

Update on Cold Temperature Effects on Geochemical Weathering

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Update on Cold Temperature Effects on Geochemical Weathering

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Executive Summary

Since the mid-1990s, the majority of new mine development and mine closure in Canada has focussed on the northern regions. In response to this activity, the Mine Environment Neutral Drainage (MEND) Program sponsored a series of projects involving review of literature and some data collection to increase the understanding of mine waste behaviour under cold conditions and to evaluate opportunities to exploit low temperatures for control of acid rock drainage (ARD). Over the past ten years, data on low temperature effects have been collected at several sites. The current review, to compile this data, was commissioned by MEND.

The scope of this review covered eight mechanisms that were either expected to occur differently at low temperatures, or were unique to low temperature conditions: oxidation rates of iron sulphide minerals; oxidation rates of other sulphide minerals; activity of different types of bacteria; solubility and reactivity of acid buffering minerals including carbonates and silicates; formation and solubility of secondary minerals (weathering products); freeze concentration effects; physical exposure of minerals due to freeze-thaw processes; and solubility of oxygen in waters used to flood reactive wastes. The primary focus of the report was on understanding these mechanisms at small scales although implications to full scale facilities were considered.

Materials for the review were obtained from the authors' files, contact with mining companies and consultants, and through a general literature search. The majority of information obtained related to specific sites. Fourteen case histories were compiled and form the basis for the review findings. Overall, the authors found that specific information on the reactivity of iron sulphides at low temperatures has been collected from eleven sites and seven of these had comparative temperature data from laboratory testwork. These data indicated rate reductions at low temperatures were generally consistent with the Arrhenius Equation, though some exceptions were apparent, which could be related to compounding effects caused by the temperature differences. Data on the reactivity of other sulphides was very limited.

Considerable progress has been made on understanding the activity of bacteria at low temperatures. It is clear that bacteria can be active at sub-zero temperatures and that bacteria adapt to low temperature conditions.

Specific information on the relative solubility and reactivity of acid neutralizing minerals was not found. Theoretical calculations demonstrate that carbonate minerals are more soluble under cold conditions. This represents a potential opportunity for blending of waste rock since it means that alkalinity may be more available. No relevant data on the weathering of silicates at low temperatures was found. A specific issue caused by the solubility of carbonates at lower temperatures is the greater solubility of heavy metals (e.g. zinc and cadmium) which can be expected. This may explain the observation from testwork that zinc leaching increases as the temperature falls. Specific data on

the solubility of other secondary minerals at lower temperatures were not obtained, but in general lower temperatures should result in lower solubility.

Freeze concentration can be an important effect since it results in increasing dissolved concentrations of contaminants and freezing point depression. The former can result in expulsion of waters containing unacceptable concentrations during freezing. The latter is important because it may prevent waste from freezing.

The effect of physical exposure due to freeze thaw has potential implications for the exposure of reactive minerals to oxidizing conditions. No specific references to the geochemical implications of this process were found.

Finally, the solubility of oxygen in water is greater at lower temperatures than higher temperatures but the decrease in oxygen diffusivity is expected to offset this effect. Specific case studies to demonstrate this effect were not found.

The authors concluded that the main technology gaps exist in the areas of specific methods for low temperature testwork; understanding of the reactivity of sulphide minerals other than the main iron sulphide minerals at low temperatures; the effect of temperatures on the dissolution and weathering of carbonates and silicates; and understanding of the low temperature solubility of secondary minerals (particularly carbonates). The opportunities to harness low temperature conditions to limit ARD and metal leaching remain the same as were identified in previous MEND studies, with the possible addition of blending as an opportunity because carbonates are more soluble at lower temperatures. Limited research has been completed on the effect of low temperatures on the geochemical performance of mine waste management facilities. Research to address some of these gaps is recommended.

Practitioners who wish to invoke the benefit of low temperatures should complete suitable testwork for minesite characterization projects because the data demonstrating the effects of low temperatures are sparse and indicate site specific effects. Larger scale experiments conducted on site are highly recommended.

Résumé

Depuis le milieu des années 1990, la plupart des ouvertures et des fermetures de mine au Canada ont eu lieu dans le Nord du pays. Conséquemment, une série de projets ont été lancés dans le cadre du Programme de neutralisation des eaux de drainage dans l'environnement minier ou NEDEM, ceux-ci comprenant l'étude d'ouvrages et la collecte d'une certaine quantité de données, en vue d'approfondir les connaissances sur l'évolution des rejets miniers dans un milieu froid et d'évaluer des moyens de profiter du climat froid pour maîtriser le drainage minier acide (DMA). Au cours des dix dernières années, des données sur les effets des températures froides ont été recueillies sur plusieurs sites. La présente étude a été entreprise pour compiler ces données dans le cadre du NEDEM. L'étude portait sur huit phénomènes qui devaient se présenter différemment ou uniquement à faible température, soit le taux d'oxydation des sulfures de fer et des autres sulfures, l'activité de diverses bactéries, la solubilité et la réactivité des minéraux neutralisant, y compris les carbonates et les silicates, la formation et la solubilité des minéraux secondaires (issus de l'altération), les effets de concentration par le gel, les changements physiques dus au gel et au dégel, ainsi que la solubilité de l'oxygène dans les eaux servant à submerger les rejets réactifs. L'étude visait principalement à mieux comprendre ces phénomènes à petite échelle et, dans une moindre mesure, à en étudier les effets dans des installations grandeur réelle.

Les données utilisées aux fins de l'étude sont tirées des dossiers des auteurs, d'échanges avec des sociétés minières et des experts-conseils, ainsi que de recherches documentaires générales. Elles portent pour la plupart sur des sites particuliers. Au total, 14 cas ont été regroupés à l'appui de l'étude. Dans l'ensemble, les auteurs ont constaté que des données sur la réactivité des sulfures de fer à faible température ont été recueillies sur 11 sites, dont sept sur lesquels des données comparatives sur la température ont été obtenues lors d'essais en laboratoire. Ces données montraient que les diminutions de taux à faible température correspondaient généralement aux résultats de l'équation d'Arrhenius, hormis quelques exceptions évidentes pouvant être attribuées à l'effet composé des différences de température. Quant aux données sur la réactivité des autres sulfures, leur portée était très limitée.

Les connaissances sur l'activité bactérienne à faible température ont été considérablement approfondies. Il s'avère que des bactéries peuvent être actives à des températures inférieures au point de congélation et s'adapter à de telles conditions.

Aucune donnée sur la solubilité et la réactivité relatives des minéraux neutralisant n'a été trouvée. Des calculs théoriques ont démontré que les minéraux carbonatés sont plus solubles à faible température. Cela pourrait permettre le mélange des stériles, en raison d'une alcalinité disponible potentiellement supérieure. Aucune donnée pertinente n'a été trouvée sur l'altération des silicates à faible température. La solubilité des carbonates à faible température a pour effet particulier d'accroître celle des métaux lourds (p. ex. le zinc et le cadmium), ce qui pourrait expliquer la lixiviation accrue du zinc observée lors d'essais au fur et à mesure que la température baissait. Aucune donnée sur la solubilité d'autres minéraux secondaires à faible température n'a été obtenue, mais la solubilité devrait être inférieure à basse température.

Les effets de concentration dus au gel peuvent avoir un impact significatif, car ils entraînent une augmentation des concentrations de contaminants dissous, laquelle peut mener à l'expulsion des eaux renfermant des concentrations inacceptables, de même qu'un abaissement du point de congélation, qui s'avère important puisqu'il peut prévenir le gel des rejets.

Les changements physiques des minéraux dus au gel et au dégel peut exposer des minéraux réactifs à des conditions oxydantes. Toutefois, aucun renseignement sur les répercussions géochimiques de ce phénomène n'a été trouvé.

Enfin, la solubilité de l'oxygène dans l'eau est plus grande à faible température qu'à température élevée. Cependant, la diminution de la diffusivité de l'oxygène devrait contrebalancer cette augmentation de la solubilité. Aucune étude de cas sur ce phénomène n'a été trouvée.

Les auteurs ont conclu que les principales lacunes techniques et de données concernent les méthodes d'essai à faible température, la réactivité des sulfures autres que les principaux sulfures de fer à faible température, l'effet de la température sur la dissolution et l'altération des carbonates et des silicates, ainsi que la solubilité à faible température des minéraux secondaires (surtout les carbonates). Hormis la possibilité de mélanger les rejets miniers grâce à la plus grande solubilité des carbonates à faible température, les moyens d'utiliser des conditions froides pour maîtriser le DMA et la lixiviation des métaux demeurent les mêmes que ceux relevés lors d'études antérieures rattachées au NEDEM. Peu de travaux de recherche ont été exécutés au sujet de l'effet des températures froides sur la performance géochimique des installations de gestion de rejets miniers. On recommande donc d'effectuer davantage de recherche pour combler les lacunes susmentionnées.

Les spécialistes qui souhaitent présenter les avantages des températures froides devraient exécuter des essais complets à l'appui de projets de caractérisation de site minier, car les données témoignant des effets de telles températures sont rares et rattachées à des sites particuliers. Il est fortement recommandé de réaliser des expériences à grande échelle sur chacun des sites.

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1 Introduction

1.1 Background

Since the mid-1990s, the majority of new mine development in Canada has focussed on the diamond resources in the Northwest Territories (NWT) and Nunavut resulting in three diamond mines (Ekati, Diavik and Jericho). There has also been considerable activity related to the closure of older mine sites including the Giant and Colomac Mines in the NWT, Nanisivik Mine, Nunavut and the large Anvil Range Mining Complex near Faro, Yukon. At the same time, a new mine was permitted in central Alaska (Pogo) and research on cold temperature effects has occurred at the Red Dog Mine in northwestern Alaska. Some limited research has also occurred in northern Europe.

In response to this activity, and recognizing that low temperatures have potentially significant effects on chemical reactions, the Mine Environment Neutral Drainage (MEND) Program sponsored a series of projects from 1993 to 1997 to compile the state-of-knowledge on acid rock drainage (ARD) under cold conditions. In the intervening time, collection of data has continued at many sites and interest has also shifted from solely ARD to the more general effects of contaminant leaching under any pH conditions (e.g. Stantec Consulting 2004). Therefore, in 2005, MEND commissioned this project to update the understanding of the effect of low temperatures on geochemical processes.

1.2 Scope

The scope of the project was provided in a proposal to MEND dated December 24, 2004.

This project is a literature review focussed on new information collected subsequent to the last MEND report on this topic (issued in 1997) to avoid repetition and duplication of earlier findings. As noted above, the review was broadened to cover geochemical processes in general as they related to sources of ARD, including:

- Oxidation rates of iron sulphide minerals.
- Oxidation of other sulphide minerals.
- Activity of different types of bacteria.
- Solubility and reactivity of acid buffering minerals including carbonates and silicates.
- Formation and solubility of secondary minerals (weathering products).
- Freeze concentration.
- Physical exposure of minerals due to freeze-thaw processes.
- Solubility of oxygen in cold waters.

The primary focus of the review was on the state of knowledge of fundamental geochemical mechanisms at small scales (i.e. mineral grains up to small laboratory tests). Under low temperature conditions, large scale effects can be very significant. For example, trapped heat produced by sulphide mineral oxidation can offset the benefit of low temperatures on the rate of sulphide

oxidation, and seasonal climatic effects in the "cold climates" can result in heating of wastes comparable to warmer climates.

1.3 Acknowledgements

The original motivation and scope for this study was provided by Dr. William Price (NRCan, CANMET).

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2 Methods

2.1 Collection of Materials for Review

Two approaches were used to collect the materials for the review.

The first approach involved compilation of available information from company files and contact with other individuals working at specific sites.

The second approach involved compilation of key words for a literature search. Groups of key words used in the search are shown in Table 1. Within the groups, the search was by "OR". Between pairs of the groups "AND" was used.

Mine Wastes	Cold	Acid Mine Drainage	Geography	Weathering	Other	Authors
Mine wastes, Tailings, Waste rock	Freezing, Permafrost, Cold temperature, Low temperature, Ice, Cryogenic, Cold region, Cold climate	ARD, Acid rock drainage, AMD, Acid mine drainage, Prediction, Modelling, Modeling, Water treatment, Control, Prevention	Northern, Arctic, Boreal, Tundra, Alpine, Russia, Northern Europe, Alaska, Yukon, Northwest Territories, Nunavut, Iceland, Greenland, Norway, Sweden	Geochemistry, Oxidation, Neutralization, Weathering, Sulfide, Sulfide mineral, Sulphide, Sulphide, Sulphide minerals, Pyrite, Inhibition, Arrhenius, Rate, Soil, Bacteria, Microbial, Mineral weathering, Activity, Reactivity, Reactant, Carbonate solubility	Freezing point depression, Freeze concentration, Unfrozen solute, Unfrozen porewater, Unfrozen film	Elberling, B, Jamieson, H, Godwaldt, R.C., Nicholson, R, Kyhn, C Blowes, D Bigger, K

Table 1. List of keywords used for literature search

Databases searched included, dialog, EI Compendex, GeoRef, Web of Science, WorldCat, ProQuest Digital Dissertations, CISTI.

2.2 Compilation of Information

Examination of the available literature and documents obtained as part of the review indicated that there is little fundamental research in the area of the effect of low temperatures on the weathering of mines wastes. For example, the authors are not aware of any direct attempts to evaluate the effect of temperature on the oxidation rates of different types of sulphide minerals. The majority of research undertaken at mine sites addresses specific waste management questions for the site. Therefore, the interpretation of information derived from these studies must be placed in the context of site-specific information such as the geological, environmental and mining setting. To compile the information, a template was developed so that comparisons could be made. This approach also exposed deficiencies in the studies and provided a basis for defining minimum information requirements for future projects.

The template also included a section where specific information on the eight areas indicated in Section 1.2 could be recorded.

Appendix A contains summaries of case histories for 13 different mines and one region (Kolyma Lowland, Siberia). Studies of mine waste weathering processes are proceeding at a larger number of sites than indicated by Appendix A. The compilation only covers sites for which comparative (different temperatures) data on geochemical processes or specific cold processes (e.g. freeze concentration) are being obtained. This excludes a number of high profile sites at which geochemical processes at high latitude or altitude are being documented. For example, the Anvil Range Mining

Complex (Yukon) is undergoing extensive closure studies involving geochemical studies but the studies are designed to characterize site conditions rather than specifically document the effect of low temperatures. All mine sites in Canada have lower average annual temperatures than those used for laboratory tests and conceivably provide an opportunity to evaluate the effect of low temperature conditions. Operators should always recognize that generation of heat by sulphide oxidation can offset the benefits of low site temperatures.

3 Findings

3.1 Previous MEND Studies

MEND sponsored several projects in the 1990s on the issues related to management of reactive mine wastes under cold conditions. An update on the applications of closure technologies was completed in 2004. Brief summaries and commentaries on these reports are provided below:

- MEND Project 6.1 Preventing AMD by Disposing of Reactive Tailings in Permafrost. Geocon 1993. This project reviewed the available information on disposal of tailings in permafrost environments. The document primarily focussed on engineering approaches available for freezing of tailings. A few case studies were presented but information was mainly for moisture and temperature profiles. Geochemical data were generally not discussed.
- MEND Project 1.61.2. Acid Mine Drainage in Permafrost Regions: Issues, Control Strategies and Research Requirements. Dawson and Morin 1996. This project thoroughly reviewed the state of knowledge on ARD in permafrost environments including mechanisms, control strategies and research priorities. In terms of processes it was concluded that acid generating and metal leaching reactions are not stopped at low temperatures, and that these processes can continue under sub-zero conditions resulting in heat generation and thawing. No evidence was found to show that oxidizing and bacterial agents are inactive at low and sub-zero temperatures. Freezing of wastes was identified as a significant opportunity for limiting water contact and providing containment of reactive wastes provided that thawing did not occur. Geochemical case study information was very limited. The report provided extensive review of data on maintaining frozen conditions due to its importance in containing reactive wastes.
- MEND Project 1.61.1. Review and Assessment of the Roles of Ice, in the Water Cover Option and Permafrost in Controlling Acid Generation from Sulphide Tailings. CANMET 1997. This project considered the role of ice and snow in the water cover option for management of reactive tailings and the role of permafrost in the management of reactive tailings. The study concluded that an ice cover isolates the tailings from turbulence and exchange of oxygen with the atmosphere; however, concerns were identified with the effect of ice scour and physical disturbance of tailings during break-up. The latter was expected to result in suspension of tailings and possible oxidation effects. Disposal of tailings in

permafrost was identified as a promising technology. It was noted that disposal in unsaturated sub-zero conditions is not sufficient to limit oxygen access and limit acid generation. It is also necessary to raise the permafrost table to encapsulate the waste in ice. This conclusion was consistent with those presented by Dawson and Morin (1996).

- MEND Workshop W.014. Managing Mine Wastes in Permafrost Zones. May 8, 1997. Nine papers were presented at this workshop. Most papers were focussed on physical and engineering aspects of reactive mine waste management. Two papers summarized MEND Reports 1.61.2 and 1.61.3, and two papers provided northern research priorities on behalf of MEND and Indian and Northern Affairs Canada (DIAND) (Norecol Dames & Moore (1994).
- MEND Project 1.61.3. Column Leaching Characteristics of Cullaton Lake B and Shear (S) Zones Tailings Phase 2: Cold Temperature Leaching. Davé and Clulow 1996. This project evaluated the reactivity of two samples of tailings from the Cullaton Lake Mine containing relatively high sulphur content (2.3%) and NP (45 kg CaCO₃/t) (B Zone Tailings) and lower sulphur content (0.4%) and NP (2 kg CaCO₃/t) (S Zone Tailings). Appendix A provides a discussion of the project results. Temperature effects were not clearly demonstrated by the experiment though ARD was generated at low temperatures (2°C).
- MEND Project 1.62.2. Acid Mine Drainage Behaviour in Low Temperature Regimes Thermal Properties of Tailings. Norwest 1998. This project obtained data on the thermal properties of tailings. One of the conclusions was that a large decrease in hydraulic conductivity was found as the temperature was lowered due to the decrease in residual liquid water.
- MEND Project 5.4.2d. MEND Manual Volume 3 Prevention and Control. SENES Consultants Limited and URS Norecol Dames & Moore, 2001 (pages 4-273 to 4-323). This section of the MEND manual summarizes in some detail MEND research completed during the 1990s (that is, MEND reports 6.1, 1.61.1 to 1.61.3). The section's primary focus is on the physical, rather than chemical, aspects of using cold conditions to control reactive mine wastes.
- MEND Project 1.61.4. Covers for Reactive Tailings Located in Permafrost Regions Review, Holubec 2004. This report provides a review of the physics of using permafrost to encapsulate reactive tailings. Data from four sites (Raglan Mine, Nanisivik Mine, Lupin Mine and Rankin Inlet) were reviewed in detail. The report did not evaluate the chemical effects of cover placement except for some water chemistry data from the Lupin Mine.

