2* Sampling points and water types at Iron Duke Mine



 $12$ 





Figure 2.5 Water chemistry at Iron Duke Mine



<span id="page-21-0"></span>Table 2.3 Groundwater chemistry in the vicinity of the sludge lagoons. TDS = Total dissolved solids; EC = Electrical conductivity; all concentrations in mg/l.

#### 2.3 PARTICULATES AND **GASES**

Many sulphides will burn spontaneously in air once ignited. The autogenous reaction proceeds rapidly in the temperature range 900-1300K (with little or no fuel requirement). Roasting is the partial or complete oxidation of metal sulphide minerals (MS) with release of sulphur dioxide and is often used for the benefaction of metal sulphide flotation products. The sulphur dioxide liberated (Equation 10) may be collected and used to produce sulphuric acid for use in ore processing.

$$
MS(s) + 1.5O2(g) \rightarrow MO(s) + SO2(g)
$$
 (10)

<span id="page-22-0"></span>In Chile there are a number of documented cases of workers becoming intoxicated from smelter fumes. Mendoza (1993) measured urine arsenic in workers at a smelting plant at Copiapo in northern Chile. He found an average concentration of 0.2mg/l. The workers were removed from exposure and the As concentration dropped to O.l2mg/l except for two workers who ate shell fish and fish. These last two workers were asked not to eat fish for **8** days and retested when the As concentration was found to be 0.03 to O.O5mg/l. Normal urine arsenic levels are  $\langle 10\mu g/l \rangle$  over 24hrs, and diets high in seafood can result in increased concentrations of urine arsenic due to the presence of non-toxic organoarsenic compounds (Adams et al., 1993; Farrow et al., 2000). According to the magazine *Mineria Chilena* Volume 144 of 1993 p23, there are no set limits for As emissions from smelters in Chile, but clearly, in this case, smelter emissions are an important source of exposure.

#### 2.4 PROCESS WATER

Cyanide is used in mineral processing as a conditioner in froth flotation and in larger quantities in gold processing. According to Souren (2000) the **US** mining industry alone used 70 million kilograms in 1989 and cyanidation is still the process method of choice for many gold mining operations. Notwithstanding the large volumes of cyanide used and with the exception of the disasters previously alluded to, there is little evidence for widespread environmental impact from cyanide use and disposal. Data from the Witwatersrand, South Africa (Smith et al., 1984) show a distinct lack of impact from gold mine tailings seepage with regard to cyanide, whilst there is evidence of impact from other mine related chemicals. Smith and Mudder (1991) also commented on numerous mine tailings and heap leach facilities in Arizona, California, Nevada, South Dakota and South Carolina where routine monitoring programmes showed no impact on groundwater quality. This may reflect low source term concentrations (100 to 300 ppm CN) and low mass loading (as facilities were lined). In many cases attenuation of cyanide in the unsaturated zone may be an important process.

Cyanidation uses solutions of sodium and potassium cyanide (USEPA, 1994) as leaching agents. The main stages of the process are leaching of the finely crushed ore followed by treatment with activated carbon in carbon-in-leach or carbon-in-pulp tanks to sorb the gold-cyanide complex. The carbon is removed from the tank for further treatment to recover the gold.

#### <span id="page-23-0"></span>**2.4.1 Cyanide Chemistry and Degradation**

The CN<sup>-</sup> anion contains one sigma and 2 pi bonds, and two empty bonding orbitals, which gives the anion the following behavioural characteristics.

- Pseudo-halogen behaviour i.e. NaCN is similar to NaCl
- Back bonding utilising empty anti-bonding orbitals that enables stable complex formation
- A triple bond, which can be easily broken, and accounts for cyanate / thiocyante formation.

Cyanide compounds NaCN and KCN dissociate in water according to the following equations:



Free cyanide refers to the concentration of CN' and of the weak acid HCN in solution.

$$
CN^{\cdot} + H_2O \Leftrightarrow HCN + OH^{\cdot}
$$
 (13)

The state of the above reversible reaction, (13), is critical in the gold-cyanide extraction processes. At pH 10.3 (or greater), free cyanide in process slurry water or heap leach interstitial fluid will be in the form CN. Should the pH fall to 8.5 or less then HCN is the dominant species and because of its low boiling point and high vapour pressure liable to be lost from solution through volatilisation. In order to maintain the required high pH either lime or sodium hydroxide is added to the leach solution.

