

RS33/RS65

Draft-01

February 21, 2007

RS33/RS65 – Hydrometallurgical Residue Characterization and Water Quality Model – NorthMet Project - DRAFT

Report Prepared for
PolyMet Mining Corp.

Report Prepared by



February 2007

RS33/RS65

Draft-01

February 21, 2007

**RS33/RS65 – Hydrometallurgical
Residue Characterization and
Water Quality Model –
NorthMet Project - DRAFT**

PolyMet Mining Corp.

P.O. Box 475
County Road No. 666
Hoyt Lakes, MN 55750-0475
USA

SRK Consulting (Canada) Inc.
Suite 800, 1066 West Hastings Street
Vancouver, B.C. V6E 3X2

Tel: 604.681.4196 Fax: 604.687.5532
E-mail: vancouver@srk.com Web site: www.srk.com

SRK Project Number 1UP005.001

February 2007

Executive Summary

The processing and recovery of NorthMet Project ore to recover commodity metals will involve conventional flotation to produce a sulfide concentrate followed by hydrometallurgical treatment of the concentrate to recovery commodity metals. The hydrometallurgical process will produce five residues:

- Leach residue (silicates);
- Gypsum residue (calcium sulfate);
- Raffinate neutralization residue (calcium sulfate);
- Fe/Al residue (oxide); and
- Mg residue (oxide).

For final disposal, all residues will be mixed to create a single “combined residue” product which will be placed in lined disposal cells.

Samples of the residues were obtained by pilot testing and subjected to mineralogical and chemical tests to understand the composition and leaching characteristics of the residues. Except for the leach residue which is material remaining after initial leaching of the mineral concentrate, the residues are composed dominantly of calcium sulfate (mainly gypsum). The leach residue contains natrojarosite. The combined residue is also composed mainly of gypsum but natrojarosite will also be a component of this residue.

Except for the Mg residue, the individual residues were acidic to varying degrees. The combined residues were non-acidic in the time frame of the tests due to buffering minerals in the Mg residue but the presence of natrojarosite indicated that the combined residues could be acidic at some time in the future. To ensure that the combined residues do not become acidic resulting in accelerated leaching of metals held in the oxide components, additional base material (e.g. lime or limestone) will be added to offset the acid potential of the natrojarosite.

Results of the EPA1311 test shows that the residues are not classified as hazardous.

A variety of leaching tests have shown that leachate chemistry reached chemical equilibrium with the solids, and that the initial leach produced the highest concentrations of most parameters. The initial contact solution chemistry from the combined residues was used to indicate the chemistry of pore water in the hydrometallurgical residue disposal cells both during operation and at closure.

Table of Contents

Executive Summary	i
1 Introduction	1
1.1 Background	1
1.2 Objective	1
1.3 Design and Consultation Process	1
1.4 Structure of Report.....	2
2 Water Chemistry Prediction Methods	3
2.1 Theoretical Method	3
2.2 Analog and Empirical Methods	3
2.2.1 Analog	3
2.2.2 Empirical.....	3
2.3 Method Selected	4
3 Program Design	5
3.1 Process Background	5
3.2 Geochemical Background	5
3.3 Data Requirements	6
3.4 Overall Program Design.....	6
4 Sampling and Analytical Methods	7
4.1 Metallurgical Program	7
4.1.1 Ore Composite Preparation.....	7
4.1.2 Generation of Residue Samples	7
4.2 Dissolution Testwork	8
4.2.1 Mineralogy	8
4.2.2 Analytical Methods	8
4.2.3 Quality Assurance/Quality Control	10
4.2.4 Interpretation Methods	11
5 Results	12
5.1 Solids Characteristics.....	12
5.2 Description of Leachate Chemistry	17
5.2.1 EPA 1311	17
5.2.2 EPA 1312	17
5.2.3 Price (1997) Method.....	17
5.3 Description of Kinetic Test Leachate Chemistry	18
5.3.1 Sequential Shake Flasks.....	18
5.3.2 Humidity Cells	19
5.3.3 MDNR Reactors	20
6 Interpretation of Dissolution Testwork	22
6.1 General Interpretation of Leachate Chemistry	22
6.1.1 Saturation Indices.....	22
6.1.2 pH Control on Metal Concentrations	24
6.2 Trend Evaluation	26
6.2.1 Trends in Leachate Chemistry Shown by Testwork.....	26
6.2.2 Trends Beyond Testwork Time Frame.....	28
6.3 Comparison of Results with Other Testwork Programs	28