A general conclusion from the review of earlier MEND reports was that the concepts are still relevant and that the findings remain appropriate

3.2 Specific Mechanisms

3.2.1 Introduction

Table 2 lists the 14 case histories reviewed in Appendix A, and summarizes the information concerning the specific mechanisms available from each site. Locations of the sites in North America are shown in Figure 1.

In Table 2 an "A" designation indicates a site for which quantitative low and high temperature data, or specific data, are available for a low temperature process. A "B" designation indicates that the data are speculative or qualitative. As seen in the table, the majority of useful data cover differences in oxidation rates for iron sulphide minerals. Some of these studies provided spin-off conclusions on oxidation rates for other minerals.

Site	Location	Average Annual Temperature (°C)	Oxidation rates of iron sulphide minerals	Oxidation of other sulphide minerals.	Activity of different types of bacteria.	Solubility and reactivity of acid buffering minerals including carbonates and silicates.	Formation and solubility of secondary minerals (weathering products).	Freeze concentration.	Physical exposure of minerals due to freeze-thaw processes.	Solubility of oxygen in waters used to flood reactive wastes
Critronen Fjord Project	North Greenland	-17	В		В					
Cullaton Lake	NWT	-	В							
Diavik Diamond Mine	NWT	-12	А			В				
Ekati Diamond Mine	NWT	-12	А			В		В		
Keno Hill Mining District	Yukon	-3.6					В	В		
Maarmorilik (Black Angel) Mine	Greenland	-8	В		В					
Nanisivik Mine	Nunavut	-13.5	А							
North Kolyma Lowland Region	Russia	-				В				
Pogo Mine	Alaska	-	А	А						
Rankin Inlet Mine	Nunavut	-11	А				В	Α		
Red Dog Mine	Alaska	-6	А	А						В
Stekenjokk Mine	Norway	0								А
Urad Mine	Colorado	-	В							
Windy Craggy Project	British Columbia	-	А	А						

Table 2. List of sites and relevant information

Notes:

A – Comparative data available on high and low temperatures or good information on a specific cold temperature mechanism.

B – Qualitative data on cold temperature effects.



Figure 1. Locations of sites in North America.

Coverage of other areas is weak. For example, there is little information available in the reactivity of acid buffering minerals under cold conditions that is relevant to mine waste characterization. Limited material was found on the related effects of the solubility of oxygen in water and freeze concentration, and no information was found on the effect of freeze-thaw processes on the exposure of reactive minerals and how this might relate to the long term performance of geochemical wastes.

The following sections of the report summarize specific findings.

3.2.2 Oxidation of Iron Sulphides

The effect of low temperatures on sulphide mineral oxidation is usually described by the Arrhenius equation that relates temperature to reaction rates:

$$k=A.e^{(-Ea/RT)}$$

or to indicate relative reaction rates at different temperatures:

$$\ln(k_1/k_2) = E_a(T_1 - T_2)/(RT_1T_2)$$

where k_1 and k_2 are the reaction rates at temperatures T_1 and T_2 (in Kelvin), E_a is the activation energy of the reaction, and R is the gas constant. The value of E_a varies according to the type of mineral involved. MEND 1.21.2 indicated a range of 50 to 60 KJ/mol for pyrrhotite (Nicholson and Scharer (1998). Kamei and Ohmoto (1999) derived a range of 47 to 85 KJ/mol for pyrite oxidized by dissolved oxygen. Figure 2 shows the calculated effect on rates relative to the typical temperature of laboratories (20°C). The difference in rates with respect to temperature increases as the activation energy increases. The equation indicates that the expected rate ratio for refrigerated tests (about 4°C) and room temperature tests is 0.24 to 0.31.



Figure 2. Decrease in oxidation rate predicted by the Arrhenius equation for activation energies of 50 and 60 KJ/mol

Site	Number of Tests	Mineral	Rate Ratio (Fridge/Room)		
Calculated		Pyrrhotite, pyrite	0.24 to 0.31		
Diavik	4	Pyrrhotite	0.3 to 0.4		
Ekati	2	Pyrite	0.26		
Nanisivik	2	Pyrite and sphalerite	0.41		
		Pyrite	0.53		
Pogo	4	Arsenopyrite	0.29		
		Pyrite	0.4 to 0.8		
Red Dog Mine	4	Pyrite	1		
		Pyrite	0.37, 0.40		
		Pyrite	0.11		
		Pyrite and sphalerite	0.11		
Windy Craggy	11	Pyrrhotite, pyrite	0.34 to 0.67		

Table 3.	Differences	between	oxidation	rates for	or Ial	boratory	/ ex	perimen	Its

Six sites had specific comparative data from a total of 27 individual tests (Table 3). In most cases, the tests were conducted in parallel using the MEND (1991) humidity cell test protocol although variations in the procedure can be expected because different laboratories were used. The Ekati Mine, Nanisivik Mine and some of the Red Dog Mine tests were conducted in sequence. That is, the test was started at room temperature then transferred to a refrigerator. Some of the Windy Craggy testwork was conducted using the Sobek *et al.* (1978) humidity cell procedure. Data from the Cullaton Lake project (Davé and Clulow 1996) are not included because tailings were tested in columns. The tests were performed in sequence and comparison of oxidation rates was complicated by homogenization of samples when the temperature was changed.

The rate ratios show that the observed ratios are often comparable to predicted ratio from the Arrhenius equation, that is, the ratios are least of the same order of magnitude as calculated from the equation. Some sites showed lower rates than indicated by theory (i.e. less than 0.24), while others showed little or no change due to temperature effects. Some of the small differences in rates (Red Dog Mine, Pogo Mine pyrite examples) were a result of low calculated oxidation rates from sulphate concentrations near the detection limit for the analytical method which obscured the temperature change effects. The Windy Craggy 0.67 ratio is for massive pyrrhotite. This difference could be explained by a lower activation energy (17 KJ/mol) but this may not be the only explanation. The Diavik samples also contained pyrrhotite but showed a greater rate reduction.

The cases of high rate reductions (low rate ratios) for Red Dog Mine need to be examined cautiously. One of the Red Dog samples was massive pyrite that oxidized very rapidly under room temperature. When the test was transferred to the fridge, pH increased (from 1.8 to 2.4), and the oxidation rate dropped by a factor of 0.11. A similar result was obtained for a tailings sample. The drop in oxidation rate may be a function of the change in pH which may have been sufficient to reduce the effect of oxidation by ferric iron in favour of oxidation by oxygen. The decrease in oxidation rate is therefore not just a function of reduced reactivity caused by the temperature decrease but a dual effect of reduction in oxidation rate resulting in an increase in pH and reduced solubility of ferric iron. A similar effect was seen in a Pogo Project sample (not reflected in Table 3) in which lower temperatures resulted in lower oxidation rates and significant delay to onset of acidic conditions. This resulted in significantly different pHs between the tests.

In addition to the above sites, Elberling *et al.* (2000) measured oxygen uptake rates under laboratory and field conditions. The authors concluded that the rates observed were very similar under both conditions and also similar to oxygen uptake rates under more temperate conditions. These findings indicate a rate ratio near 1.

From this data compilation, it is apparent that the reduction in rates observed in laboratory tests for most sites are more or less consistent with the Arrhenius equation when the effect of pH is not significant. (i.e. the change in temperature did not cause a major shift in pH). Use of the equation in scale-up predictions from laboratory to field conditions is acceptable provided that other factors such as heating caused by exothermic reactions are also considered.. Conservatively, in the absence of site

specific data, the higher end of the ratio range (0.31) should be used to calculate rate reduction in the absence of site specific data. The implication of cold temperatures to depletion of neutralizing minerals is discussed in Section 3.2.5.

Little data were located on the effect of low temperatures on the field behaviour of reactive waste rock that could be related to iron sulphide oxidation rates. Red Dog Mine (Alaska), Faro Mine (Yukon) and Equity Silver Mine (British Columbia) provide three examples where reactive rock has oxidized sufficiently to result in high internal temperatures in the pile and ARD. Also low temperatures without significant heating effects at the Sä Dena Hes Mine (Yukon) have not limited neutral pH leaching of cadmium, zinc and manganese from rock and tailings (Day and Bowell 2005).

3.2.3 Oxidation of other Sulphide Minerals

The Arrhenius equation indicates that the activation energy (E_a) of the sulphidic mineral is the main factor affecting its oxidation rate with respect to temperature, but all sulphide minerals should qualitatively oxidize at lower rates under low temperature conditions with differences in their E_a determining differences in rate ratios.

Ahonen and Tuovinen (1991) determined activation energies for pyrite (95.5 KJ/mol), chalcopyrite (77 KJ/mole), sphalerite (45 KJ/mol) and pyrrhotite (40 KJ/mol). Tallant and McKibben (2005) reported 14.5 KJ/mol for arsenopyrite The range of activation energies for these sulphide minerals indicate possible rate ratios varying from 0.1 (pyrite) to 0.7 (arsenopyrite). According to the Arrhenius equation that relates relative reaction rates at different temperatures, as described above, these differences imply that leaching of parameters associated with pyrite would show significant variability with changing temperatures but arsenopyrite may be less affected.

The opportunity to evaluate these effects in the case studies is limited to Pogo (arsenopyrite), and Nanisivik, Red Dog and Windy Craggy (sphalerite).

For arsenopyrite, the value of the data is limited. Arsenic in particular is strongly affected by sorptive processes (which are in turn affected by pH) and therefore any differences in release rates may be due to secondary mineral solubility rather than oxidation rates. Tests for Pogo showed low arsenic release rates (0.01 to 0.02 mg/kg/week) under all conditions. One test containing mainly arsenopyrite showed much lower arsenic release than expected based on the sulphate release rate indicating that arsenic was most likely stored in the sample as a secondary mineral component rather than leached. Therefore, conclusions about the effects of temperatures on sulphide oxidation could not be made. One column test in tailings for Pogo showed a 0.3 rate ratio.

Kinetic tests on Red Dog waste rock samples showed a range of zinc leaching effects for sphalerite. Two tests weathering at neutral pH showed increases in zinc release after the sample was refrigerated. For one sample, the increase was by a factor of 1.7 to 1.9 and occurred steadily for three years. A third sample showed a strong decrease in zinc leaching (by a factor of 0.17). Humidity cells tests on waste rock from the Windy Craggy Project consistently showed higher release rates for zinc under cold conditions. The increase was 1.4 and 2.1 for two non-acidic tests. For humidity cell pairs in which the room temperature test started to generate acid, the increase in zinc leaching under cool conditions was 1.4 and 1.7. The same data set showed that copper leaching occurred at lower rates under lower temperatures for some tests. The rate ratio varied from 1 to 0.7 (excluding one acidic room temperature test for which the decrease was 0.33).

Humidity cells tests were conducted on tailings and shale waste rock from the Nanisivik Mine. Both tests were started at room temperature. After 26 weeks of testing at room temperature, the tests were refrigerated. Zinc release from the tailings humidity cell followed a decreasing trend through both room temperature (prior to 26 weeks) and refrigerated (after 26 weeks) conditions with no apparent effect from refrigeration. The decreasing trend in zinc release may have obscured the effect of refrigeration. In contrast, refrigeration of the shale sample clearly showed that zinc leaching occurred three times more rapidly under refrigerated conditions.

In conclusion, the data available on effects from other sulphide minerals are limited. No data for leaching of many important metals were available. Results for two Red Dog tests, all four Windy Craggy tests, and one Nanisivik test showed that zinc leaching may accelerate under low temperature conditions. By extension cadmium, which is commonly associated with sphalerite, would be expected to leach more rapidly at low temperatures. This is not consistent with the behaviour predicted by the Arrhenius equation. A possible explanation is that zinc is leaching from sulphides and then being re-precipitated as another mineral that is more soluble (i.e. less likely to precipitate) under lower temperatures. This is discussed further in section 3.2.5.

For sites where pH neutral leaching of contaminants at low temperatures is important, site-specific testing is needed to investigate the effects of lower temperatures.

3.2.4 Activity of Different Types of Bacteria

Elberling (2001a) discussed viable bacteria in permafrost environments, including:

- psychrophiles (cold-loving, optimal temperatures for growth below 15°C but active below zero); and
- psychrotrophs (cold-tolerant, optimal temperatures for growth above 15°C but active below zero).

Elberling reported that viable microorganisms occur in permafrost to depths of at least 18 m and in material older than 70,000 years. Rivkina *et al.* (2000) also reported significant numbers of viable bacteria present in permafrost that is 1 to 3 million years old in the arctic and possibly older in the Antarctic.

Sulphide oxidizing bacteria in particular have been documented at a number of sites in the Canadian Arctic as well as Northern Greenland. Price (2001) documented the presence of microorganisms in various environs with an emphasis on cold environments, and clearly illustrated the presence of microbes in glacial ice and permafrost. Of particular note is a reference by Price regarding the Citronen Fjord in Greenland (83°N) in which a species of *Thiobacillus* bacterium was found existing at pH 0 and a temperature of about -30°C for the winter months.

Elberling (2001a) compared the temperature-dependent biotic activity of sulphide oxidizing bacteria collected from temperate latitudes and arctic latitudes (Figure 3). Optimum temperature for activity was 7-8°C lower for the bacteria collected from the arctic versus the temperate climate, illustrating that bacteria can adapt to survive in colder environments.



Figure 3. Relative changes in biological oxidation rates of pyrite collected from temperate latitudes (open symbols) and arctic latitudes (closed symbols). Curves showing temperature dependence of biological activity (Elberling 2001a).

Studies at the Nanisivik Mine (see case study this section) indicated a uniform decrease in the biological and chemical oxidation rates with temperature consistent with the Arrhenius relationship for temperatures above zero. Below 0°C, there is a greater deviation from the Arrhenius equation with a more linear relationship demonstrated (Elberling 2001b).

Godwaldt *et al.* (1999) reported an improved model to the Arrhenius equation for bacterial oxidation, termed the "square root model" and given by the equation:

$$\sqrt{k} = b.(T - T_{min})$$

Where k is the specific growth rate, b is the slope of the regression line, T is the temperature of concern and T_{min} is the temperature, in Kelvin, where the regression line cuts the temperature axis.

Field and lab measurements at Nanisivik showed biological activity to temperatures as low as -4° C. Similar experiments at Rankin Inlet (Appendix A) indicated that the activity became negligible at temperatures of approximately -10° C. Godwaldt *et al.* (1999) also referenced food science studies that demonstrated that bacteria are capable of germinating at -6° C. Rivkina *et al.* (2000), based on lab experiments, suggested that measurable metabolic activity of permafrost bacteria is possible at temperatures down to at least -20° C. Tumeo and Guinn (1997) reviewed the mechanism of bioremediation of hydrocarbons by bacteria capable of mineralizing petroleum hydrocarbons in cold climates and reported that bacterial respiration occurs at temperatures as low as -5° C. Clearly, while the minimum temperatures vary between studies, sub-zero biological activity has been measured both in the field and in the laboratory at various sites.

Price (2001) purported that at temperatures as low as -30° C, metabolic rates become so low that the bacterial population that exists primarily along liquid 'veins' within ice is unlikely to be limited by availability of nutrients. While the activity of bacteria at these temperatures may be low, Price suggests that they can survive at populations on the order of 1×10^4 cm⁻³ for periods of time greater than 100,000 years.

The presence of unfrozen water (i.e. presumably what Price (2001) refers to as liquid 'veins') makes mass transfer of ions and liquid possible and therefore a key variable in bacterial survival. Rivkina *et al.* (2000) reported that the thickness of the unfrozen water content film around the bacteria may dictate the viability. The thickness is dependent on temperature and typically decreases from about 15 nm at -1.5° C to about 5 nm at -10° C. Ultimately, the slow build-up of diffusion gradients progressively slows and perhaps stops the movement of nutrients towards the bacteria and waste products away from the bacteria. Rivkina *et al.* (2000) correlate the thickness of the unfrozen water film, the overall unfrozen water content and the level of stationary phase, or when population growth stops (Figure 4).

Observations with respect to carbon cycling are also pertinent to understanding the behaviour of bacteria in these environments.



Figure 4. Levels at which bacterial growth reaches a stationary phase, measured amounts of unfrozen water, and calculated thicknesses of unfrozen water films in permafrost plotted verses temperature (Rivkina *et al.* 2000).

There is an exponential increase in soil respiration with increasing temperature (as indicated by the Arrhenius equation). The increase in the CO_2 production rate per 10°C (Q10) is routinely used to characterize the temperature dependence of CO_2 efflux from various soil types and temperature ranges. In general, the Q10 is higher in low temperature environments (values between 2 and 4) Elberling and Brandt (2003).

3.2.5 Solubility and Reactivity of Acid Buffering Minerals

As for all chemical reactions, the theoretical effect of temperature on the rate (kinetics) of dissolution of acid-buffering minerals (such as carbonates and silicates) can be predicted by the Arrhenius equation. However, an important factor in the availability of alkalinity for acid buffering is the solubility of carbon dioxide in water. This is a temperature dependent process which also affects the solubility of acid buffering minerals. Carbon dioxide dissolves in water to form carbonic acid (H₂CO₃), which in turn reacts with carbonates and silicates to release alkalinity (for example):

 $CaCO_3 + H_2CO_3(g) \rightarrow Ca^{2+} + 2HCO_3^{-1}$

 $CaAl_2Si_2O_8 + 2H_2CO_3 + H_2O \rightarrow Ca^{2+} + 2Al_2Si_2O_5(OH)_4 + 2HCO_3^- + 4H_2O$

The significance of this effect for carbonates can be calculated thermodynamically (Figure 5). The calculation using MINTEQA2 (Allison *et al* 1991) shows that the greater solubility of carbonic acid at lower temperatures results in a lower pH (about 5.5 at 4°C) compared to greater than 5.6 at 20°C. This translates to 1.4 and 1.6 times the solubility of calcite and dolomite at lower temperatures. The reactivity of silicates is more complex since the reaction products may remain on the surface of the mineral and inhibit further weathering but the presence of more acidic conditions from dissolved carbon dioxide could result in more aggressive carbonic acid weathering conditions.

Of the information reviewed, none of the studies directly attempted to evaluate the effect of temperature on buffering mineral reactivity. The focus was usually on quantifying the effects on sulphide reactivity. The Diavik Project included one pair of column tests operated on granite waste rock containing very low sulphur concentrations. The resulting leachate chemistry was evaluated as part of this review (Figure 6). The low temperature test showed lower alkalinity, potassium and sodium release. There was no detectable difference for calcium and magnesium. Since carbonate content was probably very low, the leachate chemistry most likely indicated weathering of silicates. The lower concentrations are probably reflecting the decrease in rates indicated by the Arrhenius equation.