Volatilisation of HCN is the main process involved in removal of cyanide in discharge lagoons. The necessary lowering of pH is through uptake of  $CO<sub>2</sub>$  from the atmosphere and dilution by rainwater. A modelling and field study carried out by Simovic et al. (1984) has also demonstrated that the main mechanisms for the natural degradation of cyanide were volatilisation of free cyanide and metallo-cyanide decay. Temperature was found to have the greatest effect on volatilisation rate and the process was complete within 48 to 72 hours.

Cyanide degradation and attenuation mechanisms that operate in groundwater systems are adsorption, chelation and precipitation, bacterial degradation, and hydrolysis to formate.

The metal and oxygen content of the water, pH and aquifer mineral composition affects these mechanisms.

Ford-Smith (1964) reported that 28 elements are capable of forming complexes with cyanide, with 72 metal cyanide complexes possible. The toxicity of metal cyanide complexes is generally due to the dissociation of the complex into free cyanide. At pH 4.5, zinc and copper cyanides (typically found in mineral processing waters and classed as weak acid dissociable (wad) metal cyanide complexes) may dissociate to free cyanide.

Metal cyanide complexes may also form intermediate complexes on route to the formation of more stable compounds that remove free cyanide from the environment as precipitates. The ferrocyanide ion  $(Fe(CN)<sub>6</sub><sup>4</sup>)$  and ferricyanide ion  $(Fe(CN)<sub>6</sub><sup>3</sup>)$  form insoluble salts with Fe, Cu, Ni, Mn, Pb, Zn, Cd, Sn and Ag. Tightly bound iron cyanide complexes produce free cyanide very slowly, hence reducing toxicity.

Cyanide moves only a short distance through soil before being converted to nitrate or fixed by trace metals through chelation. Initial anion complex formation with Fe, followed by precipitation with a transition metal cation also stabilises cyanide in the soil environment. Biodegradation under anaerobic conditions is not nearly as efficient as under aerobic conditions. The limit for effective anaerobic degradation was found by Coburn (1949) to be 3 mg/l cyanide, while at higher concentrations cyanide is toxic to micro-organisms. In terms of adsorption, soils with a high anion exchange capacity (AEC) are more likely to attenuate cyanide (Alessi and Fuller, 1976). Soil minerals with a high AEC include kaolin, chlorite, gibbsite and iron oxides. Chatwin and Trepanowski (1987) found that the magnitude of cyanide adsorption in soils was correlated with the organic carbon content where it is bound or oxidised to cyanate. The oxidation process is described by equation (14).

$$
CN + 0.5O2 + enzyme \rightarrow CNO
$$
 (14)

Cyanide also reacts with sulphur to form thiocyanate, which is much less toxic than cyanide.

$$
S_x^{2} + CN^{-} \to (S_{(x-1)})^{2} + SCN^{-}
$$
 (15)

McGill et al. (1985) found that chalcopyrite, chalcocite and pyrrohotite contributed a significant proportion of their sulphur content to thiocyanate production. However, the sulphur content of sphalerite and pyrite was relatively non-reactive.

<span id="page-25-0"></span>As the pH of the system falls, HCN can be hydrolysed by a different route to give formic acid or ammonium formate, as follows:



A lower pH favours formic acid formation. The rate is slow, but the reaction may be effective under a variety of conditions including those found in saturated relatively anaerobic aquifers.

#### **2.4.2 Arcturus Mine**

For the purposes of the current study, the Arcturus Mine in Zimbabwe was selected as a case study site. Arcturus Mine is located on the SE limb of the Harare Greenstone Belt and is the main producer of the Arcturus goldfield (32.48t gold produced to 1992). The gold is restricted to discrete shear zones and there are six major reefs characterised by **a**  gold-arsenopyrite-pyrrhotite mineral association.

**At** Arcturus Mine the tailings are removed to a tailings dam facility and the supernatant, cyanide solution is either recycled into the process stream or decants into a lined evaporation pond. Excess process water is discharged to a system of lagoons where the retention time is sufficient to allow natural degradation of any cyanide present prior to discharge to surface water, Figure 2.6.