6.4	Effect of Process Variations	29
6.5	Conclusions.....	29
7	Pore Water Chemistry Prediction	30
7.1	Operational Model.....	30
7.1.1	Explanation of Modeling Approach	30
7.1.2	Inputs to Water Quality Model.....	30
7.1.3	Results.....	30
7.1.4	Conclusions.....	30
7.2	Closure and Post-Closure Model	30
8	Conclusions	31
9	References.....	32

List of Tables

Table 4-1: Proportions (by Wet Weight) for Combined Residues	7
Table 5-1: Mineralogy of Residues	13
Table 5-2: Elemental Composition of Residues.....	14
Table 5-3: Acid-Base Accounting Results.....	15
Table 6-1: Saturation Indices for Humidity Cell Leachates	23
Table 6-2: Summary of Maximum Concentrations Observed in Humidity Cell Leachates	26

List of Appendices

Appendix A: Flotation Tailings and Hydrometallurgical Residue Geochemical Characterization Plan	
Appendix B: Leachate Extraction Test Results	
Appendix C: Leachate Chemistry Graphs	
Appendix C.1: Sequential Shake Flask	
Appendix C.2: Humidity Cell	
Appendix C.3: DNR Reactor	
Appendix D: Scatter Plots Showing Metal Concentrations Compared to pH	

Report CD: Leachate Chemistry Results

1 Introduction

1.1 Background

PolyMet Mining Inc. (PolyMet) is proposing to develop the NorthMet Project (Dunka Road Project of US Steel) near Babbitt, Minnesota. As a part of the Minnesota Department of Natural Resources (MDNR) “Permit to Mine” process a complete “mine waste characterization” is required (Minnesota Rules Chapter 6132.1000).

The processing and recovery of NorthMet Project ore to recover commodity metals will involve conventional flotation to produce a sulfide concentrate followed by hydrometallurgical treatment of the concentrate to recovery commodity metals.

The residues from hydrometallurgical treatment will be disposed as a single combined residue. As there are indications (but no certainty) that a market can be found for the gypsum residue, this report focuses on the disposal of combination of all residues with gypsum residue as described in the Detailed Project Description (PolyMet 2007) but with reference to testwork results for combined residue without gypsum.

All residues will be disposed in lined cells. Design concepts for the cells are provided in RS28T (Barr 2007).

1.2 Objective

The objectives of the characterization studies were to evaluate the mineralogical and chemical properties of the residues and predict the chemistry of pore waters in the residues. This information is an input into the prediction of overall water quality at the hydrometallurgical residue disposal cells.

1.3 Design and Consultation Process

The characterization plan for the residues was developed in consultation with the MDNR (SRK 2005) (Appendix A). The plan covers characterization of both tailings from the flotation process and the hydrometallurgical residues from recovery of commodity metals. Characterization of the hydrometallurgical residues was started in February 2006 following generation of the residues from pilot plant testing between August 29 and October 11, 2005 and agreement on the characterization methodologies with MDNR.

1.4 Structure of Report

This report combines results of two studies. RS33 provides results of characterization of the hydrometallurgical residues whereas RS65 is the prediction of pore water chemistry.

The structure of the RS65 report, which was a combination of RS33 and RS65 was agreed with the MDNR. The final version of the report outline was transmitted to the MDNR on April 26, 2006. The agreed outline has been followed. If any sections are redundant, the section heading is shown with a brief note to explain why the section is no longer relevant.

2 Water Chemistry Prediction Methods

2.1 Theoretical Method

The theoretical method considers the rate at which components of the residues might dissolve and their final solubility. This approach is potentially applicable to the hydrometallurgical residues because they are composed primarily of discrete fully oxidized mineral phases. Solution chemistry in the pores is expected to be controlled mainly by dissolution of these phases possibly with formation of new minerals. Oxidation reactions are not expected to be significant because the residues are the product of a strongly oxidizing process.

Numerous computer modeling programs are available to predict solubility of minerals including MINTEQA2 (e.g. Allison et al 1991) and PHREEQC (Parkhurst and Appelo 1999). Other programs couple solubility, reaction paths and reaction rates (e.g. React Bethke 2005). The main limitations of these programs are thermodynamic databases and the rate expressions for mineral reactivity. For common minerals, solubility constants are well-established but for trace elements, the solubility of co-precipitated phases are site-specific and not provided in the database, which limits the value of the theoretical method as a standalone approach. However, it can be combined with the empirical approach, as described below.

