

**Red Dog Mine
Closure and Reclamation Plan**

SD D2: Supporting Geochemical Review and Interpretation

**Red Dog Mine Closure and
Reclamation Plan**

**Supporting Geochemical Review
and Interpretation**

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1 Introduction

As a component of the Application for a Solid Waste Permit for the Red Dog Mine, SRK (2003b) prepared a report consolidating all available information on the geochemical behaviour of waste rock, pit walls and tailings at the mine. The report was prepared to in part to satisfy some of the requirements in the Action Plan (AMEC 2002).

For the Closure and Reclamation Plan, a water and load balance has been prepared to allow comparative evaluation of potential closure options. Important inputs to the closure plan include the chemistry of water originating from the various sources, and the long term stability of the inputs. A number of factors exist that can cause steady and abrupt decreases and increases in water chemistry. The purpose of this document is to evaluate the potential for changes in water chemistry at Red Dog Mine using the existing database consolidated by SRK (2003b). This report includes:

- An overview of mechanisms that might cause long term changes in water chemistry.
- A brief review of the existing database to identify any changes in water chemistry.
- Evaluation of evidence for long term changes in water chemistry.
- Discussion of implications for load balance predictions at Red Dog Mine.

The data tables and graphs in SRK (2003b) should be referred to in conjunction with the current report.

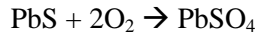
2 Mechanisms Causing Long Term Changes in Water Chemistry

Conceptually, a number of mechanisms can result in both long term decreases and increases in metal loadings from open pit walls, waste rock dumps and tailings. The main explanation for long term decrease in metal loadings is the depletion of mineral sources. In the case of sulfide mineral oxidation, the depletion of the source results in smaller reactive surface area that reduces the rate at which the remaining mineral can be depleted. The overall trend is exponential. The oxidation rate curve typically decreases rapidly at first then becomes flatter resulting in sustained relatively low oxidation rates compared to initial conditions. Depletion effects of this type are commonly observed in laboratory tests and some small-scale field tests (Norecol Dames & Moore 1991) but are rarely observed at full scale probably because at full scale, overlapping effects mask the decreases from individual components. Furthermore, at Red Dog the reactive minerals occur in many different forms ranging from fine grained (framboidal), to massive, and veined. Each of these forms will react differently, resulting in a non-uniform decay.

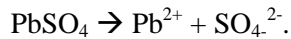
An additional factor is that the chemistry of seepage typically reflects the dissolution of oxidation products (either pre-existing or produced by mining) rather than primary oxidation processes. Dissolution of these minerals may be affected by solubility controls. In this case, the depletion of the oxidation products controls the long term decrease in loadings and will be affected by the occurrence of these minerals.

A number of processes can result in increase in metal loadings, including:

- **Depletion of acid buffering minerals.** Depletion of acid buffering effects is usually the best documented effect at mine sites. Many mineral wastes contain at least some carbonate minerals which initially hold the pore water chemistry at near neutral pH. Under these conditions, the well known biological catalysts are not effective. As the carbonate buffers are depleted, pH usually decreases to the next available buffer, which may be dissolution of aluminum silicates or iron hydroxide. As the pH decreases, oxidation accelerates releasing higher metal loads. Also, previously formed secondary minerals stable under higher pH conditions are dissolved and metal loadings increase.
- **Solubility product effects.** Loadings of metals occurring as relatively weakly soluble secondary minerals can be affected by solubility product effects. This effect can be explained by the dissolution reaction for lead sulfate. Lead sulfate (anglesite) forms by the oxidation of galena:



and is sparingly soluble according to the reaction:

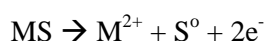


The solubility product (k_{sp}) for this reaction is written:

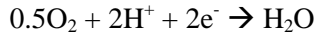
$$k_{sp} = a_{\text{Pb}^{2+}} \cdot a_{\text{SO}_4^{2-}}$$

The “a” in the equation is activity or approximately concentration. Since k_{sp} is a thermodynamically-defined constant, lead concentration varies inversely with sulfate concentration. As a result, a decrease in sulfate concentration (for example, due to depletion of more soluble sulfate salts) can result an increase in lead provided that lead sulfate can dissolve. Reaction rate reductions at low temperatures may be a factor. Barium shows similar behaviour as lead potentially resulting in increased barium concentrations as sulfate concentrations decrease.