At Arcturus Mine a total of sixteen samples were collected [\(Table 2.4\)](#page-27-0) for analysis as follows :

- Seven process water samples
- Three surface water samples
- **Six** groundwater samples including seepages from the old tailings piles.

Full chemical analyses are provided in Appendix A.

The process waters have been subdivided into two groups:

- 1. Those deriving from the tailings pond
- 2. Those deriving from the process water discharge lagoon

At the tailings pond, supernatant liquid is transferred to a lined evaporation pond, while any excess water is collected in a second unlined pond and interceptor trench. Groundwater quality is monitored at the interceptor trench by a shallow monitoring borehole. Two surface water samples were taken one upstream from the tailings lagoon and one downstream of the lagoon.

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No tailings facility impact was detected on the surface water quality and the slight increase in alkalinity in the upstream sample is probably an unrelated feature. For the purposes of looking at the major element chemistry, Stiff Plots (Tonjes et al., 1995) have been used as they enable a very good visual appreciation of chemical trends.

Figure 2.7 is a Stiff plot for the surface water samples collected in the vicinity of the tailings pond and in the case of Z39 the discharge from the process water lagoon. Sample Z6 represents the supernatant liquid on the tailings; Z5 was collected from a lined overflow pond, Z4 is from a second unlined pond, the sample Z3 was collected from a sump. All of the samples are characteristically of Na-Ca- $SO_4$  type. The size of the Stiff polygons is proportional to the total dissolved solids content and the fact that the polygon shapes are very much alike indicates that the main mechanism is dilution between the tailings pond and the interceptor trench. At the same time there is a reduction in the pH as determined in the field from  $9.62$  in the tailings pond down to  $5.58$  in the interceptor trench. This is probably due in part to absorbed atmospheric  $CO<sub>2</sub>$ . At the measured pH values cyanide would be unstable and HCN would be the dominant species, and given the large surface area of the ponds its volatilisation would be rapid and complete.



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Figure 2.6 Location of sampling points at Arcturus Mine



<span id="page-27-0"></span>Table 2.4 Sample locations and water types at Arcturus Mine



Figure 2.7 Stiff plot for tailings pond water and process water discharge

#### $2.5$ **ARSENIC**

Arsenic is the twentieth most abundant element in the earth's crust and is very commonly associated with base metal deposits occurring as the sulphide minerals: arsenopyrite FeAsS, orpiment  $As_2S_3$ , and realgar  $As_2S_2$ . Arsenic is also a component of some complex copper sulphides such as enargite and tennantite (Read, 1962).

Arsenic is derived from mine wastes by a similar process to the generation of AMD (equation 19):

$$
4FeAsS + 13O2 + 6H2O = 4Fe2+ + 4AsO43+ + 4SO42+ + 12H+
$$
 (19)

Under the range of Eh and pH conditions encountered in soils arsenic may be present as As(II1)-arsenite species or As(V)-arsenate species (Thornton and Farago, 1997). Although the speciation of arsenic is redox-controlled it can also be affected by the action of bacteria and fungi, e.g. forms of the bacterium *Thiobacillus* have been identified as having a role in producing ferric arsenate-sulphate precipitates (Leblanc et al., 1996). Temporal variations between arsenate and arsenite have been observed in the Waikato River (New Zealand) (Cullen and Reimer, 1989). In this river system arsenate is usually high, however, during spring and summer arsenite may predominate. The study suggested that the algae **A.** *oscillaroides* may be responsible in part for the reduction of  $As(V)$  to  $As(III)$ .

Several mining-related cases of arsenic releases into the environment are documented in the literature. Perhaps the most notorious releases of arsenic are from Richmond Mine, situated at Iron Mountain, California. Here the mineralisation consists of massive sulphide deposits in veins that have been mined since the 1860's. The portal effluent (Alpers et al., 1992) has a mean pH of 0.8 and high concentrations of zinc (700- 2600mg/l) and copper (120-650 mg/l). Nordstrom et al. (2000) describe discharges and seepages of AMD in the mine with negative pH values as low as -3.6 and dissolved metal content as high as 200 g/l. Measured arsenic concentrations in the same discharges are as high as 850 mg/l (Nordstrom and Alpers, 1999).