Figure 5. Theoretical solubility of calcite and dolomite and pH of carbonic acid as a function of temperature. $pCO_2 = 10^{-3.5}$ atm.



Figure 6. Major element leachate chemistry for granitic waste rock leach columns (Diavik Project). Open symbols are low temperature test.

The increased solubility of carbonate minerals at low temperatures has a number of implications:

- **Delivery of Alkalinity.** The higher solubility of carbonates at lower temperatures implies that more dissolved alkalinity will be delivered to acid generating rock particles than at higher temperatures. This combined with the slower sulphide oxidation rate provides a favourable mechanism for neutralization of acid near the sulphide grain, instead of relying on contact with solid alkalinity. Cold temperatures therefore might be more favourable for blending of acid generating and acid consuming waste rock (e.g. Mehling *et al.* 1997).
- Alkalinity Flushing. The greater solubility of alkalinity suggests that low temperature laboratory tests may see higher alkalinity flushing rates than room temperature tests. This, in conjunction with lower oxidation rates potentially complicates interpretation of NP depletion and could lead to excessively conservative NP/AP criteria for acid generating rock. Alkalinity flushing is not expected to be a significant concern at full-scale facilities because the water to solid ratio is usually much lower than in laboratory tests. At full-scale, carbonates are more soluble at lower temperatures but nonetheless pore waters will saturate with respect to carbonate minerals limiting the flushing effect. At large scales, the alkaline demand created by oxidizing sulphides almost invariably exceeds the simple dissolution of alkalinity by infiltrating water.
- Solubility of Metal Carbonates. The ideal solubility of metal carbonates is expected to be greater at lower temperature. Under neutral pH conditions, the concentrations of a number of metals (including cadmium, copper, manganese, nickel, zinc) are often predicted to be controlled by the solubility of their carbonates (e.g., Day and Bowell 2005). Therefore, the concentrations of these metals in drainage may be higher at colder sites. For example, the solubility of zinc carbonate (smithsonite) is 14 mgZn/L at 20°C compared to 19 mgZn/L at 4°C (pH 7). This may explain the observed increase in zinc concentrations for colder tests at Red Dog and Windy Craggy (see Section 3.2.3) operating at neutral pH though the leachate concentrations were usually lower than the ideal solubility of smithsonite. Day and Bowell (2005) found secondary zinc carbonates with solubility much lower than smithsonite.

3.2.6 Formation and Solubility of Weathering Products

Secondary mineral products can include sulphates, carbonates and oxides. Generally, the solubility of minerals decreases as the temperature decreases. For example, thermodynamic calculations indicate that at 5°C the solubility of gypsum results in a sulphate concentration of 1275 mg/L but at 20°C the concentration is 1354 mg/L. This illustrates the importance of considering temperature when solubility is calculated using thermodynamic models. Similar effects are expected for other minerals, though the validity of the predictions depends on the thermodynamic data and the degree to which individual minerals show ideal thermodynamic behaviour. The solubility of carbonates was described above and is the reverse of this trend due to the greater solubility of carbon dioxide in water at lower temperatures.

Mobility of soluble components in the north can be complicated by processes such as the development of reducing conditions under an ice cover and the associated increase in concentrations of certain parameters under ice and potential remobilization of constituents upon thaw (Kwong, 2001). Adsorbed metals on common secondary minerals such as iron oxy-hydroxides may desorb from the structure under reducing conditions and become readily available for flushing. In the same reference, Kwong reported the upward migration of metals during dry seasons in a tailings impoundment resulted in efflorescent salt formation on the surface. Together with incomplete oxidation of iron sulphides and the precipitation of iron sulphates rather than iron oxy-hydroxides, Kwong suggested that efflorescent salt precipitation can be more common in northern latitudes than in more temperate regions.

Further northern-specific processes occurring at the interface between the frozen and thawed soil include changing diffusion coefficients of ions (see North Kolyma lowland case study, Appendix A). For example, Alekseev *et al.* (2003) reference the diffusion coefficient in a loam at 20°C to be 10^{-6} m²/s whereas at -5° C the coefficient is reduced to 10^{-9} to 10^{-11} m²/s.

Day *et al.* (2003) suggested an important consequence of lower temperatures in the formation of ferric hydroxide precipitates at the Ekati Diamond Mine. This study showed acidic conditions in toe seeps near the disposal area for calcareous coarse kimberlite reject. The presence of acidic water was suggested as being a result of slow oxidation of ferrous iron emerging from the base of the pile. This process produces ferric iron, which then begins to precipitate as ferric hydroxide. The overall process releases acidity. Under warm conditions, this process might be expected to occur close to the calcareous pile, thereby allowing the acid to be neutralized. Under cold conditions, acid generation occurred distant from the pile and resulted in a decrease in pH to below 5. The lower pH conditions also allowed other metals (including nickel) to remain in solution when they might normally have been precipitated.

The possibility that secondary minerals formed under low temperature conditions may be different from those formed under warmer conditions does not seem to have been considered in much detail in the literature. Although, as noted above, thermodynamic models which contain temperature as a variable inherently consider that minerals may form differently under lower temperatures.

3.2.7 Freeze Concentration

Freeze concentration is important from two perspectives.

- The increase in concentration can result in waters with high toxicity (if the water is expelled) though there is no increase in chemical load; and
- The increase in concentration can cause freezing point depression resulting in liquid water at sub-zero temperatures.

Increase in Concentration

The presence of sulphate as the commonly dominant ion in mine waters means that the effect of freeze concentration can be limited for some ions. For example, during freeze concentration of a calcium sulphate water at neutral pH, the saturation limit of gypsum will eventually be reached, producing a ceiling on sulphate and calcium concentrations. In contrast, during freeze concentration of chloride containing waters the concentrations can become very high without reaching the saturation limit of a chloride mineral. Day *et al.* (2003) showed a possible example of the freeze concentration effect on magnesium-rich waters produced by weathering of waste kimberlite. In this case, the high levels of dissolved magnesium probably supported high sulphate concentrations in freeze-concentrated water due to the high solubility of magnesium sulphate. Other elements with highly soluble sulphates include potassium, sodium, iron, cadmium, zinc and nickel. As pH decreases, other elements also become highly soluble and would be further magnified by freeze concentration effects. Elements with low solubility sulphates that would be less affected by freeze concentration include barium and lead.

In carbonate-rich waters, freeze concentration would be expected to have a limited effect since carbonates of calcium, magnesium and most heavy metals have relatively low solubility when compared to sulphates. However, as noted previously, the higher solubility of carbon dioxide at lower temperatures increases the solubility of carbonates.

Freezing Point Depression

Freezing point depression as a result of solutes in the pore water has been evaluated at Nanisivik (Elberling, 2001b). Elberling reported that the pore water concentrations of Mg and SO₄ alone in 7 year old tailings at Nanisivik should account for a freezing point depression of 1° C calculated by the following simplified Van't Hoff equation:

$$\Delta T = -1.86 \upsilon m_b$$

Where ΔT is the freezing point depression, v is the number of aqueous species resulting from the dissolution of the solutes and m_b is the molarity of the solute. For a water containing only calcium and sulphate ions from dissolution of gypsum (v=2 and $m_b=0.013$ M), the freezing point depression is minor (0.04°C), but a strong acid rock drainage containing 20 g/L sulphate from dissolution of ferrous sulphate would show freezing point depression of 0.8°C. Elberling noted in this work however that deviations from this equation are expected for "high" concentrations and for electrolytes that dissociate into ions of higher valence.

Solute expulsion as a result of freezing was also studied at Nanisivik (Elberling, 2001b) and at Rankin Inlet as well as in experiments conducted by Ostroumov *et al.* (2001). Elberling (2001b) and Godwaldt *et al.* (1999) suggested that solute concentrations in the freezing front may rise to 80 times the original concentrations although is largely dependent on the rate of freezing. Goldwaldt *et al.*

(1999) reported that for freezing rates smaller than 0.1° C/day, more than 90% of the solutes were rejected from pore ice.

In the experiments by Ostroumov *et al.* (2001), the microscale at the freezing front was examined. The maximum concentration of exchangeable ions was seen located close to the surface of the ice lens that formed. An accumulation zone was seen to form in the adjacent mineral layer and usually the form of the elements were changed (i.e., exchangeable, bound etc) accompanied with a structure change of the sediment. For example, samples of frozen clay were studied with SEM and showed coagulated soil patterns during freezing resulting from a change in the form of elements in this zone. In Russia, a natural permafrost in sediment was studied that was frozen from the bottom-upwards and showed an accumulation zone located close to the upper surface of the segregated ice lens. The position of this zone relative to the ice lens reflected the direction of freezing of the material. They concluded that soluble components are transferred in the mobile form ahead of the freezing front and fixed in the accumulation zone.

Implications with respect to mine waste freezing include the development of an accumulation zone. If waste freezes predominantly from the bottom up, this accumulation zone may exist within the active zone where it is more prone to oxidation and dissolution. In the case of Rankin Inlet, a backfilled pit is essentially freezing from all sides thereby 'trapping' the solutes within the mass (Appendix A). Depending on where the accumulation and solute concentration results, the effect may be increased concentrations in water during thaw and spring freshet.

Other Factors

Mine waters may contain elevated concentrations of ions unrelated to rock weathering but which may be an environmental concern. For example, explosives residues containing nitrogen forms would also be affected by freeze concentration.

3.2.8 Physical Exposure of Minerals Due to Freeze-Thaw Processes

This process is potentially important because it may result in break-up of large particles and exposure of reactive minerals. It can also result in cracking of tailings surfaces leading to enhanced oxygen access and preferential flow paths for infiltrating water.

Observations during experimental freeze-thaw weathering by Nicholson and Nicholson (2000) implied that pre-existing flaws (visible defects such as fractures, veining etc.) are particularly important in the deterioration of stronger rocks and their direct influence is reduced in weaker rocks as the influence of other rock properties and environmental factors increases. They concluded that for stronger rocks, macro-flaws are more important than environmental conditions for rock deterioration. For weaker rocks, environmental conditions prevail.

Experimental studies conducted by Murton *et al.* (2000) consisted of permafrost aggradation (twosided freezing) and seasonal freezing and thawing (one-sided thawing) of an active layer within a large block of chalk. Temperature, unfrozen water content, surface heave and settlement as well as pressure were monitored over the duration of a year of freeze-thaw cycling. They observed that the greatest amount of heave occurred in the summer thaw cycles when the active layer approached its greatest depths. The volume of heave appeared to be dependent on the unfrozen water content. They hypothesized that the thaw-related heave is an effect of ice segregation taking place in the base of the active layer and/or top of the permafrost supplied by unfrozen water migrating downward into the still-frozen part of the chalk. This mechanism is thought to result in brecciation of material within the active layer of northern soils.

3.2.9 Solubility of Oxygen in Waters Used to Flood Reactive Wastes

The increasing O_2 solubility in cold water has been raised as an issue with respect to water covers in the cold climates. According to Elberling (2001b), the amount of O_2 in water increases by a factor of 1.4 as the temperature decreases from 15 to 0°C. He notes that with the same drop in temperature, the O_2 diffusivity decreases by a factor of 1.6. He calculates a 90% reduction in the O_2 flux at 2°C compared to that at 15°C for a 30 cm saturated sand and suggests that subaqueous disposal at low temperatures is likely to be more effective than in more temperate areas due to the greater effect of decreasing temperature on O_2 diffusivity than on its solubility in water.

Ice formation on water covers has been reported to establish seasonal gradients of decreasing concentrations of dissolved O_2 content with depth, for example at the Stekenjokk Mine in northern Sweden where Holmstrom *et al.* (2000) studied the seasonal variation in dissolved and total (suspended matter) chemistry in a water covered tailings impoundment (Appendix A).

4 Discussion of Technology Gaps

4.1 Introduction

Technology gaps need to be considered in the context of requirements for data. Typically, the requirements for ML/ARD assessment in cold climates are the same as for other climates, and include:

- Appropriate methods for characterization of wastes;
- Water chemistry prediction approaches; and
- Geochemical design criteria for prevention and control strategies.

The first two areas are discussed below because they require a significant consideration of small scale processes (release of contaminants from primary minerals and storage and re-dissolution as secondary minerals). The latter aspect considers large scale factors which are highly dependent on site specific conditions.

4.2 Characterization Methods

Characterization methods are test procedures designed to provide analogues for full-scale field behaviour that provide information for input into waste management planning and water chemistry predictions.

Static Tests

The need for specific approaches to assess cold climate effects (i.e. suppression of sulphide oxidation rates and other reactions, and increases in solubility of carbonates) indicates that special methods are needed. However, there is no need for special static methods because these are mainly surrogates for determination of mineralogy, which is an essential characterization requirement regardless of climatic conditions.

Short Term Leach Tests

Short term leach tests (shake flask extractions, meteoric water mobility procedures) to assess secondary mineral solubility are generally performed at room temperature. However, the foregoing discussion shows that temperature is an important variable for most secondary minerals. None of the studies reviewed considered this factor. Comparative specially designed solubility tests at different temperatures would address this gap.

Laboratory Kinetic Tests

It is apparent that application of results from kinetic tests performed at room temperature is not appropriate for prediction of weathering rates at lower temperatures. These tests may over-estimate weathering rates in some cases but underestimate effects due to the increase in carbonate solubility. An important consideration is the solubility of secondary heavy metal carbonates. Therefore, special kinetic test protocols are needed particularly if testing is to be performed under sub-zero conditions. Practitioners in the field have adapted the standard kinetic test protocols (Sobek *et al.*1978; MEND 1991; ASTM 2001) by operating the tests in refrigerators. Usually, tests are performed in room temperature and fridge pairs so that the majority of testwork conducted at room temperature can be calibrated to low temperature conditions. Currently, standard methods are not available for low temperature tests and reports do not always include details of the test methods. For example, some tests may be performed in a cold room where the test and all associated equipment and leach waters are maintained at the same low temperature whereas in other cases the tests may be kept in a small fridge and removed each week resulting in warming of the sample during the leach cycle.

On-Site Kinetic Tests

A few projects have built small-scale kinetic tests at the site. The limitations of these tests are well known but may be more significant under low temperature conditions. The size of these piles means that full thawing usually occurs in the pile and therefore that the pile simulates the active zone. The

size of the pile also indicates that any effects due to internal heating are not likely to be observed. Under full-scale conditions, the temperature gradient between a warm zone and low outside temperatures can lead to significant convection effects that would not be observed in small-scale piles. A gap in this area is therefore the need for guidance on the appropriate design of field tests.

4.3 Water Chemistry Predictions

Water chemistry predictions usually involve scale-up of laboratory results to full scale conditions and consideration of secondary mineral solubility. This may involve an empirical approach, a purely theoretical approach, or a hybrid. The inputs to these calculations are usually the same, and include assumptions about rates of weathering of individual mineral grains (kinetics), particle size distribution, hydrology (water balance), heat generation and transfer, chemical precipitation reactions and products (calculated from thermodynamics) and depletion effects. Several of these inputs are grain-scale processes while others depend on macroscopic features. Oxidation rates are an important small-scale input since they indicate acid generation rates and heat generation. Solubility of secondary minerals is also an important small-scale process.

For sulphide oxidation, a typical approach is to adjust reaction rates obtained at room temperatures using the Arrhenius equation. A literature value for the activation energy (E_a) value for pyrite is used to make an adjustment to reflect low temperature using the room temperature rate. It is apparent that this approach may not be appropriate if different types of iron sulphide minerals such as pyrite, marcasite and pyrrhotite (possibly containing different trace element impurities), or other sulphide minerals are present. The measured range of E_a values can include factors from 90% to 10% of the room temperature rate. The gap in knowledge is the lack of reliable estimates of E_a for typical waste sulphide minerals being oxidized by atmospheric oxygen. The literature contains experimentally derived E_a values but these reflect the use of other oxidants more related to the mineral processing industry than waste weathering.

The observed higher rate of zinc leaching under refrigerated conditions compared to room temperatures indicates that the usual assumption that all metal leaching rates are lower under cold conditions may not be valid. It is speculated that this effect is due to the higher solubility of zinc carbonates under cold conditions, but this is not known and could have important implications for water quality predictions.

4.4 Conclusions on Gaps

The following technological gaps have been identified:

- A protocol for short-term leach extractions at low temperatures is needed to assess the solubility of secondary minerals at low temperatures.
- Standardized protocols and guidelines for kinetic testing (laboratory and field) at low temperatures are needed.

- There is limited availability of activation energies for the atmospheric oxidation of most sulphide minerals to allow estimation of temperature effects.
- The leaching behaviour of heavy metals (particularly zinc) under low temperatures is not well understood.

5 Conclusions and Recommendations

5.1 Research

This review found that understanding of low temperature geochemical processes as it relates to mine waste characterization has not advanced significantly since the MEND-sponsored work in the 1990s with the possible exception of understanding of bacterially-mediated reactivity under sub-zero conditions. Data are available for more sites on reaction rate differences but these are typically not rigorous scientific experiments. Therefore, there is a need for:

- Acquisition of data on the reactivity of common sulphides as a function of temperature under conditions relevant to oxidation by gaseous oxygen.
- Studies on the short-term (in the geological sense) reactivity (kinetics and equilibrium) of common acid neutralizing minerals including carbonates and silicates.
- Evaluation of the formation and solubility of common secondary minerals (kinetics and equilibrium), with particular emphasis on pH neutral conditions.
- Evaluation of the effect of galvanic processes on low temperature oxidation rates.

A separate category of processes cover downstream reactions which appear to operate differently at low temperatures and can influence the chemistry of mine drainage. For example, oxidation and precipitation of iron to form ferric hydroxides may influence acid generation and the efficacy of sorption processes to naturally attenuate metals. Oxidation of nitrogen compounds to degrade explosives residues was not considered in this review but falls into a separate category.

The review found that there is little standardization of test procedures as they relate to low temperatures. Static test procedures are interchangeable between climatic conditions, but short-term kinetic test conditions are affected by environmental conditions and almost every project approaches low temperature testing in a different way. It is recommended that:

- The performance of extraction tests (like shake flask tests and meteoric water mobility procedures) be evaluated rigorously and standard methods developed to provide consistency between researchers.
- The protocols used for low temperature humidity cell tests be standardized so that data produced by testing at different sites be compared.

• Field kinetic test designs be evaluated for their suitability to truly simulate field conditions.