- **Galvanic effects.** Galvanic effects refer to processes occurring when semi-conducting materials with different rest potentials are in contact with each other. Rest potential is defined as the equilibrium electrode potential at zero net anodic or cathodic current. When two minerals with different rest potentials are connected (ie in contact) in a salt containing solution, the rest potentials determine which of the minerals behaves as the cathode and anode. The generalized anode reaction for a metal sulfide (MS) is:



It indicates oxidative dissolution. The cathode reaction is:



The mineral with the lower rest potential behaves as the anode and therefore dissolves while the mineral with the higher potential is the cathode and is protected from oxidation. For example, if pyrite (FeS₂) and sphalerite (ZnS) are in contact, sphalerite oxidizes releasing dissolved zinc whereas pyrite does not oxidize until the sphalerite is depleted. Rest potentials for these minerals and others (compiled by Kwong et al 2003) are shown in Table 1.

Table 1: Rest Potentials of Selected Sulfide Minerals (compiled by Kwong et al 2003)

Mineral	Rest Potential (volts)
Pyrrhotite	-0.28
Sphalerite	-0.24
Galena	0.28
Covellite	0.42
Chalcocite	0.44
Chalcopyrite	0.52
Pyrite	0.63

3 Review of Water Chemistry Database

The monitoring database for waste rock stockpile seeps, pit walls and tailings seepage were reviewed to determine if existing water quality is stable or shows any evidence of long term increases or decreases. The review was based on the data provided in Appendices F, G and H in SRK (2003b) with the addition of monitoring data from the 2003 open water season.

3.1 Main Waste Rock and Overburden Stockpiles Seepage

Overall review of the database for waste rock seeps monitored for more than a year indicated that there are few indicators of long term changes. Seasonal effects are strong and may obscure subtle shifts in the data. Only MWD 7 and 17 show what appears to be a long term increase in TDS. This appears to be controlled by increasing sulfate and magnesium rather than zinc or iron.

Controls on solution chemistry were evaluated using MINTEQA2, though the results are approximate because the ionic strengths of the seepage waters are greater than 0.5. Above this level, the calculation of activity coefficients is not reliable using the Davis Equation. The following controls were identified and are logical:

- The highest calcium concentrations are probably limited by gypsum dissolution.
- Magnesium concentrations are well below magnesium sulfate soluble limits.

- The highest zinc concentrations are theoretically limited by the dissolution of zinc sulfates and silicates.
- Lead concentrations are limited by lead sulfate (anglesite) formation.
- Dissolved iron likely is dominantly in the ferrous form and is well below soluble limits for ferrous sulfates.

Two seeps are monitored at the Overburden Stockpile. These seeps are consistently pH-neutral and there are no increasing or decreasing trends. Sulfate was not monitored historically.

3.2 Open Pit Sump

The Open Pit Sump has shown an erratic decrease in pH from highs above 5 to below 4. At the same time TDS has increased from 5,000 mg/L in the late 1990s to between 5,000 and 10,000 mg/L currently. The increase in TDS is driven by increases in all major ions (sulfate, zinc, iron and magnesium).

3.3 Tailings Seepage

Tailings seepage has shown declining pH from above 6 in 2000 to currently below 6. At the same time alkalinity decreased from between 100 and 200 mg CaCO₃/L to near undetectable. The dominant ions in solution are sulfate and calcium. TDS appeared to decline from 1998 to 2000 but is now erratic between 2000 and 4000 mg/L. Calcium began to increase in 2001.