The Summitville gold mine operation in Colorado was abandoned, due to bankruptcy, by the operator in December 1992 (Pendleton et al., 1995). As well as the cyanide heap leaching pads, large volumes of waste rock were left on the surface and AMD and cyanide leach solutions were present. The sources of AMD include flows from adits, seeps from waste rock piles and ponds which develop on the surface as a consequence of rainfall. According to Plumlee et al. (1995) the waters draining the adits and waste dumps have pH values ranging from 2.3 to 3.2 and arsenic concentrations ranging over an order of magnitude from 100 to 4000 ppb. The same authors also recognised the role of evaporation in producing soluble heavy metal salts as a secondary source of contamination citing the formation of highly acidic metalliferous ponds and puddles after summer thunderstorms as evidence of this process.

Bech et al. (1997) identified phytotoxic effects around the Mina Turmalina copper mine located in the Peruvian Andes to the north-east of Chiclayo. Limited plant performance was attributed to potentially toxic arsenic concentrations that were found in all soil samples tested, the highest value recorded was 7670 mg/kg. Similar concentrations of As are also reported for soils in the vicinity of abandoned mine dumps in Zimbabwe

<span id="page-30-0"></span>(Jonnalagadda and Nenzou, 1996). Armienta et al. (1997) attribute the arseniccontaminated groundwater of the Zimapan Valley in Mexico to its interaction with mineralised As-bearing rocks. Arsenopyrite, scorodite and tennantite were identified as probable source minerals.

In the Mother Lode District of Tuolumne County, California, Savage et al. (2000) have determined that As is released into the environment as a result of the weathering of mine wastes. The weathering products were found to be primarily goethite with arsenic content up to 1260 ppm, while jarosite and gypsum may contain up to 1300 ppm arsenic. These workers also identified that arsenic content increases with total iron reflecting the efficiency of arsenic removal by sorption and coprecipitation with iron compounds. As previously described (Williams and Smith, 1994), arsenic is recorded as a component of the AMD at the Iron Duke Mine in Zimbabwe. Arsenic removal from the natural system is postulated to be due to coprecipitation with iron oxyhydroxides (ochre) in the Yellow Jacket River. Williams (2001) in reviewing data for 34 mining localities covering a range of metallogenic types and climatic settings proposed that in most cases arsenopyrite is the primary arsenic source. It was postulated that in-situ oxidation generally results in the formation of scorodite (FeAsO<sub>4</sub>.2H<sub>2</sub>O) which has limited solubility under a range of Eh/pH conditions, and hence constrains arsenic mobility. The exception was the Ron Phibun tin mining district in Thailand where post-alluvial tin mining groundwater rebound has been linked to increased arsenic in drinking water (Fordyce et al., 1994; Williams et al., 1996). This is believed to be due to the solution of arsenopyrite oxidation products formed during the mining phase of groundwater drawdown. It should be noted that the role of scorodite as an appropriate candidate for arsenic immobilisation has been questioned by Roussel et al. (2000) who point out that its solubility exceeds drinking water standards irrespective of the pH.

Lee et al. (2000) describe mean concentrations of around 110 mg/kg arsenic in paddy soils (range 13-642 mg/kg) and 104 mg/kg in farmland soils (range 16-444 mg/kg) in the vicinity of Da Duk Mine, **S.** Korea. The arsenic dispersal from the mine site is attributed to sediment transport and irrigation with contaminated surface water. Crops grown in the Da Duk area contain elevated concentrations of arsenic especially rice  $(0.3 - 0.6 \text{ mg/kg})$ As) and Chinese cabbage (0.65 mg/kg As). A comparison with UK values quoted by MAFF (1982) are useful in demonstrating that the arsenic concentrations at Da Duk are elevated. The MAFF report indicates a range of <0.01-0.01 mgkg for cabbage and 0.08- 0.28 mg/kg for rice.