The reviewers found a lack of good quality case studies documenting the performance of mine waste facilities under low temperature conditions. Many sites are monitored because the drainage chemistry is an issue but there is a need for case studies to show that waste management has resulted in acceptable water quality. Good examples of ongoing monitoring to assess performance under low temperature conditions include the INAP test pile at Diavik Diamond Mines and monitoring of several facilities at the Ekati Diamond Mine.

The value of case studies was often limited by the lack of consistent data on basic characteristics and reporting.

5.2 Mine Site Characterization

Many existing and proposed mines in Canada operate under average temperature conditions lower than the typical conditions used for laboratory testing. This review has confirmed the well known fact that temperature influences reaction rates and equilibrium conditions. The usual assumption that temperature reduces reaction rates holds true, and therefore the use of laboratory-derived reaction rates for water quality prediction is conservative; however, leaching of contaminants is more likely to be controlled by the thermodynamics of secondary mineral dissolution which in some cases (carbonates in particular) may result in higher concentrations in pore waters at low temperatures compared to high temperatures.

It is recommended that:

- At mine sites where temperature is potentially an important factor and is being invoked to support significantly lower reaction rates, test work should be completed to obtain reaction rates under low temperatures, and the effect of exothermic processes on raising reactions should be considered.
- In addition, the solubility of secondary minerals should be evaluated to determine effects on concentrations of potential contaminants.

It should be noted that temperature is one of several "scale-up" factors commonly used and that temperature effects are probably better constrained than some other factors. For example, temperature effects probably span less than an order-of-magnitude but hydraulic factors (e.g. permeability) can easily span several orders-of-magnitude.

6 References

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Appendix A

Case Histories

CITRONEN FJORD PROJECT

LOCATION

Description	Citronen Fjord exploration project in North Greenland
Latitude	83°N
Elevation	Unknown
CLIMATIC REG	IME
Precipitation	Not applicable
Temperature Range	Average annual temperature below -17° C Summer temperatures relatively high due to a large orographic sheltering effect from the inland ice, July-Aug (1993-1996) had average temps between 5 and 10°C with a max of 14°C and a min of -3° C.
Permafrost Zone	Continuous. Depth to permafrost table in dry gossans was 50-70cm, in near saturated areas depth less than 10cm. In Aug 1996, ground temperatures varied between 5 and 12°C in the top 10 cm.
MINING	
Status	Proposed mine.
Mine Life	Not applicable
Mining Method	Not applicable
Waste Rock Management	Not applicable
Ore Processing and Tailings Disposal	Not applicable
GEOLOGY	
Summary Geological Description	Primary targets were the reported gossans and sulphide showings in the Lower Palaeozoic sediments at Citronen Fjord. Three main stratiform sulphide sheets occur within a 200 m thick stratigraphic sequence composed of massive and bedded pyrite with variable amounts of sphalerite and minor galena. Host rocks consist of dark argillaceous rocks of the Amundsen Land Group (late Ordovician to Early Silurian), primarily cherts and shales with siltstones and mudstones as well as carbonate debris flow conglomerates derived from nearby southern carbonate shelf. The deposit is likely of lead-zinc sedimentary-exhalative origin formed by
	precipitation of metal sulphides on the sea floor.
Mineralogy	Pyrite $[FeS_2]$, sphalerite $[(Zn,Fe)S]$ and galena $[PbS]$. Pyrite described as massive to dendritic-textured representing vent-facies deposition. Other metal sulphides are bedded. Carbonate intergrowths reported.
Surficial Geology	Lower Palaeozoic sediments and gossans.

CITRONEN FJORD PROJECT

GEOCHEMISTR	Y
Geochemical Overview	 Concentrations of selected elements in the fresh sulphide-rich rocks and in the overlying gossan were reported (see Tables 1 and 2, Elberling and Landgahl, 1998). The organic content in the gossans are negligible. The fresh sulphide rocks are described as being comprised of 30% carbonate minerals and 70% sulphide minerals. The gossan overlying the fresh rock shows depletion in elements near the surface, and potentially an enrichment zone due to reprecipitation of elements as they are leached from the surface. Pore water extracted from the gossan were pH between 1 and 2. Fe concentrations
	between 10,000 and 50,000 ppm, Zn between 600 and 7000 ppm, Pb between 10 and 40 ppm with Ni, Cd and Cu up to 3 ppm. The pH of water in small streams in the area reported pH values of 3 downstream of the gossan and between 7 and 8 downstream of non-gossaneous areas. Ferric hydroxides abundant between gossan and the receiving river (Eastern River).
Low Temperature Geochemical Aspects	<i>Effect of temperatures on oxidation rates</i> : O ₂ uptake rates within the dry areas varied between 9.7 x 10^{-2} and 39.7 x 10^{-2} mol/m ² /day, with an average of 19.8 x 10^{-2} mol/m ² /day. Rates were about a factor of 10 less at moist and wet sites. The authors reported that these rates are on the same order as rates measured in temperate zones (e.g. Sudbury) for similarly sulphidic materials.
	 <i>Effect of temperature on bacterial activity:</i> Preliminary bacteria number analysis of the gossan indicated the numbers at this site were similar to those found in mining areas in temperate regions. Price (2001) references the identification of a species of Thiobacillus bacteria at Citronen Fjord that exist at pH 0 and temperatures of ~ -30°C in the winter months.
	Effect of temperature on solubility and reactivity of acid buffering minerals: No data Effect of temperature on solubility of secondary minerals:
	No data Solute freeze-concentration effects:
	No data <i>Effect of freeze-thaw processes on mineral exposure:</i> No data
	Solubility of oxygen in water covers: No data
	<i>Ice barrier effects on oxygen and water movement</i> No data

CITRONEN FJORD PROJECT

	Freezing point depression of mill supernatant and tailings porewater
	No data
OTHER	
INFORMATION	SOURCES
References	 Elberling, B. and Langdahl, B.R. (1998) Natural heavy-metal release by sulphide oxidation in the high arctic. Canadian Geotechnical Journal, vol. 35 (1998), pp. 895-901. Price, P.B. (2001). Life in solid ice? Unpublished report presented at Workshop on Life in Ancient Ice, June 30 to July 2, 2001, 21 pp. Van der Stijl, F.W. & Mosher, G.Z. 1998: The Citronen Fjord massive sulphide deposit, Peary Land, North Greenland: discovery, stratigraphy, mineralization and structural setting. Abstract in Geology of Greenland Survey Bulletin 179, 40 pp.
Permissions for Unpublished Data	Not applicable
Case Study Prepared by:	Shannon Shaw

TABLES (from Elberling and Langdahl, 1998)

					(-)	
	Fe	S	Cu	Pb	Zn	Cđ	Ca
Rock 1	25.5	28.7	0.001	0.29	1.0	0.002	12
Rock 2	25.5	29.1	0.001	0.27	1.25	0.003	12

Table 1. Concentrations of selected elements in fresh sulphide-rich rocks (% by weight).

Table 2. Concentrations of selected elements in gossanous soil at oxygen consumption site 1 (% by weight).

Depth below							
the surface							
(cm)	Fe	S	Cu	Pb	Zn	Cd ^a	Ca
0-5	14.7	5.4	0.002	0.07	0.08	_	5
5-10	16.6	3.6	0.002	0.18	0.12	_	3
10-15	17.8	4.8	0.002	0.09	0.09	_	4
15-20	20.4	2.6	0.003	0.50	0.15	_	1
20-25	19.7	3.7	0.003	0.45	0.19	_	3
25-30	23.3	3.5	0.003	0.34	0.23	_	2
30-35	22.9	2.9	0.003	0.62	0.21	_	1
35-40	25.0	2.3	0.003	0.37	0.25	_	1
40-45	19.8	5.8	0.003	1.42	0.22	—	б
45-50	25.6	1.0	0.003	0.26	0.31	—	3

"Below the detection limit of 0.5 ppm.

Table 3. Summary of sites and oxygen uptake rates.

Station No.	Thickness of unfrozen gossan (cm)	O ₂ flux (mol/m ² per day;×10 ⁻²)	Soil characteristics (colour, grain size, and water content)
1	67.6	9.7	Red, yellow sand; dry
2	62.1	13.7	Grey, yellow sand; dry
3	61.4	3.8	Grey silt; moist
4	65.0	15.2	White, grey sand; dry
5	58.8	39.7	Red sand; dry
б	52.6	17.5	Red sand; dry
7	62.0	38.2	Red sand; dry
8	35.0	11.8	Red sand; dry
9	51.0	24.3	Red sand; dry
10	51.0	11.5	Red sand; dry
11	15.0	3.2	Grey fine sand; wet
12	29.0	16.8	Red sand; dry
13	17.6	5.3	Grey fine sand; wet

CULLATON LAKE MINE

LOCATION

Description	Closed, Cullaton Lake and Shear Lake Mines, Nunavut
Latitude	61°16'N
Elevation	Unknown
CLIMATIC REG	IME
Precipitation	Unknown
Temperature	Unknown
Kange	
Permafrost Zone	Discontinuous
MINING	
Status	Closed mine.
Mine Life	4 years
Mining Method	Underground
Waste Rock	Unknown
Management	
Ore Processing	300 tonne per day gold mine using cyanide leaching
and Tailings	
Disposal	
GEOLOGY	
Summary	The gold mineralization in the B-Zone of the Cullaton Lake Mine is hosted by
Geological	sulphide iron formations. The mineralization at the S-Zone is contained in altered
Description	shears, breccia zones, pyritic shears and pyritic and sericitic impure quartzite. The host rocks for S. Zone were orthoguartzite, shale and siltstone
	nost rocks for 5-20ne were orthoquartzite, state, shale and sitistone.
Mineralogy	Unknown
Surficial	Lower Palaeozoic sediments and gossans.
Geology	
GEOCHEMISTR	Y
Geochemical	Chemical characteristics of the tailings samples are provided in the attached table.
Overview	

CULLATON LAKE MINE

Low	Effect of temperatures on oxidation rates:
Temperature	This project evaluated the reactivity of two samples of tailings from the Cullaton
Geochemical	Lake Mine containing relatively high sulphur content (2.3%) and NP (45 kg CaCO ₃ /t)
Aspects	(B Zone Tailings) and lower sulphur content (0.4%) and NP (2 kg CaCO ₃ /t) (S Zone
	Tailings). Sulphate sulphur content of the samples was elevated and influenced
	leachate chemistry. Both samples were initially weathered at 2°C for two years and
	then at 10°C for 1 year. The study complemented an earlier project on the same
	materials which was performed at 25°C (Davé 1992). The overall value of the data
	collected for the project was limited by removal from the columns and
	homogenization of the samples between the 2°C and 10°C temperature stages. This
	procedure would have disrupted any layering that may have developed as a result of
	surface oxidation and would have distributed weathering products from the oxidized
	to the unoxidized tailings Furthermore, the onset of acidic conditions at the beginning $f(t) = 10^{\circ}$
	of the 10°C period for the B Zone sample (see figure below) prevented the direct
	comparison of oxidation rates for the lower subshur semple which concreted exide loophete
	similar concern existed for the lower surpline sample which generated actual reachate during the 2° C period, which continued during the 10° C period. It appeared that
	sulphate released increased during the 10° C period but this may have been due to
	homogenization of the sample and re-distribution of sulphate from the oxidized
	tailings Both tests demonstrated that ARD was produced at low temperatures
	Effect of temperature on bacterial activity:
	No data
	Effect of temperature on solubility and reactivity of acid buffering minerals:
	No data
	Effect of temperature on solubility of secondary minerals:
	No data
	Solute freeze-concentration effects.
	No data
	Effect of freeze-thaw processes on mineral exposure:
	No data
	Solubility of oxygen in water covers:
	No data
	Ice barrier effects on oxygen and water movement
	No data
	Execting point depression of mill supernatant and tailings portunater
	No data
	110 uuu

OTHER

CULLATON LAKE MINE

INFORMATION	INFORMATION SOURCES			
References	Davé, N. K., 1991, Column Leaching Characteristics of Cullaton Lake B and Shear Zones Tailings Phase 1 - Room Temperature Leaching, Energy Mines and Resources Canada, Division Report, September 1991. Davé, N. and Clulow, V. 1996. Column Leaching Characteristics of Cullaton Lake B and Shear (S) – ZONES Tailings Phase 2: Cold Temperature Leaching. MEND Project 1.61.3.			
Permissions for Unpublished Data	Not applicable			
Case Study Prepared by:	Stephen Day			

Appendix A - Case Histories

Parameter / Element	B - Zone	Shear (S) Zone
Al (%)	1.62 ± 0.008	0.47 ± 0.003
Ba (μg/g)	83.6 ± 0.6	101.5 ± 0.8
Ca (%)	2.37 ± 0.032	0.09 ± 0.002
Cd (µg/g)	<10	<10
Co (µg/g)	<10	16.1 ± 0.52
Cr (µg/g)	36.4 ± 0.2	24.4 ± 0.2
Cu (µg/g)	45.4 ± 0.3	15.5 ± 0.3
Fe (%)	20.07 ± 0.085	2.96 ± 0.01
K (%)	0.305 ± 0.07	0.15 ± 0.025
Mg (%)	0.88 ± 0.006	0.057 ± 0.003
Mn (%)	0.09 ± 0.0003	0.01 ± 0.0001
Na (%)	0.14 ± 0.001	0.06 ± 0.002
Ni (µg/g)	60.6 ± 10.8	48.6 ± 1.1
Total phosphorus (% P)	0.06 ± 0.014	0.009 ± 0.006
Pb (µg/g)	65.8 ± 1.9	48.4 ± 0.9
Total sulphur (% S)	2.63 ± 0.32	0.49 ± 0.1
Soluble sulphur (as % S)	0.32 ± 0.01	0.09 ± 0.01
Total sulphide sulphur (as % S)	2.31 ± 0.33	0.4 ± 0.11
Ti (%)	0.069 ± 0.0008	0.012 ± 0.0002
V (µg/g)	58.6 ± 2.0	15.4 ± 0.4
Zn (µg/g)	45.7 ± 0.4	12.1 ± 0.1
Zr (µg/g)	53.1 ± 3.0	44.4 ± 1.2
Total acid generation potential, kg	72.2	12.5
Total alkalinity, kg CaCO ₃ /tonne	45.36	2.0
Net neutralization potential, kg CaCO ₃ /tonne	-26.84	-10.5

Chemical Characteristics of Tailings Samples, Cullaton Lake Mines



Leaching Results for Cullaton Lake Tailings. Blue and red lines are the B and S zone tailings, respectively. The 2°C period is shown as filled symbols and the subsequent 10°C period as open symbols. Data from spreadsheets included with MEND Report 1.61.3 (Davé and Clulow 1996).

DIAVIK DIAMOND MINE

LOCATION	
Description	Approximately 300 km northeast of Yellowknife and 30 km southeast of the Ekati Diamond Mine in NWT, Canada
Latitude	64°30'(N)
Elevation	416 masl
CLIMATIC REG	IME
Precipitation	375 mm, 60% as snow
Temperature Range	Daily Annual Average -12°C
Permafrost Zone	Continuous
MINING	
Status	Operating
Mine Life	~2.5 years to date (2003 to present)
Mining Method	Open pit.
Waste Rock Management	Conventional waste rock disposal involving segregation and management of granite and xenolith-bearing granite containing variable but very low sulphur concentrations.
Ore Processing and Tailings Disposal	Conventional water-based kimberlite processing results in production of coarse and fine waste products.
GEOLOGY	
Summary Geological Description	Diamondiferous kimberlite pipes hosted by tonalite-quartz diorite and 2-mica granite which intruded metaturbidites. The latter were incorporated into the granite as xenoliths.
Mineralogy	The mineralogy of the granitic rock includes potassium feldspar, albite and quartz with lesser muscovite and biotite. Biotite is locally altered to chlorite.
	Biotite schist is composed principally of quartz, albite and biotite with lesser sillimanite and garnet. Sulphide occurs primarily as pyrrhotite. Pyrite, marcasite and chalcopyrite are present in very minor quantities.
Surficial Geology	Primarily glacial till.
GEOCHEMISTR	Y
Geochemical Overview	The sulphide and carbonate content of the granitic rocks is very low. This rock is described as "inert". The biotite schist as low median sulphur content (0.16%) but ranges from 0.01 to 0.56%. Negligible buffering capacity is present. Biotite schist is therefore considered to be potentially acid generating.

DIAVIK DIAMOND MINE

Low	Effect of temperatures on ovidation rates.
Temperature	As part of the environmental assessment process for the project 35 column tests and
Geochemical	$4 16 \text{-m}^3$ on-site leach pads were operated. The on-site tests were operated as
Aspects	laboratory equivalents, of which three were operated under both room and cold (4°C) conditions (Table 1). Data were obtained for about two years of laboratory and field testing. The field tests were reported to be frozen for nine months of the year. No flow measurements were obtained from the pads. Table 1 provides a summary of the four field tests and laboratory equivalent data.
	The three comparative laboratory column tests showed little difference for the pure granite sample but lower oxidation rates for two samples composed of pure biotite schist sample developed acidic leachate (with pH as low as 2.8), and sulphate concentrations from 85 to 472 mg/L. The cold equivalent sample also produced acidic leachate (lowest pH 3.4) but sulphates were 36 to 124 mg/L representing about a factor of 3 difference. This difference is equivalent to that predicted theoretically by the Arrhenius equation. The test containing a rock type mixture at room temperature showed pH depression to 4.7 whereas the refrigerated equivalent test did not. Comparison of sulphate release cannot be made on the same basis. The lack of flow measurements for the leach pads precludes direct comparison of release rates. The two tests containing pure biotite schist generated acidic (pH 4.6) leachate and sulphate concentrations were elevated compared to the granite pads. The pad containing 20% biotite schist did not produce acidic leachate and sulphate release
	was not substantially different from the non-acidic pads. Effect of temperature on bacterial activity:
	No data
	<i>Effect of temperature on solubility and reactivity of acid buffering minerals</i> One pair of column tests containing granitic rock with low very sulphur oxidation rates provides some data on the relative reactivity of silicate minerals for room and refrigerated conditions. The low temperature experiment produced lower alkalinity, potassium and sodium release. There was no detectable difference for calcium and magnesium. Potassium and sodium originate from weathering of silicates (biotite and possible K-feldspar and plagioclase). Calcium and magnesium may originate from weathering of carbonate minerals or silicates (plagioclase and/or biotite). The data only suggest that alkalinity release is slower under lower temperatures. Alkalinity can be released by dissolution of carbonates and weathering of feldspars by carbonic acid. <i>Effect of temperature on solubility of secondary minerals:</i> No data
	Solute freeze-concentration effects: No data

DIAVIK DIAMOND MINE

	<i>Effect of freeze-thaw processes on mineral exposure:</i> No data
	Solubility of oxygen in water covers: No data
	<i>Ice barrier effects on oxygen and water movement</i> No data
OTHER	•

The International Network on Acid Prevention is sponsoring construction of a fully instrumented test pile. No results have been published to date.