4 Discussion of Long Terms Loading Changes

4.1 Sulfide Depletion Effects

The waste rock seepage database does not show any indication of decrease in loadings resulting from depletion of sulfides. However, the majority of humidity cell tests on waste rock and tailings showed evidence of depletion of sulfur, iron and zinc. This indicates that individual sources deplete relatively rapidly, but this is not apparent in the seepage data for the reasons indicated in Section 2.0.

4.2 Depletion of Acid-Buffering Minerals

Depletion of acid-buffering minerals results in pH transitions usually occurring in steps separated by periods during which pH remains relatively stable. Steady decreases in pH may also occur, which usually reflects depletion of a series of weak buffers. No sharp pH changes have been observed in seepage from waste rock. The Main Waste Stockpile seeps are strongly acidic. Based on the presence of some acid buffering capacity in the rock indicated by acid-base accounting a short period of non-acidic conditions may have occurred very early in construction, but the seeps were not monitored at that time. The declining pH in the Open Pit Sump may reflect the consumption of buffers in the pit

walls, but could also be due to changes in the proportions of different types of waters in the pit walls, or galvanic effects (discussed below).

The majority of humidity cell tests (see SRK 2003a) showed either a rapid initial transition to strongly acidic conditions, or stable non-acidic conditions (Kivalina Shale, Ikalukrok Shale). These latter samples contained high neutralization potentials. Two humidity cells containing Ikalukrok Barite (HC 3) and Silica Rock (HC 7) contained no detectable carbonate but did not generate acid immediately. HC 3 showed erratic pH between 5 and 7 for a year before being terminated. HC 7 generated leachate with pH near 6 for nearly two years then showed a decrease in pH to near 3 over about a year period. The lack of carbonate minerals in these samples indicates that these pH effects are not related to depletion of carbonate minerals but more likely indicate a galvanic effect (discussed below).

In general, changes in pH due to depletion of buffering minerals probably occurred early in the history of the Main Waste Rock Stockpile. The NP of most waste rock is very low and was probably depleted shortly after deposition. In contrast, the rock composition of the Overburden Stockpile indicates that non-acidic conditions will probably be maintained.

4.3 Solubility Product Effects

Barium, lead and calcium loadings are potentially affected by solubility product effects. The inverse relationship between barium and lead sulfate is readily apparent (for example, see Figure 9 in SRK 2003a) in leachates from humidity cells. In both cases, the highest barium and lead concentrations are associated with the lower sulfate concentrations. Lead release from the humidity cells clearly increased as sulfate release decreased, and vice versa. The relationship is not apparent in the field data, possibly due to the effects of problems with the sulfate analysis, seasonal variations and the lack of long term sulfate trends.

In the very long term, sulfate concentrations in waste rock seepage (both Main and Overburden Stockpiles) can be expected to decrease resulting in increasing lead and barium concentrations and loadings.

4.4 Galvanic Effects

Sphalerite and pyrite are the dominant sulfide minerals at Red Dog followed by galena and marcasite. As shown in Table 1, sphalerite oxidation is strongly preferred over pyrite oxidation. The expected effects of preferential sphalerite oxidation would be near molar equivalence of zinc and sulfate in leachates, and non-acidic leachate because the zinc sulfide oxidation reaction does not generate acid. In fact, sphalerite always has an iron sulfide component and therefore some release of iron and possible acidification can be expected. Any pyrrhotite inclusions in sphalerite would be expected to oxidize with sphalerite as shown in Table 1.

Preferential oxidation of sphalerite is shown by field and laboratory data, as discussed below.

Seepage from the waste rock dumps contains on average about twice as much zinc as iron (on a molar basis). This might be explained by the presence of more zinc than iron sulfide in the waste rock, but in fact, iron in sulfide form is estimated to exceed zinc in sulfide form by a factor of about four. It is possible that iron could be attenuated within the waste rock by formation of secondary minerals but at the pHs observed, ferrous and ferric iron are expected to be highly mobile and there is only limited evidence of solubility constraints for zinc or iron.