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## **2.5.1 Fachinal Mine, Chile**



Table 2.5 Some chemical parameters for Fachinal Mine waters (concentrations in mg/l)

Table 2.5 and Figure 2.8 provide some information on arsenic concentration at the Fachinal Mine in Patagonia, **S.** Chile. In a 1999 interview with the Operations Manager of the mine (Anon, 1999b), the ore processing was described as flotation to produce a pyrite-rich concentrate from vein deposits containing gold and silver. The concentrate was exported to Japan for refining. The tailings were disposed to a tailings dam in the Laguna Los Juncos (also known locally as Laguna Verde) catchment, Figure 2.8. This particular lake does not directly connect to Lago General Carrera, a major, inland, fresh water body and at the time of visiting the water level in the smaller lake was falling due to evaporation. Four monitoring boreholes have been constructed down hydraulic gradient from the tailings dam, BH-S4 is designed to monitor a lined leachate collection pit below the tailings dam and BH-S11 / BH-S5/ BH-S13 monitor the down gradient flow to Laguna Verde. The results would seem to indicate that surface water runoff from the mine site is the most contaminated with respect to arsenic. The surface water bodies, the main receptors, show elevated arsenic concentrations in excess of  $150 \mu g/l$  and concentration due to evaporation may be an important concentrating mechanism.

Groundwater concentrations do not seem to indicate contamination arising from the tailings lagoon nor any clearly defined trend. This is thought to be due to the nature of the mineralisation, which occurs in veins, and might also explain the disparity in the results from the two adit drainage samples, C40 and C44.

#### **2.5.2 Andacollo, Chile**

The town of Andacollo in north-central Chile is an ancient centre of gold and copper mining. Gold is produced from strata-bound and manto deposits as well as vein and placer-style mineralisation (Reyes 1991, Oyarzun et al., 1996). Old tailings piles are found within the area of residential town housing and groundwater samples collected from wells in the town indicate that the groundwater is contaminated with concentrations of As, Pb, Cd and, to a lesser extent, MO, which exceed the WHO guideline values (Figure 2.9). Attempts to assess the level of groundwater contamination using MINDEC have proved unsuccessful, however, due to the complex history and spatial distribution of contamination sources within the town, and uncertainties regarding recharge rates and probable groundwater gradients.

Water samples: Fachinal Mine



Groundwater samples: Andacollo



Sample concentration / WHO drinking water guide value

# 3 Mining-related Arsenic Contamination in Korea

Lee et al. (2000) describe mean concentrations of around 110 mg/kg arsenic in paddy soils (range 13-642 mgkg) and 104 mgkg in farmland soils (range 16-444 mgkg) in the vicinity of Da Duk Mine, **S.** Korea. The arsenic dispersal from the mine site is attributed to sediment transport and irrigation with contaminated surface water.

Da Duk Mine is located about 200 km to the southeast of Seoul and was one of the largest Au-Pb-Zn mines in Korea (Figure 3.1). During its period of operation, mainly in the 1950s, the mine produced over 20 kg of Au, 50 kg of Ag and thousands of tons of Pb and Zn. The mineralisation is a hydrothermal replacement type with galena (PbS), sphalerite  $(ZnS)$ , chalcopyrite (CuFeS<sub>2</sub>), pyrite (FeS) and arsenopyrite (FeAsS) in quartz veins. The host rock is a mixture of pyrite (FeS) and arsenopyrite (FeAsS) in quartz veins. Precambrian and Jurassic granitoid rocks. The mine was closed in 1984 and large amounts of mine wastes including tailings have been left untreated. These materials have been dispersed down slope by surface erosion and by rain and wind action into lower lying agricultural land. Leachate discharged from the tailings flows into the Da-Duk creek, the main stream in the study area. The impact of AMD waters is easily recognisable in the field by yellowish red (orange ochre) precipitates along the entire stream channel.

Samples of tailings, soils and sediments were taken for chemical analysis. Stream sediment and water samples were mainly collected downstream from the tailings. Random samples of crop plants were also taken and included rice, red peppers, sesame leaves, bean leaves, radish leaves and Chinese cabbage. Fingernail samples were taken from farm workers living in proximity to the mine area.

A number of researchers have developed *in vitro* tests to measure the bioaccessible fraction of a chemical taken up from a soil sample under simulated gastrointestinal conditions (Ruby et al., 1993, 1996; Williams et al., 1998). Soil samples from agricultural land around the Da-Duk mine were selected for human bioaccessibility testing and in this study, the SBET test, a simplified *in vitro* method, was used to determine bioaccessibility of arsenic and heavy metals.