INFORMATION SOURCES		
References	Data files submitted as part of the environmental assessment and licensing.	
Permissions for Unpublished Data		
Case Study Prepared by:	Stephen Day	

Lab Test	Rock Type	Lab Outcome		Site Test Pad
				Equivalent
		Ambient	4oC	
SUB CR1	Granite (100%)	104 weeks (2 week cycle), pH 6.5 to 8.1, SO ₄ <1 to 3 mg/L	44 weeks (2 week cycle), pH 6.7 to 7.7, SO ₄ <1 to 3 mg/L	110 weeks (7 samples), pH 6.9 to 8.5. SO ₄ 100 to 285 mg/L
SUB CR2	Granite (85%), Pegmatite (15%)	10 weeks (2 week cycle), pH 7.6 to 8.1, SO ₄ 2 to 10 mg/L	No test	110 weeks (7 samples), pH 8.0 to 9.0. SO ₄ 18 to 262 mg/L
SUB CR3	Granite (6%), Biotite Schist (20%), Pegmatite (12%), Diabase (2%)	104 weeks (2 week cycle), pH 4.7 to 6.9, SO ₄ 22 to 52 mg/L	96 weeks (2 week cycle), pH 6.5 to 7.6, SO ₄ 6 to 38 mg/L	110 weeks (7 samples), pH 7.2 to 8.5. SO ₄ 32 to 301 mg/L
SUB CR4	Biotite Schist (100%)	104 weeks (2 week cycle), pH 2.8 to 7.3, SO ₄ 85 to 472 mg/L	96 weeks (2 week cycle), pH 3.4 to 7.6, SO ₄ 36 to 124 mg/L	110 weeks (7 samples), pH 4.6 to 6.9. SO ₄ 357 to 934 mg/L

Granite Leach Column Operated at Two Temperatures - Diavik Project



EKATI DIAMOND MINE

LOCATION

Description	Approximately 20 km east-northeast of Lac de Gras and 30 km northwest of the Diavik Diamond Mine in the NWT, Canada
Latitude	64°44'(N)
Elevation	469 masl
CLIMATIC REG	IME
Precipitation	Total 299 mm, with 46% (138 mm) as snow (Lupin A station)
Temperature	Annual average temperature= $-12^{\circ}C$
Range	Range: -30.4°C (Jan) to 11.5°C (Jul) (Lupin A station)
Permafrost Zone	Continuous
MINING	
Status	Operating
Mine Life	~7 years (1998 to present), expected mine life of at least 25 years.
Mining Method	Open pit and underground
Waste Rock	The majority of pipes are hosted by granitic rock types which are disposed in
Management	conventional waste rock dumps. At the Misery Pipe, several pipes occur at the contact
	rock dump has been constructed to enhance cooling of the rock.
Ore Processing	Fine processed kimberlite is discharged to the Long Lake Containment Facility
and Tailings	(LLCF) consisting of 4 cells for tailings placement and 1 cell for settling and
Disposal	clarification of water.
	at the Panda Pipe.
GEOLOGY	
Summary	Diamondiferous kimberlites thought to be Mesozoic or Cenozoic in age and emplaced
Geological	into Archean granitic and schistose rocks of the Slave tectonic province, and much
Description	later diabase dykes associated with the Mackenzie Dyke Swarm.
Mineralogy	Kimberlites have conventional mineralogy consisting of fresh and altered ultramafic
	minerals (olivine and serpentine). Sulphur occurs primarily as fine-grained pyrite at
	Granite mineralogy is consistent with global characteristics. Intrusion of kimberlite
	does not alter the granite. The granitic rocks contain negligible sulphur ($<0.05\%$)
	typically as pyrite but occasionally as chalcopyrite. Calcite also occurs rarely as
	fracture fillings. Mafic xenoliths are a common feature which may be local sources of
	Supplie (pyrite and chalcopyrite enrichments). Biotite schist contains low concentrations of sulphur ($\sim 0.2\%$) primarily as fine-
	grained pyrite and pyrrhotite. Calcite is rare.
Surficial	Glacial till, glacio-fluvial deposits, glacio-lacustrine sediments and lacustrine
Geology	deposits.

EKATI DIAMOND MINE

GEOCHEMISTRY			
Geochemical Overview	The kimberlites are non-acid generating due to the high concentrations of carbonate (calcite) and silicate (magnesium) neutralization potential and low concentrations of pyrite. Neutral pH leaching of elements occurring in pyrite (nickel and molybdenum) is apparent in laboratory tests and in seepage from the CKR disposal area. Granitic rocks have very low reactivity. While carbonate neutralization potential is negligible, sulphur content is also very low and kinetic testing has shown that weathering of silicates by carbonic acid produces enough alkalinity to offset acid generation by oxidation of sulphides. Schists at the Misery Pipe and Pigeon Pipe have been shown to generate ARD under laboratory conditions. Generation of ARD under field conditions for the schist has not been demonstrated.		
Low Temperature Geochemical Aspects	<i>Effect of temperatures on oxidation rates</i> : A laboratory kinetic test on diabase from the Fox Pipe showed that reduction of temperatures from room to refrigerated resulted in a decrease in oxidation rates from about 23 mg/kg/week to about 6 mg/kg/week (ie a factor of about 3.8). Similar factors were observed for zinc (3.2) and nickel (3.1). It is apparent from the extensive seepage monitoring network that oxidation of pyrite occurs under the cold temperatures at the site. The coarse kimberlite reject pile has drainage containing several thousand mg/L and elevated Ni and Mo concentrations. However, the effect of freeze-concentration in this setting is probably significant and the elevated sulphate concentrations cannot be attributed to rapid oxidation under pH neutral conditions. The high sulphate concentrations are also partly supported by the abundance of magnesium. Several years of monitoring at the Misery Waste Rock Storage area has not detected ARD. This appears to indicate that the measures designed to enhance low temperature conditions within the pile are being successful either by limiting oxidation of the sulphide or by ice encapsulation.		
	Effect of temperature on bacterial activity: No data Effect of temperature on solubility and reactivity of acid buffering minerals: No data		
	<i>Effect of temperature on solubility of secondary minerals:</i> No data		
	<i>Solute freeze-concentration effects:</i> Thermal monitoring of the CKRSA demonstrates that internal temperatures are consistently very close to freezing implying that freezing of trapped process water is occurring, likely resulting in freeze concentration of waters. This may partially explain the highly concentrated nature of waters observed draining from the pile.		
	<i>Effect of freeze-thaw processes on mineral exposure:</i> No data		
	Solubility of oxygen in water covers: No data		

EKATI DIAMOND MINE

Ice barrier effects on oxygen and water movement
No data

OTHER

Acidic seepage apparently unrelated to ARD is seen at Ekati. In some cases, the acidic water is very dilute and the water is believed to originate from natural decay in tundra soils. Therefore, tundra water is typically slightly acidic but has very low ion concentrations. In the CKRSA, acidic seepage has been observed. This is suspected to be due to ferrous iron release in reducing conditions (perhaps produced by interaction of CKR with tundra, and subsequent slow oxidation and hydrolysis under cold conditions producing ferric hydroxide precipitates and low pH water. Since the acid generation does not occur in contact with the calcareous CKR, the acidity is detected as low pH of surface water.

INFORMATION SOURCES		
References	 Day, S., Sexsmith, K. and Millard, J. 2003. Acidic Drainage From Calcareous Coarse Kimberlite Reject, Ekati Diamond MineTM, Northwest Territories, Canada. Proceedings of the Sixth International Conference on Acid Rock Drainage. SRK Consulting, 2003. 2002 Waste Rock Storage Area Seepage and Waste Rock Survey Report. Prepared for BHP Billiton Diamonds. February 2002. 	
Permissions for Unpublished Data	Not applicable	
Case Study Prepared by:	Stephen Day	

KENO HILL MINING DISTRICT

LOCATION

Description	Approximately 350 km north of Whitehorse in central Yukon, Canada
Latitude	63°56'(N)
Elevation	Average elevation of mining at 760 m.
CLIMATIC REG	IME
Precipitation	Total 346 mm, with 42% (145 mm) as snow (Mayo Airport station)
Temperature Range	Annual average temperature= -3.6°C Range: -26.9°C (Jan) to 15.6°C (Jul) (Mayo Airport station)
Permafrost Zone	Discontinuous
MINING	
Status	Closed with regional exploration on-going
Mine Life	~75 years (1914-1989)
Mining Method	Underground and open pit (from1977 onwards)
Waste Rock Management	Waste rock often used for construction, riprap etc., but piles, in particular those associated with open pit operations exist.
Ore Processing and Tailings Disposal	The Keno Hill silver-lead-zinc mining district is one of the richest and most productive silver camps in North America. Historic production amounts to over 210 million ounces of silver, 350,000 tons of lead and 210,000 tons of zinc from both underground and open-pit operations. The district is a world-class silver camp with more than 160 km of known vein strike length, 65 identified deposits or prospects and a documented history of production from 34 deposits. The property produced more than 200 million ounces of silver between ~1914 and 1989. Tailings from the Elsa mill were deposited in a storage facility covering an area of 0.65 km ² .
GEOLOGY	
Summary Geological Description	Three main rock types are described as Devonian-Carboniferous Earn Group metasedimentary and metavolcanic rocks (carbonaceous phyllite, siliceous phyllite and porphyritic phyllitic felsic metavolcanic rocks), Early Carboniferous Keno Hill quartzite (with lenses of cholritic phyllite and rare limestone) and Late Triassic meta- diorite.
Mineralogy	Carbonate veinlets are reported in all the rock types. Ore mineralogy includes argentiferous galena [PbS] and silver-containing sulphosalts such as freibergite [(Ag,Cu,Fe) ₁₂ (Sb,As) ₄ S ₁₃]. Associated gangue minerals reported included sphalerite [ZnS], pyrite [FeS ₂], manganiferous siderite [(Mn,Fe)CO ₃] occurring in quartz veins. Secondary minerals identified in the waste rock include limonite [Fe-hydroxides], pyrolusite [MnO ₂], cerrusite [PbCO ₃]and anglesite [PbSO ₄].

KENO HILL MINING DISTRICT

Surficial	Local gravel 'sumps' at the base of slopes. Hillsides are mantled by bouldery sand
Geology	and clay with locally modified solifluction since glacial melting. Stream bottoms
	generally consist of pebble to boulder sized rock fragments and lag from glacial
	deposits.
GEOCHEMISTR	Y
Geochemical	No data
Overview	
Low	Effect of temperatures on oxidation rates:
Temperature	No data
Geochemical	Effect of temperature on bacterial activity
Aspects	No data
	Effect of temperature on solubility and reactivity of acid buffering minerals:
	No data
	Effect of temperature on solubility of secondary minerals:
	Water quality and stream sediment sampling and analysis suggest that there is
	formation of soluble secondary minerals during the dry season (including winter)
	creating a temporary metal storage through the cryogenic precipitation of hydrozingite $[Zn (CO) (OH)]$.
	streams with high concentrations of Zn flowing over microbial growth in late spring
	through fall. The metals sorb onto the body walls of bacteria forming a microbial mat
	or organic litter on the stream bed. During winter and progressive freezing, the
	concentrations of dissolved constituents in the water increases due to ice segregation.
	Sorbed metals provide nucleation sites for secondary mineral formation resulting in
	further accumulation. Unless the microbial mat is rapidly buried, the metals will
	largely redissolve after the thaw and spring freshet.
	Evaluations of the tailings indicate unward migration of constituents through
	capillary action during the summer when evaporation is highest. Precipitates
	included gypsum [CaSO ₄ 2 H ₂ O] and bianchite [(Zn,Fe++)(SO ₄) 6 (H ₂ O)] resulting in
	a surface enrichment of contaminants.
	Solute freeze-concentration effects.
	No data
	Effect of freeze-thaw processes on mineral exposure:
	Solubility of oxygen in water covers:
	No data
	Ice barrier effects on oxygen and water movement
	No data
OTHER	
UTHER	

KENO HILL MINING DISTRICT

INFORMATION SOURCES		
References	Kwong, Y.T.J., Roots, C.F., Roach, P. and Kettley, W. (1997). Post-mine metal transport and attenuation in the Keno Hill mining district, central Yukon, Canada. Environmental Geology, vol. 30(1/2), pp. 98-107.	
Permissions for Unpublished Data	Not applicable	
Case Study Prepared by:	Shannon Shaw	

MAARMORILIK MINE (BLACK ANGEL)

LOCATION	
Description	In the inner part of the Uummannaq fjord system of West Greenland
Latitude	71°07'N
Elevation	Unknown
CLIMATIC REG	IME
Precipitation	Total = <120mm
Temperature Range	Average annual temperature = $-8^{\circ}C$
Permafrost Zone	Continuous permafrost at a depth of 1.4 m in summer
MINING	
Status	Closed (in 1990)
Mine Life	17 Years (1973-1990)
Mining Method	Underground
Waste Rock Management	Waste rock placed above ground in dumps
Ore Processing and Tailings Disposal	During operations, the mine processed ~ 11 million tonnes of ore. Tailings were discharged into a small adjacent fjord named Affarlikassaa that is separated from the outer fjord by a small sill. On closure, some of the inter-tidal
	tailings were placed further underwater and some were placed on land. Those on land were covered in 1991 with 40 to 70 cm of sediments consisting primarily of carbonate minerals
GEOLOGY	
Summary Geological Description	The deposit is a carbonate-hosted zinc-lead-silver massive sulfide deposit of SEDEX or MississippI Valley-type origin. Host rocks are Proterozoic calcitic to dolomitic marble a basal quartzite unit and intercalations of anhydrite-bearing marble and semipelitic schists. The ore forms flat-lying, highly deformed lenses up to 30m thick. The massive ore consists of sphalerite, galena, and pyrite, with accessory pyrrhotite, chalcopyrite, tennantite and arsenopyrite.
Mineralogy	The deposit is reported to consist of 24-30% pyrite [FeS ₂], 14-15% Zn (assuming as sphalerite, ZnS) and 4% Pb (assuming as galena PbS). Fine tailings (<2mm) consisted of ~ 50% carbonates in equal proportions of calcite [CaCO ₂] and dolomite [CaMg(CO ₂)] 15 to 40% pyrite [FeS ₂] 1-2% sphalerite [ZnS]
	and less than 1% galena [PbS]. Coarse tailings (>2mm) contained less than 1% sulfides and 99% other silicate minerals.
Surficial Geology	No data

MAARMORILIK MINE (BLACK ANGEL)

GEOCHEMISTRY		
Geochemical Overview	Reported contamination from marine disposal and waste rock dumps consist of heavy metals in water, dust and concentrate pollution. The metal concentrations in the waste were reported as 0.89±0.2%Pb, 2.7±0.4% Zn and 0.12±0.002% Cd. The tailings pH values were reported to vary between 8.1 and 9 s.u.	
Low Temperature Geochemical Aspects	<i>Effect of temperatures on oxidation rates</i> : Somewhat low oxidation rates (on the order of 0.1 moles/m ² /d) are seen in this material, partially as a result of temperature and partially as a result of near neutral pH conditions. Depth profiles of temperature, O_2 and CO_2 concentrations, SO_4 and activity are shown in Figure 2 from Elberling <i>et al.</i> , 2001). Results show that sulfide oxidation and carbonate dissolution occur in the active zone beneath a cover in the tailings.	
	<i>Effect of temperature on bacterial activity:</i> Almost negligible biotic activity was seen in this study, however it is primarily attributed to the high pH environment.	
	<i>Effect of temperature on solubility and reactivity of acid buffering minerals:</i> No data	
	<i>Effect of temperature on solubility of secondary minerals:</i> No data	
	Solute freeze-concentration effects: No data	
	<i>Effect of freeze-thaw processes on mineral exposure:</i> No data	
	Solubility of oxygen in water covers: No data	
	<i>Ice barrier effects on oxygen and water movement</i> No data	
OTHER		

INFORMATION SOURCES	
References	Elberling, B., Asmund, G. Balic-Zunic, T. Rohwerder, T. and Sand, W. (2001). <i>Reactivity of covered sulfidic waste near Maarmorilik in West Greenland</i> . Mining in the Arctic, Olsen, Lorentzen & Rendel (eds.), 2001, pp. 11-16.
Permissions for Unpublished Data	Not applicable
Case Study Prepared by:	Shannon Shaw

FIGURES (from Elberling et al., 2001)



Figure 2. Depth-dependent ground temperatures, pores gas composition, solid sulfate content and total heat output at 20°C from oxidizing pyritic waste. The thick solid line across the inert cover represents linear regression of oxygen concentrations ($r^2 > 0.99$) and bars represent standard deviations

LOCATION

Description	Located on Baffin Island, Nunavut, Canada approximately 750 km north of the Arctic Circle.
Latitude	73°02'N
Elevation	~ 400 m
CLIMATIC REG	IME
Precipitation	Total average annual precipitation = 125 mm; [note 240 mm from Cassie and LeDrew, 2001] Proportion as snow = not recorded.
Temperature Range	Average annual temperature = -13.5 °C; [note -15.2°C from Cassie and LeDrew, 2001] Monthly average range = see Figure 1 from Kyhn and Elberling, 2001
Permafrost Zone	Continuous. Permafrost boundary in tailings moved from a depth of ~1m in mid July to 1.5 m in mid August.
MINING	
Status	Started production in 1976, operations ceased in September 2002.
Mine Life	~ 26 years
Mining Method	In the Main Lens, mining was by room and pillar methods, but in the smaller satellite zones, production methods included drift and slash stoping with some cut and fill stoping.
Waste Rock Management	No data
Ore Processing and Tailings Disposal	Ore was crushed in a jaw crusher and a cone crusher and grinding was by rod and ball mill. Lead flotation was carried out in six rougher cells and zinc flotation is carried out in 24 cells. Concentrates were dried in rotary dryers and were trucked 3 km to the storage shed at the ship loading dock.
	Flotation tailings were pumped through a 4 km pipeline to the West Twin Lake tailings disposal area. Some tailings were deposited "on land" (Elberling <i>et al.</i> , 2000).
	The tailings disposal area was divided into an upper Surface Cell for solids and a lower Reservoir for storage of supernatant water. A frozen-shale upstream constructed dike separates the two cells (Cassie and LeDrew, 2001).
GEOLOGY	
Summary Geological Description	The Nanisivik sulphide deposits are hosted in carbonate rocks of the Society Cliffs Formation. The various Nanisivik deposits aggregate more than 50 million tonnes of massive sulphides. Barren massive pyrite bodies are by area the most extensive, and contain the largest sulphide tonnages. Zones carrying sphalerite are present within the massive pyrite bodies, but are really more restricted and also confined to a restricted vertical interval. All known significant sphalerite deposits are in horsts adjacent to the Keystone Graben.