2.2 Analog and Empirical Methods

2.2.1 Analog

The analog method involves direct prediction of the dissolution of residues by comparison with similar hydrometallurgical processes involving pressure oxidation of copper sulfide concentrates. Similar processes include the CESL Copper Process (TeckCominco, Undated) which involves moderate pressure oxidation of copper concentrates using chloride as a catalyst and production of residues containing leach residue, iron oxide, elemental sulfur and gypsum, and Outokumpu's HydroCopper™ process (Outokumpu 2006) which also produces iron oxide and elemental sulfur but no gypsum. These are comparable to the NorthMet process, which will result in production of jarosite as a product of sulfide oxidation and gypsum due to acid neutralization. The differences in the processes obviously limit the direct comparison of the performance of residues.

2.2.2 Empirical

The empirical method involves the use of testwork to simulate the leaching behavior of residues. The limitation of this approach is usually that the ratio of leachate to solid in testwork is often much higher than under field conditions due to the practical need to produce enough water for analysis. The results can be scaled up to field conditions by assuming that the concentration will increase in proportion to the decrease in liquid to solid ratio. Such scale-up calculations can produce very high concentrations that are not realistic.

2.3 Method Selected

The selected method is primarily empirical (i.e. based on testwork) but with evaluation of data using thermodynamic considerations, if practical, to place constraints on concentrations indicated by scale-up of laboratory results. The steps used to generate water quality predictions are therefore:

- Evaluation of overall leachate chemistry using the SpecE8 module of the Geochemist's Workbench (Bethke 2005) to determine if major elements are near chemical saturation.
- Comparison of trace metal concentrations with pH to determine if concentrations are constrained by pH.
- Scale-up of metal concentrations to reflect under-saturation indicated by SpecE8 and the pH relationships.
- Development of final predictions for pore water chemistry.

3 Program Design

3.1 Process Background

Hydrometallurgical processing will result in production of the following residues composed dominantly of the indicated minerals or mineral groups:

- Leach residue (silicates);
- Gypsum residue (calcium sulfate);
- Raffinate neutralization residue (calcium sulfate);
- Fe/Al (Iron/Aluminum) residue (oxide); and
- Mg residue (oxide).

The process flow sheets are provided in Appendix A. The pilot plant run that generated the residues for testing had a separate Fe/Al Removal Stage. Subsequent refinement of the flowsheet has combined this stage with Raffinate Neutralization which means that the raffinate neutralization residue and the Fe/Al residue will be combined in the full scale plant and are generally referred to singularly as raffinate neutralization residue.

3.2 Geochemical Background

The residues are mainly chemical products in which the original concentrate components are oxidized to sulfates and hydroxides, and dissolved.

- Sulfur from the sulfide minerals is oxidized to jarosite and soluble sulfate. The latter is precipitated as calcium sulfate through the neutralization process;
- Iron released from sulfide and silicate minerals is precipitated as hydroxide; and
- Magnesium and aluminum released from silicate minerals are precipitated as hydroxides.

Copper is recovered in the process by electro-winning to produce copper anodes. Nickel, cobalt and zinc are recovered as a mixed hydroxide product. Platinum group metals and gold are recovered as concentrate product.

Incomplete dissolution of the silicate and sulfide minerals results in the generation of a fourth residue; a mineralogical leach residue.

Because these products represent near-complete dissolution, oxidation and neutralization of the concentrate, the chemistry of contact waters is expected to be controlled mainly by the simple

dissolution of the compounds. Oxidation of residual sulfide minerals may occur from the leach residue but this effect is expected to be minor.

Overall, the process of dissolution of neutralization products is unrelated to the composition of the ore and is not expected to vary in the long term except by depletion.

3.3 Data Requirements

The primary requirements for the test program were therefore:

- Mineralogical characterization of residues to provide a basis for understanding the dissolution of the residues; and
- Dissolution tests to investigate the solubility of the minerals.

3.4 Overall Program Design

The overall program design included the following components:

- Production of individual and combined residues using a pilot plant (see RS32 Part III, Barr 2006).
- Mineralogical characterization of residues.
- Determination of solids elemental characteristics.
- Performance of various types of leaching experiments at different solid to liquid ratios to determine the dissolution behavior of the residues.

4 Sampling and Analytical Methods

4.1 Metallurgical Program

4.1.1 Ore Composite Preparation

Preparation of the ore composite is described in ER03 (PolyMet, in preparation).

4.1.2 Generation of Residue Samples

Sulfide concentrates were prepared by a pilot flotation plant in which the copper sulfate was evaluated as a reagent to improve flotation of sulfide minerals. Two concentrates were prepared in the pilot plant. One concentrate was prepared with the use of copper sulfate, and a second was prepared without the use of copper sulfate. Both residues were subsequently leached in the hydrometallurgical process. PolyMet has since decided that copper sulfate will be used. Therefore, it was agreed (in consultation with MDNR, SRK 2005) that characterization testwork would be performed on the residues generated by leaching of the concentrate that was produced with copper sulfate. The exception is the leach residue for which both residue samples are being tested.