### 3.1 SOURCE TERM CHARACTERISATION

High mean concentrations of 8782 mg/kg As, 8.3 mg/kg Cd, 489 mg/kg Cu, 3638 mg/kg Pb and 919 mg/kg Zn were found in the tailings. Mean concentrations of As, Cd, Pb and Zn in soils are significantly higher than for world average soil reported by Bowen (1979) while Cu concentration is similar to the world average soil. In particular, high mean concentrations of As  $(110 \text{ mg/kg}$  in paddy,  $104 \text{ mg/kg}$  in farmland, and  $156 \text{ mg/kg}$  in mountain soils, respectively) are present to the extent that crops produced on them would normally be considered unfit for human consumption.

Crops containing elevated concentrations of arsenic are rice  $(0.3 - 0.6 \text{ mg/kg})$  and Chinese cabbage (0.65 mg/kg). Ranges and means of element concentrations in crop plants around the Da-Duk Mine are shown in Table 3.1. **A** comparison with UK values quoted by MAFF (1982) are useful in demonstrating that the arsenic concentrations at Da Duk are elevated. The MAFF report indicates a range of  $\langle 0.01 - 0.01 \rangle$  mg/kg for cabbage and 0.08-0.28 mg/kg for rice. Compared to normal concentrations in rice grains grown on a

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Table 3.1 Arsenic concentration (mg/kg) in a variety of food crops. (Where the number in the brackets is  $>1$  the value is a mean)





Figure 3.1 Location of the Da-Duk mine and sample locations. Red dots are soils and tailings and blue dots are water samples.

non-polluted area in Korea (Rhu et al., 1988), mean concentrations of 0.39 mg/kg As and 0.08 mg/kg Cd are elevated in rice grains from the mine area. High concentrations of 8.35 mg/kg As and 0.52 mg/kg Cd in rice stalks were also found. Rice is generally grown under both reducing and oxidising conditions and stalks sampled under oxidising conditions were found to contain higher metal concentrations than those sampled under reducing conditions. This agrees with a study by Jung and Thornton (1997) that demonstrated that the availability of metals decreases under submerged, reducing conditions due to precipitation and sorption onto iron compounds.

High concentrations of 1578 mg/kg As were found in stream and sediment concentrations and decreased with distance from the tailings probably as a consequence of dilution by mixing with uncontaminated sediments. The impact is detectable for about 500 metres down stream from the tailings. Iron and As concentration in stream waters decreases rapidly downstream with rising pH

as a result of coprecipitation in Fe-oxyhydroxides onto the stream bed. This mechanism of As removal is well documented elsewhere (e.g. Pierce and Moore, 1982; McClean and Bledsoe, 1992).

## 3.2 EXPOSURE PATHWAYS AND RECEPTORS

In order to define the pathways and receptors a conceptual model needs to be developed and in the case of the receptors in the vicinity of Da-Duk mine this is best achieved with a cartoon as illustrated in Figure 3.2. The pathways and receptors identified are as follows:

- 1. Effluents and leachates entering groundwater and surface water.
- 2. Contaminated sediment entering surface water bodies.
- **3.** Contaminated surface water used for irrigation and drinking.
- 4. Dispersal of particulate matter onto agricultural soils.
- 5. Soil ingestion by farmers
- **6.** Plant uptake of contaminants
- 7. Ingestion of contaminated plants.

In the following risk analysis only pathways (5) and (7) are assessed. In terms of soil data the results of SBET tests have been used and results indicate that between **6** and 22% of As is bioaccessible.

Arsenic is a documented human carcinogen as well as a toxic heavy metal (WHO, 1993). Toxic risks are defined for non-carcinogenic exposures, and evaluated in terms of a Hazard Quotient (HQ). The HQ is the ADDRfD where **RfD** is the reference dose and ADD is the average daily dose. A toxic risk exists for HQs>l. Compounds deriving from mine sites either constitute a toxic hazard or a carcinogenic hazard. Toxic hazard estimates are expressed relative to a reference dose concentration. The reference dose is an exposure that can occur over a prolonged period without ill effect.

Carcinogenic risks are statements of probability. Individual excess risk is an estimate of the probability that an individual *will get* cancer from an exposure, *not* the probability of dying from it. It is calculated from Risk =  $1$ -exp{-(SF x LADD)}. The LADD is the average daily dose averaged over a lifetime and SF is the slope factor, i.e. the gradient of the laboratory determined dose - response curve. Carcinogenic compounds differ from systemic toxic compounds in that there is no lower limit for the existence of cancer risk.