	The Main Zone deposit is 3 km long, oriented east-west, and broadly "T" shaped, with a flat-topped upper section. The keel section of the deposit extends to about 80 m below the upper section. While it is vertical, no obvious controlling structures are observed. In places, flat-lying wings of sulphides extend out laterally from the keel zone. Internal structures in the ore zones tend to be complex, ranging from massive and banded to chaotic and brecciated. Banding tends to be subhorizontal in both the upper section of the Main Zone and the keel section of the deposit, but it may be parallel to dipping dolostone contacts in some areas. As well, the ore is porous in places and large irregular zones of ice are present in some faces underground. The accepted geological model is a Mississippi Valley Type (MVT). These are post- depositional, carbonate hosted deposits (InfoMine, 2005).
Mineralogy	Fresh tailings are comprised of roughly 50-85% pyrite $[FeS_2]$ with the remainder made up of dolomite $[CaMg(CO_3)_2]$ and residual amounts of sphalerite $[ZnS]$ and galena $[PbS]$.
Surficial Geology	No data
GEOCHEMISTR	Y
Geochemical	Tailings generally well buffered to pH values between 7.4 and 7.7. Sulphate is the
Overview	dominant oxidation product (accounts for >98% of sulphur species), also identified thiosulphate, polythionates and elemental sulphur. Oxidized and reduced zone interface in subaerial tailings at a depth of 20 to 40 cm. A thin Fe(OH) ₃ hardpan is associated with the interface (Elberling, 2005). Pore water collected below 40cm is buffered. Pore water concentrations in the oxidation zone after precipitation events are similar to that below the interface, but after dry periods are acidic (pH as low as 2.3) with elevated Zn, Pb, Cd and SO ₄ (see Table 1). Oxygen concentrations dropped from atmospheric to below detection (0.1%) at all sites. O ₂ penetration reached ~ 30cm in well drained areas (water content ~ 10%) and only ~ 2cm in wet areas (water content ~ 30%). Temperatures during sampling near 13°C near the surface, 4-6°C at 60cm depth and reached 0°C at the permafrost level.
Low Temperature Geochemical	<i>Effect of temperatures on oxidation rates:</i> Chemical oxidation accounted for 50 to 100% of the total activity with an average of 65% (see Table 2, Elberling <i>et al.</i> , 2000).
Aspects	Field measured O_2 uptake rates measured at 3 locations in moles/m ² /d = 0.40±0.06 (well drained 6 yr old tailings); 0.0055±0.008 (wet 6 yr old tailings); 0.39+/-0.05 (well drained ½ yr old tailings). Field measurements of oxygen uptake at temperatures less than -4°C were not possible with the equipment used due to freezing, but measurements under snow cover with temperatures of -1 to -3°C showed oxidation rates in the winter of approximately 20-25% of the rates measured during the summer. Heat output converted to O ₂ uptake from laboratory experiments were generally in good agreement with field measurements with values in moles/m ² /d = 0.43±0.03 (well drained 6 yr old tailings); 0.0027 (wet 6 yr old tailings); 0.38 (well drained ½ yr old tailings). The authors indicate these rates are similar to those seen in more temperate regions.

Low Temperature Geochemical Aspects	The O_2 uptake rate decreased with decreasing soil temperature in the well-drained tailings sites indicating that the sulphide oxidation rate is dependent on the soil temperature in unsaturated materials (see Figure 3, Elberling <i>et al.</i> , 2000). Summer oxidation rates may be 2 to 3 times higher than average monthly rates on an annual basis (Elberling <i>et al.</i> , 2003). Due to low O_2 uptake rate in wet materials, little variation is seen with changing soil temperature. A Q_{10} value (temperature coefficient) is used to describe the change in rate (chemical and biological oxidation rate) for every 10°C change in temperature. The value above $-2^{\circ}C$ was ~ 2 , but below $-2^{\circ}C$ was much greater at ~ 10 (see Figure 1, Elberling, 2005). The change was attributed to trapping of gases rather than a decrease in microbial activity below freezing temperatures due to a similar shift in experiments where all microbes were exterminated with chloroform. Comparative humidity cell data provided by Mattson (personal communication) show that oxidation rates were lower when temperature was reduced for a sampling of tailings and waste rock. Zinc release however appeared to increase.
	<i>Effect of temperature on bacterial activity:</i> Calorimetric results indicate bacterial activity accounts for roughly $1/3^{rd}$ of the current sulphide oxidation or activity throughout the range of temperatures tested (roughly 13° C to -3° C).
	Microorganisms identified included strongly acidophilic, lithotrophic iron(II) (<i>Thiobacillus ferrooxidans</i>) and sulphur (<i>T. thiooxidans</i>) oxidizing bacteria, moderately acidophilic lithotrophic, thiosulphate oxidizing bacteria (<i>Thiomonas intermedia</i>) and chemoorganotrophic microorganisms (COT) in the upper zones to a depth of 25cm.
	Microorganisms were not detected in samples from the reduced zone below 30cm of the buffered tailings nor from the fresher (1/2 yr old) tailings in either zone. The microbial oxidation therefore is limited when pH is high.
	Temperature itself could not account for increased or reduced bacterial activity, significant activity near 0°C in well-drained, poorly buffered tailings was measured.
	<i>Effect of temperature on solubility and reactivity of acid buffering minerals:</i> Pore water chemistry changed over time in the unsaturated zone of the tailings. The greatest variability was seen in the reaction zone (i.e. between the leached oxide zone and the saturated zone). Figure 5 from Elberling, 2001 shows the variations in a number of parameters on a seasonal basis.
	Increased acid production (and decreasing pH) over the season as temperatures increase from July to September is accompanied by an increase in concentrations of Mg and to a lesser extent Ca due to dolomite dissolution. Elberling anticipates that the Ca is attenuated somewhat by gypsum precipitation due to the smaller increase as compared to Mg. Increasing concentrations of sulphate in pore water during the monitoring period was assumed to be a result of sulphide oxidation and corrected for evaporation (by comparison with Cl changes) and gypsum precipitation (by comparison with Mg:Ca ratios). Sulphate concentrations were compared to O_2 consumption rates over the same period of time with very close agreement in the

calculated O_2 uptake rates by both methods (0.22 vs. 0.19 mol $O_2/m^2/d$).
<i>Effect of temperature on solubility of secondary minerals:</i> No data
<i>Solute freeze-concentration effects:</i> High concentrations of dissolved weathering products decreased the freezing point by a few degrees. Unfrozen water was observed at temperatures at least as low as -10° C (Elberling, 2005). Relatively good matches between observations and modeling using FREZCHEM to predict the amount of unfrozen water content were found in freezer experiments (Figure 7 from Elberling, 2001).
<i>Effect of freeze-thaw processes on mineral exposure:</i> No data
Solubility of oxygen in water covers: No data
Ice barrier effects on oxygen and water movement:
At freezing temperatures, decreasing temperatures increase the fraction of water freezing thereby potentially trapping gas containing O_2 . Elberling, 2005, hypothesized that the physical trapping of O_2 limits the amount of O_2 available for oxidation and may partially account for the increased Q_{10} value below -2°C at Nanisivik.
Increasing water content in tailings towards the lake reduced the near-surface effective diffusion as well as the O_2 uptake by a factor of ~ 100 (Figure 5, Elberling <i>et al.</i> , 2003). Freezing has shown no significant effect on the diffusivity in tailings with a water saturation of less than 30%. Above 30%, freezing decreases the diffusivity by up to an order of magnitude compared to unfrozen tailings up to a saturation of 70% (see Figure 5, Elberling 1998).
Effect of thermal dry covers:
Kyhn and Elberling (2001) discuss the effects of thermal dry covers on two test pads constructed to encapsulate the tailings within the permafrost zone and ensure the active zone remains within the cover materials, essentially by forcing the frost table upwards. One cover consisted of 2m of shale (TP1), the other consisted of 1.7m of shale and 0.3m of sand and gravel on top (TP2). Temperatures and thermal conductivities were measured with depth in both test pads. Results were used to calibrate a model using WinSoil to analyze heat and water transport in the material.
Thermocouple readings in TP1 show temperatures at the cover/tailings interface from -15° C to -10° C in Feb and March and between -2° C and -0.5° C in August and September. Slightly warmer winter temperatures were recorded at the interface in TP2 reaching -7.2° C. Modeling of a snow cover indicated snow (as little as 5 cm) may have a dramatic impact on the temperature regime within covered tailings (see Figure 7 from Kyhn and Elberling, 2001). Modeling of various cover thicknesses was included (see Figure 8 from from Kyhn and Elberling, 2001) however snow cover was not considered.

	within the permafrost zone, however chemical and biological oxidation can continue below 0° C and snow cover can greatly impact the temperature regime in the thermal cover and beneath it.
OTHER	

INFORMATION SOURCES

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Permissions for Unpublished Data	Bruce Mattson, November 7, 2005.
Case Study	Shannon Shaw
Prepared by:	Stephen Day

FIGURES (from Eberling, 1998)



Figure 5. Oxygen diffusion coefficients in partly saturated tailings from Nanisivik (m^2/s). Mean values of 3 measurements are shown as dots and the 95% confidence interval of 5 replicates are shown as bars. Solid curves have been drawn by hand to simplify the display. The dashed line represents a fitting equation from Reardon & Moddle (1985) that is based on measurements on unfrozen sandy tailings

FIGURES (from Eberling et al., 2000)



Fig. 1. Normalized activity of pyrite oxidation vs. temperature. Solid squares (\blacksquare) represent calorimetric measurements of samples from Nanisivik Mine and the straight line a linear fit for temperatures between 6°C and 20°C ($r^2 = 99\%$ — maximum and minimum measured values are indicated with bars). Normalized pyrite oxidation activity based on dissolved iron production data from Langdahl and Ingvorsen (1997) are included for comparison. Open circles (\circ) represent chemical rates and solid circles (\bullet) microbial rates. The Arrhenius plot based on the activation energy observed by Langdahl and Ingvorsen (1997) is shown as a dashed line.



Fig. 2. Depth dependent related data for well-drained tailings deposited 6 years ago. A: oxygen gas concentration (\blacktriangle) and temperature (O) prior to sampling, B: measured heat output at 10°C (\bullet), and total heat output (—) corrected according to on-site temperatures using the linear relationship shown in Fig. 1.



Fig. 3. Temporal trends in air temperatures (\bullet), soil temperatures (\blacktriangle), precipitation (solid bars), and oxygen uptake rates (\blacksquare) measured from the 15th of July to 18th of August 1998. The site consists of well-drained tailings deposited 6 years ago. Simulated oxygen uptake is shown as a thick solid line.

FIGURES (from Elberling, 2001)



Figure 5. Temporal trends in concentrations of metals, selected cutions and anions, and pH in pore water collected at five depths within the unsaturated zone of a well-drained tailing profile.


Figure 7. Unfrozen water content (percent of total water content) in mine tailings collected August 7, 1998, from the upper oxidized zone (20 cm) and lower reduced zone (80 cm). Observations are compared to FREZCHEM simulations.

FIGURES (from Kyhn and Elberling, 2001)



Fig. 1. Daily mean temperatures (dashed line), net radiation (solid line) and precipitation (bars) from June 1998 to June 1999 in Nanisivik, Canada.



Fig. 7. Predicted ground temperatures at 2 m of depth in Test pad 1 as a result of various snow cover regimes: no snow (dashed line), 5 cm (thin solid line), 25 cm (thick solid line) and 50 cm (very thick solid line) of snow. Meteorological driving variables are based on observations of the period 1995–1996 as representative years. Only the air temperature (solid line) is shown.



Fig. 8. Predicted ground temperatures at the cover/tailings interface below covers of 1 m (thin line), 2 m (solid line), and 3 m (thick solid line). Simulated cover material represents characteristics observed for material in Test pad 1. Meteorological driving variables are based on 1995–1996 observations, but without any snow.

FIGURES (from Eberling et al., 2003)





Spatial trends in oxygen uptake from the surface of reactive 7-yearold tailings disposed along a transect, representing well-drained to fully saturated conditions. *Filled squares* represent results of oxygen uptake by closed gas chambers, while the *open square* represents oxygen uptake measured as the oxygen concentration gradient in mine tailings covered by 10 cm of water

Appendix A - Case Histories

FIGURES (from Eberling, 2005)



Fig. 1. Oxygen consumption rates observed in pyritic mine tailings incubated at temperatures from -12 to $12 \,^{\circ}$ C. Exponential fits are shown as straight dashed lines indicating a Q_{10} value of about 2 at temperatures above $-2 \,^{\circ}$ C (0.0247 $e^{0.037x}$, $r^{2}=0.99$) and a value of 10 at temperatures below $-2 \,^{\circ}$ C (0.0256 $e^{0.2328x}$, $r^{2}=0.92$). The figure insert shows rates above $-2 \,^{\circ}$ C on a linear scale.

TABLES (from Eberling et al., 2000)

Table 1

Characteristics of tailing and chemistry of suspension (average ± SD)

Sites	1 and 2 ^a	3	4
Years since deposition	б	6	0.5
Water Content	well-drained	wet	well-drained
pH	7.4±0.2	7.7±0.2	7.4±0.4
Sulfate	2668 ± 1100	2001 ± 1799	1493 ± 772
Thiosulfate	1.3 ± 0.8	3.2 ± 3.1	3.8 ± 2.3
Elemental sulfur	58±52	25 ± 23	95±108
Trithionate	9±5	3±3	98.2±63
Tetrathionate	173 ± 69	52±41	738±386
Pentathionate	34 ± 12	9±1	110 ± 70
Nitrate	8.1±6.2	7.3 ± 2.1	25.2±28.6

^aSite 1 and 2 are replicates.

Table 2

Characteristics of tailin	gs reactivity	(average + SD)
---------------------------	---------------	----------------

Sites	1 and 2	3	4
Oxygen uptake ^a (moles m ⁻² day ⁻¹)	0.40±0.06	0.0055±0.008	0.39±0.05
Heat output converted to O_2 uptake (moles m ⁻² day ⁻¹)	0.43 ± 0.03	0.0027	0.38
Chemical oxidation (percent of total oxidation)	70±14	63±29	68±9

^aSD-values for in situ oxygen uptake values represent the sensitivity of the slope estimate.

NORTH KOLYMA LOWLAND

LOCATION

Description	Near the Bolshaya Chukochya River in north-east Siberia, Russia
Latitude	$\sim 70^{\circ}$ N
Elevation	Unknown
CLIMATIC REG	IME
Precipitation	Unknown
Temperature Range	Unknown
Permafrost Zone	Continuous.
	The active layer thickness varies, but was up to 32 cm in depth, with shallower active layer where thick peat or moss cover existed.
MINING	
Status	Natural soils
Mine Life	Not applicable
Mining Method	Not applicable
Waste Rock Management	Not applicable
Ore Processing	Not applicable
Disposal	
GEOLOGY	
Summary	Soils formed from the Yedoma deposits which are mid to late Pleistocene continental
Geological Description	loamy sediments.
Mineralogy	The soils are dominated by illite, Fe-Mg Chlorite and kaolinite.
Surficial Geology	Soils are yellowish, olive and brownish colours with inclusions of humus and plant roots. Diffuse black, brown and reddish spots and microconcretions are seen.

GEOCHEMISTRY

Geochemical Overview	The Yedoma deposit is pH neutral to weakly acidic with Eh values decreasing from the surface (180-210 mV) to the frozen layer which is strongly reducing.
Low Temperature	<i>Effect of temperatures on oxidation rates:</i> No data
Aspects	<i>Effect of temperature on bacterial activity:</i> No data

Appendix A - Case Histories

NORTH KOLYMA LOWLAND

	Effect of temperature on solubility and reactivity of acid buffering minerals:
	Within the active layer there was degradation of chlorite and illite with formation of
	randomly interstratified chlorite-smectite and illite-smectite respectively. At the
	permafrost table, lepidocrocite was determined to be precipitating. The hypothesis
	presented suggests that the permatrost acts as a barrier to infiltration and results in an
	accumulation and enrichment of ferrous iron (sourced from minerals above). Low En
	and slow oxidation are reportedly important for the formation of repidocrocite.
	Effect of temperature on solubility of secondary minerals:
	No data
-	Solute freeze-concentration effects:
	No data
	Effect of freeze-thaw processes on mineral exposure:
	No data
	Solubility of oxygen in water covers:
	No data
	Ice barrier effects on oxygen and water movement
	The unfrozen water content in the Yedoma deposits is reported to be 3% at -8° C.
OTHER	

INFORMATION	SOURCES
References	Alekseev, A., Alekseeva, T., Ostroumov, V., Siegert, C. and Gradusov, B. (2003). <i>Mineral transformations in permafrost-affected soils, North Kolyma Lowland, Russia.</i> Soil Sci. Soc. Am. J. vol, 67, pp. 596-605.
Permissions for Unpublished Data	Not applicable
Case Study Prepared by:	Shannon Shaw

POGO PROJECT

LOCATION	
LOCHION	

Description	Approximately 160 km southeast of Fairbanks, Alaska, USA
Latitude	63°48' (N)
Elevation	Unknown
CLIMATIC REC	GIME
Precipitation	Total= 275 mm. Proportion as snow not available
Temperature	Average annual not available
Range	Range: -24°C (Jan) to 21°C (July)
Permafrost	Widespread
Zone	
MINING	
Status	In construction.
Mine Life	Anticipated 10 year mine life
Mining Method	Underground
Waste Rock Management	Waste rock will be segregated according to sulphur and arsenic content to address potential for acid generation and arsenic leaching. "Reactive" waste rock containing higher sulphur and arsenic concentrations will be co-disposed with dry-stacked tailings.
Ore Processing and Tailings Disposal	A bulk sulphide concentrate is produced by flotation resulting in flotation tailings which will be dry-stacked. The concentrate will be leached with cyanide to recover gold and silver. Cemented mixed leached and flotation tailings will be used as backfill in the underground mine.
GEOLOGY	
Summary Geological Description	Gold mineralization is in stacked low-angle mesothermal quartz veins approximately 7m in thickness hosted by granodiorite and gneiss.
Mineralogy	Sulphide mineralogy in the ore consists primarily of pyrite, pyrrhotite and arsenopyrite. Chalcopyrite and löllingite (FeAs ₂) are present in variable locally significant amounts. Carbonate minerals are present. Ore type sulphide minerals extend through altered rock into the host rock but in lower concentrations.
Surficial Geology	No data