Both tailings and waste rock humidity cells showed evidence of preferential sphalerite oxidation. The tailings humidity cell released more zinc than iron (on molar basis) early in the test and zinc release was steady, with iron release slowly increasing (see Figure 2 in SRK 2003a). Leachate pH was strongly acidic during this period dropping to less than 3 as iron release increased. After about a year, zinc release suddenly decreased marking nearly complete depletion of zinc contained in the original sample. Iron release also increased suddenly, and iron release then dominated zinc. Subsequently, iron release decreased as it was depleted. The correspondence of increase in iron release as zinc was completely depleted under low pH is a strong indicator that residual sphalerite in the tailings oxidized before pyrite.

Waste rock test HC 7 possibly also shows the same effect. Despite the lack of carbonate, leachate was only weakly acidic and zinc release occurred steadily at about 10 mg/kg/week. Sulfate release was also low and consistent with oxidation of sphalerite only. When pH began to decrease, sulfate release also increased, along with iron and zinc. Zinc release continued to exceed iron on a molar basis but the sulfur to zinc ratio increased indicating that oxidation of another mineral (pyrite) began to contribute to the sulfate load. The interpretation of these results is complicated by the pH change because the decrease in pH would be expected to accelerate metal release. The change in sulfur to zinc ratio in the leachates implies that the source of sulfate in the leachate changed from sphalerite-dominated to some contribution from pyrite, and this resulted in acidification of the leachate.

Results from the tailings test appears indicate that when sphalerite is consumed, sulfate release increased by a factor of about 2.7. Acidity increased by about the same factor.

Although not shown by the test work, the shift from sphalerite to pyrite oxidation would likely result in additional heating since the enthalpy of the pyrite oxidation reaction is 2.8 times the sphalerite reaction on a per mole of sulfur basis.

4.5 Implications to Load Balance Predictions

The overall implications to load balance predictions for closure planning are:

- Load inputs to the current balance for waste rock seepage can be estimated based on averages indicated by the current database.
- Long term loadings need to account for the shift in water chemistry caused by the change from sphalerite to pyrite oxidation. Sulfate conservatively may increase and be balanced by iron rather

than zinc. However, as sulfate and iron increase, ferrous sulfate solubility controls may limit the concentrations.

- Acceleration of oxidation due to heating may occur.
- Long term decline in sulfate can be expected. This could be accompanied by increasing lead concentrations. Current lead concentrations in waste rock seepage average 1 mg/L. Long term lead concentrations might increase to 10 or 20 mg/L.

The order-of-magnitude time frame for these factors can be estimated by calculating depletion of the current inventory in the waste rock.

At the current rate of zinc depletion, the zinc inventory will last at most 25 years (assuming that all zinc is available for leaching and oxidation). As the mine has been production for 15 years, the time frame for the shift to iron dominance could be in the next 10 years. In reality the transition will probably occur over several years as the different sections of the waste rock deplete.

Assuming that sulfur depletion accelerates by a factor of 3 following sphalerite depletion, the time frame for depletion of pyrite at current rates is expected to be in the order of a century, though exponential decrease in sulfate loading can be expected to occur once pyrite is the main source of sulfate and acidity.

The time frame for increased lead leaching is also of the order of centuries since sulfate concentrations must decrease substantially before lead concentrations will increase.

5 Conclusions

The source water quality database was reviewed to determine if there are any factors that could result in long term shifts in water quality including possible decreases or increases in loadings. The main factors considered were depletion of primary and secondary sulfur mineral sources, depletion of acid buffering minerals causing decreases in pH, solubility product effects and galvanic effects. The main potential long term effect is expected to be an overall shift from sphalerite to pyrite as the source of sulfate from weathering of pit walls and waste rock. This shift is expected to result in iron replacing zinc as the dominant ion in seepage and possible factor of 3 increase in acidity in seepage and heating of the waste rock. This effect is expected to occur in the next decade or so. In the long term, and following this effect, the rapid oxidation of pyrite will cause decrease in sulfate release. The inventory of pyrite is large and depletion will occur over the time frame of a century or so.

6 References

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