The SF and RfD are compound specific and may be obtained from the U.S.EPA database **IRIS**  (Integrated Risk Information System - available on the Internet).

In the soil pathway exposure occurs through direct contact with soil and ingestion during normal agricultural activities. To calculate the exposure duration **a** typical Korean farmer was interviewed to determine the working/exposure pattern. The following data is relevant to the calculations:

- (1) Working period in the fields is about seven months (210 days) from mid-March to mid-October.
- (2) About 10 hours are spent working each day (includes a stop for lunch)



Exposure pathways of Korean farmer

Figure 3.2 Conceptual model of exposure for a Korean farm worker

- (3) In the cultivation of Chinese cabbage all the work of ploughing and weeding is carried out by hand
- (4) In the cultivation of rice most work is carried out by machine
- (5) Average male life expectancy is 69 years for a male and 77 for a female. (Source: Korean **Statistics Administration**)
- (6) Average male body mass is 66kg and for a female is 55kg. (Source: Korean Ministry of Health and Welfare)

It is assumed that a female Korean farm worker begins working in the fields at the age of 12 years. The concentration of As using the SBET test was found to vary from 1.5 to 17.9 mg/kg in the soils from the Da-Duk mine. The highest concentrations were encountered in paddy soils.

The following dose calculations are made assuming that the exposure derives from arable fields only and the As mean value is 3.85 mg/kg. The soil ingestion rate has been taken from the Exposure Factors Handbook (USEPA, 1999) to be 450 mg/d and is the upper bound estimate.

According to the Korean Ministry of Agriculture a Korean farm worker has an average rice intake of 437.5 g/d of rice while unclassified plant food is said to comprise 1205 g/d. If it is assumed that green vegetables comprise the difference between the total intake and the rice and fruit intake then t a figure of 624 g/d greens is calculated. Furthermore if it is assumed that Chinese cabbage constitutes 40% of this figure then a daily consumption of Chinese cabbage amounts to 250 g/d.

The following table (Table 3.2) summarises the results of the risk calculations.



Table 3.2 Sources of risk from the food and soil pathways

It is evident that most of the toxic risk derives from contaminated food and not from contaminated soils. The soil pathway, even when using a conservative estimate for soil ingestion does not seem to be a hazard. However, the carcinogenic risk associated with both the soil and food pathway is unacceptably high. The U.S. EPA consider that and increased risk of cancer of le-6 to be the cut off for acceptable risk.

The analysis supports the view that a significant toxic risk exists in the vicinity of the Da-Duk mine site due to the consumption of locally grown rice and Chinese cabbage and that an unacceptable carcinogenic risk is associated with the soil ingestion and food intake pathways. Unfortunately no epidemiological evidence was available for the Da-Duk area to validate these risk assessment findings. However, samples of farm workers fingernails were collected in the area and analysed for arsenic content. The results were compared with a test group from Seoul.

Arsenic concentrations in hair and nails are higher than in other organs because of the high keratin content (Herber and Stoeppler, 1994). Arsenic in hair and nails reflects exposure to inorganic arsenic only and is thus also a good indicator in cases of short-term exposure i.e. for arsenic poisoning (Smith, 1964; Valentine et al., 1979). Arsenic is deposited in the nail roots from the blood stream and then migrates distally as the nails grow. Arsenic concentrations in fingernails of farm workers are higher than normal level of 0.30 mg/kg As (Liebscher and Smith, 1984), and a maximum value 1.5 mgkg As was observed. In terms of gender, As was found to be higher in male fingernails than female fingernails.

The Student's T-test comparing the arsenic concentrations in fingernails of farm workers and the control (non-farming) group indicated that there is a statistical difference in average concentration of As between the two groups at the 99.5% confidence limit.

### 3.3 CONTAMINANT TRANSPORT IN GROUNDWATER: MINDEC **ANALYSIS**

The potential for the migration of contaminants from the tailings at Da-Duk mine has been analysed using MINDEC.

The following parameters were used as input data to the program:

#### **Source term data**



Leachate composition:



### **Groundwater pathwav data**



#### **Receptor data (average S.Korean female)**



The input leachate composition corresponds to the maximum tailings effluent concentrations recorded by Lee et al. (2000). For the purposes of the analysis it has been assumed that all of the leached trace elements pass from the tailings to groundwater and the surface run-off of leachate has therefore not been considered. It has also been assumed that background levels of arsenic and trace metals in the groundwater are insignificant and can be ignored.