POGO PROJECT

GEOCHEMISTRY		
Geochemical Overview	Ore contains variable sulphide content but generally less than 2% total sulphur. Neutralization potential is low resulting NP/APs typically less than 1.	
	In contrast, the sulphur content of most waste rock is less than 1%, and the majority of waste rock has NP/AP greater than 2.	
	An extensive kinetic test program showed that the potential for acid generation was low and that leaching of arsenic was potentially the most significant issue for the project.	
Low Temperature Geochemical Aspects	<i>Effect of temperatures on oxidation rates:</i> Two pairs of waste rock humidity cells (refer to Figures 1, 2 and 3), one set of flotation tailings humidity cells and one set of leach columns were operated under room and refrigerated conditions.	
	One waste rock pair was operated on potentially acid generating gneiss (total S – 0.87%, sulphate S – 0.06%, NP 5.7 kg CaCO3/t, TIC 4.3 kg CaCO3/t, As 1477 mg/kg). The pH of the room temperature cell dropped quickly to less than 4, whereas the refrigerated test showed highly variable pH between 5.5 and 8 before eventually decreasing to near 4 after 5 years of testing. The more acidic room temperature test had higher sulphate production than the refrigerated test though the difference in pH prevents any direct conclusions about the effect of temperature on oxidation rates. Arsenic release rates were much lower for the refrigerated cell but as pH decreased eventually became similar to the refrigerated test. The main conclusion from these tests was that the lower temperatures delayed but did not prevent the onset of acidic conditions and that the refrigerated test eventually released arsenic at the same rate as the room temperature test.	
	The second waste rock pair was operated on not potentially acid generating rock from near the ore zone that contained 0.33% total S, undetected sulphate (<0.01%), NP of 52 kg CaCO3/t, TIC of 82 kg CaCO3/t and arsenic of 4311 mg/kg. Arsenopyrite was the dominant sulphide mineral in the sample (0.4%) followed by pyrite (0.2%). During the period of concurrent operation (about 1 year), pHs were identical and increased from 8 to 9. Both tests initially showed comparable sulphate but then decreased. Sulphate release from the low temperature test was barely detectable (0.4 mg/kg/week) compared to 1.4 mg/kg/week for the room temperature test, representing a ratio of 3.5. Arsenic release was initially greater for the room temperature test but after about 6 months the release rates were similar but very low (<0.01 mg/kg). This test indicated the expected decrease in overall sulphide oxidation rate for the temperature difference but it is not known which sulphide mineral was oxidizing. The low arsenic concentrations probably indicate that pyrite was oxidizing but they could be also be due to storage of arsenic in the cell.	
	The set of flotation tailings humidity cells consisted of three room temperature tests and one refrigerated test contained tailings with low sulphur (0.08%), 30 kg CaCO3/t NP and 628 mg/kg As. Leachate pHs for all tests were the same for 3 ¹ / ₄ years of testing (about 8). Sulphate release decreased for two years with the refrigerated test showing no substantial difference in release rates from the three room temperature tests. However, once sulphate release stabilized, the refrigerated test had lower rates (erratic but about 0.8 mg/kg/week) compared to the room temperature tests (1 to 2 mg/kg/week)	

POGO PROJECT

The tailings column test operated on the same materials as the humidity cell and similarly as triplicate room temperature tests and a single refrigerated test. The column tests were subaerial 3 kg tests leached weekly with 600 mL of water. All four tests produced pH roughly 8 leachate for five years. Sulphate concentrations in leachates were low (generally less than 10 mg/L) but very erratic. One room temperature column released sulphate concentrations up to 20 mg/L for over a year, and the refrigerated column had higher sulphate concentrations than any of the tests for some periods. Towards the end of the test, sulphate concentrations were between 4 and 8 mg/L and with no difference for the refrigerated column. In contrast, arsenic concentrations (Figure 4) were consistently lower for the refrigerated column (typically about 0.15 mg/L compared to up to 0.5 mg/L for the room temperature column). As for sulphate.	representing a ratio of 1.3 to 2.5. The refrigerated test consistently released less arsenic (0.01 mg/kg/week compared to 0.02 mg/kg/week). As with the waste rock tests, it is not know to what degree this represents differences in oxidation rates or storage in secondary minerals.
differences between columns were significant.	The tailings column test operated on the same materials as the humidity cell and similarly as triplicate room temperature tests and a single refrigerated test. The column tests were subaerial 3 kg tests leached weekly with 600 mL of water. All four tests produced pH roughly 8 leachate for five years. Sulphate concentrations in leachates were low (generally less than 10 mg/L) but very erratic. One room temperature column released sulphate concentrations up to 20 mg/L for over a year, and the refrigerated column had higher sulphate concentrations than any of the tests for some periods. Towards the end of the test, sulphate concentrations were between 4 and 8 mg/L and with no difference for the refrigerated column. In contrast, arsenic concentrations (Figure 4) were consistently lower for the refrigerated column (typically about 0.15 mg/L compared to up to 0.5 mg/L for the room temperature column). As for sulphate, differences between columns were significant.
<i>Effect of temperature on bacterial activity:</i> No data	<i>Effect of temperature on bacterial activity:</i> No data
<i>Effect of temperature on solubility and reactivity of acid buffering minerals:</i> No data	<i>Effect of temperature on solubility and reactivity of acid buffering minerals:</i> No data
<i>Effect of temperature on solubility of secondary minerals:</i> No data	<i>Effect of temperature on solubility of secondary minerals:</i> No data
Solute freeze-concentration effects: No data	Solute freeze-concentration effects: No data
<i>Effect of freeze-thaw processes on mineral exposure:</i> No data	<i>Effect of freeze-thaw processes on mineral exposure:</i> No data
Solubility of oxygen in water covers: No data	Solubility of oxygen in water covers: No data
<i>Ice barrier effects on oxygen and water movement</i> No data	<i>Ice barrier effects on oxygen and water movement</i> No data

OTHER

INFORMATION	N SOURCES
References	Supporting documents for the Pogo Project Environmental Impact Statement can be found at: http://www.dnr.state.ak.us/mlw/mining/largemine/pogo/index.htm
Permissions for Unpublished Data	Not applicable.
Case Study Prepared by:	Stephen Day



Figure 1. pH Trend for Waste Rock Humidity Cells



Figure 2. Sulphate Trend for Waste Rock Humidity Cells



Figure 3. Arsenic Trend for Waste Rock Humidity Cells

Appendix A - Case Histories



Figure 4. Arsenic trend for flotation tailings columns.

RANKIN INLET

Description	480 km north of Churchill
Latitude	63°6'(N)
Elevation	0 to 28 masl
CLIMATIC REG	IME
Precipitation	Total= 297 mm, with 40% as snow
Temperature	Average annual temperature = -11° C,
Range	Range: -31.9° C (Jan) to 10.4° C (July)
Permafrost Zone	Continuous permafrost zone with a mean annual ground temperature of -7 to -8° C. An average active layer thickness of 1.5m in till and gravel.
MINING	
Status	Closed
Mine Life	5 Years (1957-1962)
Mining Method	No data
Waste Rock Management	No data
Ore Processing and Tailings Disposal	Approximately 297,000 tonnes of tailings were produced during operations. Tailings had been disposed of on land in three 'ponds' and scattered on the surface. Tailings above high tide were dried and scattered on the ice, tundra and sea by wind action. Reclamation activities (1992-1994) involved relocation of tailings to an abandoned
	open pit and ponds with placement of a 1m cover of gravel intended to host the active layer and encourage permafrost development in the tailings.
GEOLOGY	
Summary Geological Description	The deposit is an Archean Ni-Cu-plantinum group elements (PGE) bearing sulphide mineralization. Host rocks consist of serpentinized pyroxenite-peridotite sill.
Mineralogy	Tailings mineralogy reported to contain 5-20% by volume pyrrhotite $[Fe_7S_8]$, with minor pyrite $[FeS_2]$, chalcopyrite $[CuFeS_2]$ and pentlandite $[(Fe,Ni)_9S_8]$. Secondary iron hydroxides [e.g. Fe(OH) ₃] rimmed pyrrhotite grains.
Surficial Geology	No data
GEOCHEMISTR	Y
Geochemical Overview	The tailings storage ponds had measured concentrations of Ni between 170 and 2500 ppb. Sulphidic, metal rich water had discharged from the tailings into Hudson Bay during annual thaws for a period of 30 years.
	Inundation of the tailings periodically by tides had led to saline pore waters and storage pond water (up to 52 ppt).

RANKIN INLET

Low	Effect of temperatures on oxidation rates:										
Temperature	Lab experiments run on various columns from temperatures of 30° C to -10° C										
Geochemical	reported O_2 fluxes below detection at -10° C, reduced but measurable O_2 uptake was										
Aspects	seen at $-2 \cup$ (see 1 able 2 from Meldrum <i>et al.</i> , 2001).										
	Effect of temperature on bacterial activity:										
	No data										
	Effect of temperature on solubility and reactivity of acid buffering minerals:										
	No data										
	Effect of temperature on solubility of secondary minerals:										
	Secondary mineral formation during lab experiments was identified as halite [NaCl],										
	epsomite [MgSO ₄ ·7H ₂ 0], birnessite [Na ₄ Mn ₁₄ O ₂₇ ·9H ₂ O] and suspected amorphous										
	experiments included mineral dissolution and on-going sulphide oxidation with										
	incremental freezing and solute exclusion to the surface of the columns.										
	incremental freezing and solute exclusion to the surface of the columnis.										
	Solute freeze-concentration effects:										
	contents in lab experiments suggested that the strongest pore water concentrations										
	resulted in the greatest degree of unfrozen water at -10° C. The high salinity of pore										
	waters (and entrapped seawater) depressed the freezing point, however reportedly had										
	little effect on the O_2 uptake rates (see Table 2 from Meldrum <i>et al.</i> , 2001).										
	Effect of freeze-thaw processes on mineral exposure:										
	No data										
	Solubility of oxygen in water covers:										
	No data										
	Ice barrier effects on oxygen and water movement										
	Field measurements and observations when drilling through reclaimed tailings										
	suggested pronounced ice bonding appears to begin at about –4°C. Unfrozen water										
	nowever was present in lab experiments down to measured temperatures of -10° C (see Table 3 from Moldrum et al. 2001) although unfrozon volumetric water content										
	decreased in all columns with each successive decrease in temperature										
	decreases in an estamnis with each successive decrease in temperature.										
OTHER											

INFORMATION SOURCES									
References	Meldrum, J.L., Jamieson, H.E. and Dyke, L.D. (2001). Oxidation of mine tailings from Rankin Inlet, Nunavut, at subzero temperatures. Canadian Geotechnical Journal, vol. 38, pp.957-966.								
Permissions for Unpublished Data	Not applicable								

RANKIN INLET

Case Study	Shannon Shaw
Prepared by:	

TABLES (from Meldrum et al., 2001)

Table 2. Average oxygen flux ($\pm 5 \mod O_2/(m^2 \cdot year)$) over the duration of the experiment in each material at each ambient temperature tested.

		Temperature (°C)								
Material	Pore fluid	+30	0	-2	-10					
Silty sand	Seawater	14	2	0	0					
Intact tailings	In situ pore water	148	19	7	0					
Cuttings	Seawater	68	3	0.5	0					
Cuttings	Distilled water	89	2	0	0					

 Table 3. Average unfrozen volumetric water content in each material tested at each ambient temperature.

		Temp	erature	(°C)	
Material	Pore fluid	+30	0	-2	-10
Silty sand	Seawater	23	16	11	1
Intact tailings	In situ pore water	32	20	15	9
Cuttings	Seawater	24	18	14	5
Cuttings	Distilled water	21	16	13	4

LOCATION

Description	Approximately 145 km north of Kotzebue, Alaska, USA
Latitude	68°1'(N)
Elevation	No data
CLIMATIC RE	GIME
Precipitation	255 to 330 mm total annual precipitation
Temperature	Mean annual temperature: -6°C
Range	Range: $-29^{\circ}C - 15.5^{\circ}C$
Permafrost Zone	Continuous
MINING	
Status	Operating
Mine Life	16 years to date (1989 to present)
Mining Method	Open Pit
Waste Rock Management	Waste rock is disposed in conventional waste rock dumps.
Ore Processing and Tailings Disposal	Ore is processed by conventional flotation technology resulting in a lead and zinc concentrates. Tailings are stored in a flooded impoundment.
GEOLOGY	
Summary Geological Description	The deposit is a Mississippian to Pennsylvanian-age black shale-hosted zinc-lead-silver deposit. The mineralization is contained in the Ikalukrok Member of the Kuna Formation. This member is underlain by the Kivalina Member. The Kuna Formation is overlain by chert and shale of the Lower Triassic to Pennsylvanian Siksikpuk Formation. The mineralization in the Ikalukrok Shales is stratabound and consists of accumulations of silica, barite and sulfides. The silica rock consists of translucent quartz grains with accessory sulfides, and occurs within and peripheral to the main mass of sulfides. The baritic facies contains accessory sulfides, silica, and rare calcite and is concentrated toward the top and periphery of the deposit.
Mineralogy	The sulfide facies is composed, in decreasing order of abundance, of sphalerite, pyrite, marcasite and galena. Chalcopyrite and pyrrhotite are minor constituents. The natural reactivity of the deposit resulted in oxidation of primary sulfide minerals to sulfates to a depth of 100 feet and deeper in the vicinity of thrust faults. At least 50 secondary sulfate minerals have been identified. These include relatively common minerals such as jarosite, siderotil, melanterite, and anglesite. Native sulfur is also present.

Surficial	Valley fill fluvial deposits.										
Geology											
GEOCHEMIST	ΓRΥ										
Geochemical Overview	Rock at Red Dog Mine is characterized by complex sulphur chemistry including iron sulphides (mainly pyrite), other sulphides (galena and sphalerite), soluble acid sulphates (jarosite), soluble base metal sulphates (eg zinc sulphate) and other sulphates (barite, anglesite). Carbonate content varies widely (including some limestones) but is negligible in most rock types.										
	The majority of rock types and all tailings are potentially acid generating. Rock types with low potential for acid generation due to the presence of carbonates may contain elevated zinc concentrations resulting in zinc and cadmium leaching at neutral pH.										
	Kinetic testing on waste rock and tailings indicates that potentially acid generating materials oxidize rapidly resulting in low pHs. Galvanic effects are apparent. Sphalerite oxidizes first, followed by pyrite.										
Low Temperature Geochemical Aspects	<i>Effect of temperatures on oxidation rates:</i> Of an original total of ten rock humidity cells started at room temperature, five cells were subsequently switched to refrigerated conditions after 41 weeks of testing. A tailings sample was tested in parallel room temperature and refrigerated humidity cells, and in subaqueous columns operated under both conditions.										
	The rock samples tested covered a wide range of characteristics (Table 1), including a sample with low sulphur and negligible potential for acid generation, samples with elevated acid potential and neutralization potential, and a sample of massive pyrite. Pyrite was the dominant sulphide in all but one sample. Pyrite content was estimated by speciating sulphur amongst barite, galena, sphalerite and sulphate as shown in Table 1.										
	Comparison of average rates before and after the transfer to refrigerated conditions is shown in Table 2. Before refrigeration, three of the tests were leaching at pH neutral or alkaline conditions, one was weakly acidic, and one was strongly acidic. The low sulphur sample (HC1) showed no effect on the low sulphate release rates by refrigerated and pH was unaffected. The lack of a significant difference may be a result of the low sulphate release rates.										
	HC 3 (barite and pyrite) showed a factor of two decrease in sulphate release and pH also increased by one unit (from 5 to 6). Sulphate release was predicted to be due to the pyrite oxidation. The reduction in sulphate release is lower than would be expected for the temperature shift and increase in pH. Zinc release decreased by a factor of 5. This decrease cannot be interpreted in the context of sphalerite oxidation due to the change in pH.										
	HC 4 and 5 were oxidizing under non-acidic conditions and comparable effects due to refrigeration. The decrease in sulphate release was comparable (2.5 to 2.7) and is consistent with expected effect of temperature. Leachate pH did not change substantially. Zinc leaching increased by a factor 1.9 and 1.7 respectively. Cell 4 continued for three more years after the test was transferred to the refrigerator and the increase in zinc leaching rate was confirmed. Cell 5 was stopped shortly after being transferred to the refrigerator. This increase perhaps suggests that sphalerite oxidation rates are greater under colder conditions, but it may also reflect accelerated leaching of										

carbonate minerals that occurs at lower temperatures. Calcium concentrations did not indicate the same effect because they were on a decreasing trend when the cells were transferred to the refrigerator.
HC 8 was oxidizing very rapidly (3.2 g/kg/week) at pH 1.8 when it was transferred to the refrigerator. The oxidation rate decreased by a factor of 9 and pH increased to 2.4. Zinc released decreased by a factor of 6. The significant decreased in oxidation rates is not consistent with expected decrease. A possible factor in this was that the rapid oxidation rate was generating sufficient heat to significantly raise internal temperatures.
The tailings humidity cells showed significant temperature effects. Over the first year, the room temperature test showed decreasing pH to near 2 whereas the refrigerated tests remained above pH 3 but with a steady decline over time. This translated to a significant difference in sulphate release (570 and 65 mg/kg/week, room and fridge respectively). Based on elevated zinc release, sulphate primarily reflects oxidation of sphalerite. The difference in oxidation rates may reflect the oxidation by oxygen under refrigerated conditions (higher pH) and oxidation by ferric iron at room temperature. The rate difference therefore may be due to several different factors. An interesting effect was that lead release was greater for the refrigerated test because sulphate concentrations were lower. This is due to the lead sulphate control on leaching.
Overall, the tailings humidity cells showed that sulphides were depleted very rapidly under room temperature conditions. Refrigerated conditions delayed this process but eventually showed comparable metal release rates to the room temperature test.
The subaqueous tailings column tests (Figures 1, 2, and 3) showed strong acidification of both the overlying water (eventual pH 3.5) and column leachate (eventual pH of 3.5) at room temperature. Stable conditions after three years of testing indicated similar pH. The refrigerated test showed moderate acidification of surface water (pH 4.5) and no acidification of leachate (pH>6). The effect of reduced metal release to the water cover and leachate under refrigerated conditions was substantial.
<i>Effect of temperature on bacterial activity:</i> No data
<i>Effect of temperature on solubility and reactivity of acid buffering minerals:</i> No data
<i>Effect of temperature on solubility of secondary minerals:</i> No data
Solute freeze-concentration effects: No data
<i>Effect of freeze-thaw processes on mineral exposure:</i> No data
Solubility of oxygen in water covers: No data
<i>Ice barrier effects on oxygen and water movement</i> No data

OTHER	
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	Day, S., Coulter, G. and Falutsu, M. 2000. Red Dog Pb-Zn Mine Closure Planning: Phase 1 Geochemical Studies – Characterization of Complex Sulfur Mineralogy. Proceedings of the 5th International Conference on Acid Rock Drainage. Denver.
Permissions	Not applicable
for	
Unpublished	
Data	
Case Study Prepared by:	Stephen Day

Table 1. Characteristics of Samples Tested in Humidity Cells.

				Analysis								S-Forms ⁵					Acid-Base Account																																																							
Cell#	Duration ^{2,9}	Sample Name	Rock Type	Paste	TIC	$\rm CO_2 NP^3$	Pb	Zn	Ba	Cu	Sulphur S,%		BaSO4	ZnS	PbS-SO4	SO4	FeS	AP^6	NP	NNP	NP/AP																																																			
	(weeks)			pH	ppm	(kg/t)	%	%	%	%	Total	WA ⁴	Sulphide	S,%	S,%	S,%	S,%	S,%	(kg/t)	(kg/t)	(kg/t)																																																			
HC-1	47	1225KS/KSS	Okpikruak	8.4	7090	59	0.003	0.03	0.77	0.006	0.14	0.01	0.13	0.18	0.01	0.00	0.01	-0.06	0.31	55	54	174.400																																																		
			Shale/Sandstone																																																																					
HC-3	47	900LB	Ikalukrok Barite	8.1	0	0	0.02	0.04	30.50	0.001	10.80	0.01	10.79	7.11	0.02	0.00	0.01	3.66	114	3	-111	0.027																																																		
HC-4	201	950EP MLS	Ikalukrok Shale	6.8	17260	144	0.17	0.72	0.01	0.006	2.68	0.05	2.63	0.00	0.35	0.03	0.05	2.25	70	91	21	1.292																																																		
HC-5	47	MIK975	Kivalina Shale	7.9	22910	191	0.01	0.00	1.15	0.003	3.75	0.01	3.74	0.27	0.00	0.00	0.01	3.47	108	166	57	1.528																																																		
HC-8	47	1025MP	Massive Pyrite	5.1	446	4	1.69	4.88	2.74	0.022	39.24	0.14	39.10	0.64	2.39	0.26	0.14	35.82	1119	0	-1119	0.000																																																		
Tailings-AMB	170	Tailings	Tailings	6.5	450	4	1.580	3.200	3.060	0.016	10.30	0.11	10.19	0.71	1.57	0.24	0.11	7.67	240	1	-238	0.005																																																		

Table 2. Effect of Temperature Reduction

Cell/Parameter	1	3	4	5	8	
Sulphate (mg/kg/week)						
R(Room T)	1.775	2.95	63.10	303.32	3249.60	
R(Fridge))	1.485	1.485	23.1675	120.285	347	
Ratio (Room/Fridge)	1.20	1.99	2.72	2.52	9.36	
Zn (mg/kg/week)	Zn (mg/kg/week)					
R(Room T)	0.005	0.55	0.06	0.05	131.34	
R(Fridge))	0.00495	0.1089	0.1107	0.09405	22.43	
Ratio (Room/Fridge)	0.98	5.07	0.52	0.58	5.86	
pH						
pH(Room T)	8.086	4.976	7.862	7.736	1.76	
pH(Fridge))	8.11	6.034	7.666	7.768	2.36	
pH	-0.024	-1.058	0.196	-0.032	-0.6	



Figure 1. pH in Subaqueous Column Leachates



Figure 2. Sulphate Concentrations in Subaqueous Column Leachates



Figure 3. Zinc concentrations in subaqueous column leachates.

STEKENJOKK MINE

Description	Northern Sweden, close to the Norwegian border in Vasterbotten county.					
Latitude	No data					
Elevation	800 m above sea level.					
CLIMATIC REG	IME					
Precipitation	Total = 1100 mm					
	Proportion as snow N/A					
Temperature	Average annual = 0° C					
Range	Monthly average range = N/A					
Permafrost Zone	No data					
MINING						
Status	Closed					
Mine Life	~ 12 years (1976 to 1988)					
Mining Method	Underground cut and fill with a small open pit					
Waste Rock	Disposed of in rock dumps.					
Management						
Ore Processing	Cu-Zn mine produced approximately 4.4 million tonnes of sulphide-rich tailings. The					
and Tailings	tailings were flooded in 1991.					
Disposal						
GEOLOGY						
Summary	The deposit is a stratabound volcanogenic Zn-Cu deposit.					
Geological						
Description						
Mineralogy	The main ore associated minerals referenced included the sulphides pyrite [FeS ₂],					
	sphalerite [ZnS], chalcopyrite [CuFeS ₂], galena [PbS], pyrrhotite [Fe _{1-x} S], covellite					
	[CuS] and minor arsenopyrite [FeAsS]. Other minerals included quartz [SiO ₂],					
	feldspars [(Ca,Na,K)(Al,Si) ₄ O ₈], sericite [KAl ₂ (Si ₃ Al)O ₁₀ (OH,F) ₂], chlorite					
	$[(Mg,Fe)_5AI(S1_3AI)_4O_{10}(OH)_8]$ and carbonates $[(Ca, Mg, Fe)CO_3]$.					
	Mineralogy of the tailings consisted of quartz $[SiO_2]$, plagioclase					
	$[(Na,Ca)Al(Si,Al)Si_2O_6]$, calcite $[CaCO_3]$, biotite $[K_2Mg_6(Si_6Al_2O_{20})(OH,F)_2]$, chlorite					
	$[(Mg,Fe)_5Al(Si_3Al)_4O_{10}(OH)_8]$, muscovite $[KAl_2(Si_3Al)O_{10}(OH,F)_2]$, sulphides					
	(predominantly pyrite $[FeS_2]$ with lesser pyrrhotite $[Fe_{1-x}S]$), amphiboles, epidote					
	$[CA_2(Fe^{3+},Al)_3(SiO_4)_3(OH)]$, gypsum $[CaSO_4^2H_2O]$ and zircon $[ZrSiO_4]$.					
Surficial	No data					
Geology						

STEKENJOKK MINE

GEOCHEMISTR	Y				
Geochemical Overview	The geochemistry of the tailings was reported to be relatively homogenous across the deposit with 19.6% Fe, 4.1% Ca, 2.8% Mg and 17.8% S and elevated levels of As (1139 ppm), Cu (2266 ppm), Pb (1458 ppm) and Zn (6829) with trace Cd, Co and Ni (ranging from 24 to 61 ppm). The pH of the water cover is circum-neutral ranging from 7.01-7.75 with lower values during the winter and a trend in decreasing values with depth under the ice.				
Low Temperature Coochemical	<i>Effect of temperatures on oxidation rates:</i> No data				
Aspects	<i>Effect of temperature on bacterial activity:</i> No data				
	<i>Effect of temperature on solubility and reactivity of acid buffering minerals:</i> No data				
	<i>Effect of temperature on solubility of secondary minerals:</i> No data				
	Solute freeze-concentration effects: No data				
	<i>Effect of freeze-thaw processes on mineral exposure:</i> No data				
	Solubility of oxygen in water covers: The water cover over the sulphidic mine tailings varies from 0.6m to 9m in depth with an average of 2m.				
	Below the ice in the winter, a redox gradient is established with anoxic or at least O ₂ - poor bottom waters. Winter concentrations of dissolved oxygen at a depth of 5m were reported to be ~ 9 mg/L compared to concentrations between 10 and 11 mg/L in the summer. Other seasonal variations with respect to dissolved elemental concentrations include Si and Al concentrations that are higher in the summer and autumn originating from the weathering of silicate minerals on surrounding slopes (and therefore in run-on). Other parameters including Ca, Mg, Na, S, As, Ba, Cd, Cu, Hg, Ni, Pb, Sr and Zn are higher during the winter due to the ice cover isolation of the pond water and diffusion from the tailings.				
	Hypotheses for these trends include the migration of elements from deeper pore waters into the water cover and/or establishment of redox conditions under ice and dissolution of Fe- and Mn-oxyhydroxides and decomposition of organic matter in the upper portion of the tailings. High concentrations of suspended Fe and Mn in the winter correspond to the depths at which higher concentrations of dissolved metals are seen supporting the hypothesis of oxyhydroxide dissolution and release of sorbed metals.				
	<i>Ice barrier effects on oxygen and water movement</i> No data				

STEKENJOKK MINE

OTHER	
INFORMATION	SOURCES
References	Holmstrom, H., Ljungberg, J., Ohlander, B. (2000). <i>The character of suspended and dissolved phases in the water cover of the flooded mine tailings at Stekenjokk, northern Sweden</i> . The Science of the Total Environment, vol. 247 (2000), p. 15-31.
Permissions for Unpublished Data	Not applicable
Case Study Prepared by:	Shannon Shaw

URAD MINE

LOCATION				
Description	Near Berthoud Pass in Colorado			
Latitude	~39°N			
Elevation	~3200 m (10,500 ft)			
CLIMATIC REG	IME			
Precipitation	Mean annual precipitation varies from 635 to 1015 mm (25 to 40 inches) per year, mostly as snowfall.			
Temperature Range	Average annual, monthly average range			
Permafrost Zone	Discontinuous			
MINING	-			
Status	Closed			
Mine Life	Approximately 7 years (1967 to 1974)			
Mining Method	Block caving			
Waste Rock Management	No data			
Ore Processing and Tailings	Approximately 14 million tons of ore containing less than 5% pyrite was crushed and processed by flotation.			
Disposal	Tailings were deposited by slurry in one of two impoundments. On closure, both tailings impoundments were covered with a 3 to 10 foot thick cover (rock, sewage sludge and wood chips) that was amended and revegetated. Tailings dams were constructed in the valley using upstream construction.			
	The tailings were reported to be silty clay to silty sand with a hydraulic conductivity ranging from $2x10^{-7}$ to $1x10^{-4}$ cm/s.			
GEOLOGY				
Summary Geological Description	The deposit was a low-grade molybdenum porphyry hosted in granite.			
Mineralogy	Molybdenite $[MoS_2]$ and pyrite $[FeS_2]$ were the only reported sulphides. Other gangue minerals not reported, although granite hosted.			
Surficial Geology	An underlying alluvium in the valley bottom was reported with a hydraulic conductivity ranging from 10^{-6} to 10^{-3} cm/s.			

GEOCHEMISTRY

Geochemical	Tailings within the vadose zone had oxidized. Pore water concentrations in the					
Overview	vadose zone reported to be pH 3.5, 30 to 400 ppm Fe, 440 to 490 ppm Mn and 2400					
	ppm SO ₄ .					

URAD MINE

Low Temperature Geochemical Aspects	<i>Effect of temperatures on oxidation rates:</i> Tailings beneath the frozen layers within the tailings facility appeared to be less oxidized and had pore water chemistry more indicative of process water. The paper hypothesized that the frozen layers played a role in the minimization of oxidation of provide tailings happened to be less.
	Effect of temperature on bacterial activity: No data
	<i>Effect of temperature on solubility and reactivity of acid buffering minerals:</i> No data
	<i>Effect of temperature on solubility of secondary minerals:</i> No data
	Solute freeze-concentration effects: No data
	<i>Effect of freeze-thaw processes on mineral exposure:</i> No data
	Solubility of oxygen in water covers: No data
	<i>Ice barrier effects on oxygen and water movement</i> The existence of ice layers within the tailings facility was hypothesized to have been formed during active tailings deposition and have remained to date, although likely diminishing with time. The presence of the ice layers has resulted in hydrologic zones within the impoundment. The zones consist of a perched water table on top of the frozen tailings layers, a longitudinal confined and unconfined flow (regional water table) beneath the frozen tailings layers, a deep regional water table and a vadose zone (see schematic in Figure 6 from Steffens et al., 1995). Each zone has a characteristic chemical signature that was used to assess the primary water sources and flow directions of the four zones. The chemistry of each zone is shown in Table I from Steffens et al., 1995). The conclusions included the assessment that the frozen layers within the impoundment acted as hydraulic barriers to vertical groundwater flow.
OTHER	

INFORMATION SOURCES

INFORMATION BOURCES				
References	 Steffens, S.D., Lewis-Russ, A., Jones, J. and Rech W. (1995). The effects of permafrost on the geochemistry and hydrology of a metal-sulfide tailings impoundment 20 years later. 1995 National Meeting of the American Society for Surface Mining Reclamation, Gillette, Wyoming, June 1995, pp. 547-559. Reclamation Success, Climax Molybdenum Company, URAD Mine http://www.mii.org/urad/climax.html 			
Permissions for Unpublished Data	Not applicable			

URAD MINE

Case Study	Shannon Shaw
Prepared by:	

FIGURES (from Steffens et al., 1995)



Figure 6. Isometric View of Groundwater Floy. Regimes

TABLES (from Steffens et al., 1995)

	Table I	
TYPICAL	CHARACTERISTICS OF TAILING PORE-WATER I	Ν
	HYDROLOGIC ZONES	
	(values in mg/l)	

Parameter	Ice	Perched Layer	Beneath Ice	Lateral Recharge ⁱ	Vadose Zone
pH	7.7	7.6	7.0	4.3	3.5
Iron	< 0.02	0.02-0.08	3.9	.6	30-400
Manganese	10	35	12	170	440-490
Spec. Cond.	2,200	1,800	1,600	2,350	3,300
Chloride	92	50-85	50	5	2-30
Sulfate	900	800	700	1,400	2,400

1. May include some effects of overlying vadose zone.

WINDY CRAGGY PROJECT

LOCATION

Description	Approximately 190 km southwest of Whitehorse, Yukon						
Latitude	59°44'(N) 137 44 W						
Elevation	No data						
CLIMATIC REG	IME						
Precipitation	Total, proportion as snow						
Temperature Range	Average annual, monthly average range						
Permafrost Zone	No data						
MINING							
Status	Proposed						
Mine Life	Not applicable						
Mining Method	Not applicable						
Waste Rock Management	Not applicable						
Ore Processing and Tailings Disposal	Not applicable						
GEOLOGY							
Summary Geological Description	Windy Craggy is a Beshi Type volcanogenic massive sulphide deposit containing primarily copper mineralization with zinc, gold, silver and cobalt deposit. The deposit is hosted by clastic sediments and mafic flows and sill. The ore body occurs at the transition between these rock types.						
Mineralogy	Massive sulphide mineralization occurs as (1) massive pyrrhotite with lesser chalcopyrite, (2) massive pyrite with lesser chalcopyrite; and (3) pyrrhotite and pyrite with lesser chalcopyrite and magnetite. A stockwork/feeder zone is present beneath the sulphide bodies. The stockwork is comprised of irregular sulphide veins within pervasively chlorite and silica altered wallrock. Sulphides within the stockwork zone consist predominantly of pyrrhotite with lesser chalcopyrite and, in places, pyrite. In general, the percentage of sulphides, and number and density of sulphide veins increases upward from the bottom or "root" to the top of the stockwork zone. Gangue minerals include quartz, carbonate, chlorite and albite. Other sulphide minerals include digenite and sphalerite with rare marcasite and arsenopyrite.						
Surficial Geology	No data						

WINDY CRAGGY PROJECT

GEOCHEMISTRY							
Geochemical Overview	Due to the nature of the mineralization and locally calcareous host rocks, rocks vary from potentially acid generating to not potentially acid generating						
Low Temperature Geochemical	<i>Effect of temperatures on oxidation rates:</i> Five samples were tested in paired humidity cells under room temperature and refrigerated conditions. One sample was also frozen at -20°C.						
Aspects	Table 2-1 (extracted from MEND report 1.61.2) shows the effect of temperature on four samples. The table indicates that sulphate release rates were always lower under low temperature conditions. The decrease in sulphate release was by a factor of 2.2 to 2.9 except in the case of BHC-16 (factor 6.6) that was more acidic under room temperature conditions. The onset to acidic conditions for this sample resulted in higher oxidation rates which are not comparable to the refrigerated test.						
	Copper release was unchanged or decreased slightly when refrigerated, except in the case of BHC-16 which showed a factor of 3 difference. The lack of change for samples at higher pHs reflects solubility controls on copper release rather than oxidation of chalcopyrite or other primary sources of copper.						
	Zinc showed higher release rates under non-acidic conditions.						
	Results for pH and sulphate for one sample of massive pyrrhotite tested at three temperatures are provided in Figures 1 and 2. The two unfrozen tests showed a decreasing pH trend with slightly higher pH in the refrigerated test. Eventually pH was the same for both tests. The frozen sample (which was thawed each week for leaching) also showed decreasing pH but at a higher level. The sulphate for both unfrozen samples was erratic but roughly similar. The average rate for room and fridge tests was 128 and 83 mg/kg respectively, representing a factor of 1.5. The frozen sample showed very low oxidation rates.						
	Metal concentrations were low in leachates from all tests (release rates less than 0.1 mg/kg/week), but the room temperature test released copper and zinc at higher rates than the refrigerated test.						
	Note that the results for the one sample tested using three different temperatures were incorrectly reported in MEND 1.61.2.						
	<i>Effect of temperature on bacterial activity:</i> No data						
	<i>Effect of temperature on solubility and reactivity of acid buffering minerals:</i> No data						
	<i>Effect of temperature on solubility of secondary minerals:</i> No data						
	Solute freeze-concentration effects: No data						

WINDY CRAGGY PROJECT

	<i>Effect of freeze-thaw processes on mineral exposure:</i> No data
	Solubility of oxygen in water covers: No data
	<i>Ice barrier effects on oxygen and water movement</i> No data
OTHER	

OTHER

INFORMATION SOURCES				
References	Dawson and Morin (1996) SRK Files.			
Permissions for Unpublished Data				
Case Study Prepared by:	Stephen Day			

Table 2-1 Statistical Summary of Reaction Rates from Humidity Cells Operated at +20°C and +6°C, Windy Craggy Project (Norecol, Dames and Moore, personal communication, 1995)

Sample	High/Low pH	Avg pH	SO4 Rate (mg/kg/wk)	Cu Rate (mg/kg/wk)	Zn Rate (mg/kg/wk)
BHC-15 +20°	7.7/5.4	7.0	27.4	1.52	5.15
BHC-15 +6°	7.9/6.5	7.4	9.44	1.46	8.76
BHC-16 +20°	7.8/2.9	4.4	289	4.78	8.58
BHC-16 +6°	7.7/5.4	6.6	44.4	1.56	11.9
BHC-17 +20°	8.9/7.3	7.8	46.1	2.07	5.11
BHC-17 +6°	9.3/7.2	8.1	17.6	1.45	10.8
BHC-20 +20°	7.9/6.9	7.4	24.2	1.55	3.44
BHC-20 +6°	8.0/7.0	7.6	11.0	1.55	4.91



Figure 1. Trends in pH for Three Humidity Cells.



Figure 2. Trends in Sulphate Release for Three Humidity Cells