The results (Table **3.3)** indicate that there is the potential at the Da-Duk site for the groundwater migration of contaminants at potentially harmful concentrations over distances of at least 2 km from the tailings over a time period which is less than the probable current age of the tailings. It should be noted that increasing the hydraulic gradient (or increasing the permeability of the aquifer medium) not only has the effect of reducing the time taken for the plume to reach any given point (Table **3.3)** but also of reducing peak plume concentrations through enhanced dilution.

Table 3.3 Time (in years) for groundwater As levels to exceed WHO drinking water guidelines at receptor site

#### **Medium sand aquifer**



(n/a indicates that the contaminant plume concentration stabilises at a steady-state value below the WHO guideline value.)

In order to establish the source to receptor distance within which arsenic is likely to pose a health risk to consumers of groundwater, the risk assessment module of MINDEC has been used. It was calculated that the arsenic concentration which would give rise to a hazard quotient of 1 is 0.011 mg/l, based on the receptor data tabulated above (i.e. body weight =  $55\text{kg}$ ; water intake = 1.5 litres / day; exposure frequency =  $365$  days) assuming that all water consumed is groundwater. With a hydraulic gradient of 0.05 and medium sand alluvial aquifer, the groundwater pathway module of MINDEC can then be used iteratively to calculate that this limiting concentration should be attained at a source to receptor distance of 2600m. At distances of less than 2600m from the source, therefore, consumers of groundwater might be subject to a significant toxic risk from arsenic.

# <span id="page-42-0"></span>4 Conclusions

Without doubt the most visible impacts of abandoned mining are derelict ground formed by waste rock piles, abandoned buildings and the sight of acid drainage, both ARD and AMD, which aesthetically is never very pleasant and in most cases is the source of serious heavy metal burden on the environment. In the operational mines and mineral processing plants visited effluents were carefully monitored and environment management systems were in place in most cases. However, site aftercare after mine closure was generally seen to be non-existent.

Literature searches, recent news and observations in Chile and Zimbabwe have emphasised that poor tailings dam construction and aftercare failure are major causes of environmental impact, see Appendix **B.** The problem was found to be a general one in Chile, but Iron Duke and Arcturus Mines in Zimbabwe had both suffered from tailings and waste rock problems in the past.

The present project concentrated on the groundwater and surface water pathway for contaminant transport away from tailings and mine sites. However, the risk assessment work on a reasonably well constrained site (in terms of data), Da-Duk Mine in Korea has demonstrated that contaminated soils and arsenic bioaccumulation by food plants pose a serious threat that certainly needs further investigation.

Air borne dispersal of contaminants from dried up tailings lagoons and waste piles is considered to be a major problem, but one about which there appears to be little information. Stabilisation of abandoned tailings should be considered as a major priority in any site remediation strategy. A possible sustainable approach would be to plant heavy metal-resistant tree species that could be harvested to supply a local fuel wood industry.

The treatment of acid drainage is more problematical in that there is a need for long-term aftercare and certainly in the past mining operators did not make financial provisions for this eventuality. As can be demonstrated with the MINDEC model the duration of the activity of the pyrite source term, the main contributor to acid drainage, runs into many decades and even minor anthropogenic disturbance tends to cause problems with renewed acid generation.

In many instances, site remediation may be necessary in order to reduce the risk to nearby inhabitants to acceptable levels. This may involve the removal or modification of the contaminant source, the re-engineering of the contaminant pathway or, in extreme cases, the relocation of the receptors. Contaminant source modification options include covering with low permeability media or using chemicals to neutralize acidity or immobilise heavy metals. Pathway re-engineering may include the construction of structures such as reactive barriers and wetlands which are intended to modify the acidity and oxidation potential of contaminated waters so that dissolved contaminants are immobilised. In many areas with a long history of mining activity there may be hundreds of potential contaminant sources and there is therefore a clear role for site prioritisation tools and guidelines with which to decide where to allocate available resources.

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Appendix  $A$ : Sample descriptions and chemical analyses for samples collected in Chile, (sample numbers prefixed C and CS) and Zimbabwe (Sample numbers prefixed Z)







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