Residues generated during the pilot plant run at SGS Lakefield were collected under supervision of Barr Engineering and shipped to Canadian Environmental and Metallurgical Inc (CEMI) in Burnaby, British Columbia, Canada for testing. SRK Consulting is responsible for supervision of the testwork described in this report.

Testing is proceeding on individual samples of each type of residue and combined residues. Residue combinations are being tested with and without the gypsum residue to allow for the option of recovery of a separate gypsum product. The proportions by wet weight of each residue in the combined samples are provided in Table 4-1. The combined residue containing all residues was received directly from the pilot plant (SGS Lakefield). The combined residue without gypsum was prepared from the component residues using the same weight proportions less the gypsum amount.

Table 4-1: Proportions (by Wet Weight) for Combined Residues

Residue	Actual Pilot Plant Observation		Projected for Commercial Scale
	All	Without Gypsum	All
Leach Residue	27%	45%	41%
Gypsum Residue	40%	0%	33%
Raffinate Residue	18%	31%	20%
Fe/Al Residue	6%	10%	NA, combined w/Raffinate
Mg Residue	8%	14%	6%

Subsequent optimization and modeling (MetSim Version U3) of the hydrometallurgical process by Bateman indicated that the proportion of the residues will be somewhat different under full scale production (see Table 4-1). Specifically, the pilot plant run that generated the residues for testing had a separate Fe/Al Removal Stage. The commercial scale flowsheet has combined this stage with Raffinate Neutralization which means that the raffinate neutralization residue and the Fe/Al residue will be combined in the full scale plant. This difference will affect the overall mineralogical make-up of the residues but will not affect overall leaching performance. Further discussion is provided in Section 6.4.

4.2 Dissolution Testwork

4.2.1 Mineralogy

Mineralogical characterization included:

- Optical Analysis on feed, product and mineral wastes (Leach Residue). Other residues were not examined optically because they are precipitates; and
- X-Ray Diffraction on all samples to determine crystalline compounds.

Residues were not examined sub-optically due to the nature of the materials.

4.2.2 Analytical Methods

Solids Characterization

A split of each sample was submitted for:

- Sulfur forms (total S, S as sulfate).
- Paste pH.
- Neutralization potential and carbonate.
- 50 elements (mostly metals by ICP scan following aqua regia (nitric and hydrochloric acids) digestion).
- Whole rock oxides. This provides total concentrations of major elements.

Leachate Extraction Tests

All samples were submitted for regulatory leach tests (EPA 1311; EPA 1312) to provide data for waste classification purposes.

A third leach procedure was used as the first step of the sequential shake flask leach procedure described below. This procedure, developed by Price (1997) for the British Columbia (Canada) Ministry of Energy Mines and Petroleum Resources, uses a lower leach ratio (1:3) to improve

detection of low levels of metals. The lixiviant was deionized water, which typically has a pH between 5 and 6. The leachate pH was not fixed as in the TCLP and SPLP methods. The extraction was performed by shaking in a glass or plastic container for 24 hours, after which the leachate was extracted and analyzed.

Extraction test results are provided in Appendix B.

Sequential Shake Flask

All samples were tested using a sequential leach procedure consisting of weekly repetition of the leach procedure developed by Price (1997) in which the solid to liquid ratio is 1:3. The procedure involved weekly leaching of roughly 300 g of solids in a plastic bottle. The leaching step consisted of addition of deionized water and agitation for 24 hours. The leachate was then decanted for analysis.

This procedure was requested by the MDNR to provide a more aggressive evaluation of residue dissolution than was perceived to occur in humidity cells.

Leachates were analyzed using the following schedule:

- Weekly – pH, oxidation-reduction potential, conductivity.
- Bi-weekly – Acidity, alkalinity, inorganic C, hardness, anions (F, Cl, SO₄).
- Four weekly (weeks 0, 4, 8, 12, etc) – Low level element scan using ICP-MS.
- Four weekly (weeks 2, 6, 10, 14, etc) – General element scan using ICP-OES.

Humidity Cell

Samples were tested in ASTM-style humidity cells in the tailings configuration. Details of the procedure are provided in Appendix A. The solid to liquid ratio is 1:0.5 (1 kg of solids leached with 500 mL of deionized water). Leachates were analyzed using the same schedule as the sequential shake flasks.

MDNR Reactor

Samples were also tested in small (75 g) MDNR Reactors for which the solid to liquid ratio is 1:2.7 (75 g of solids leached with 200 mL of deionized water). Details are provided in Appendix A. Leachates were analyzed using the same schedule as the sequential shake flasks.

Kinetic Testwork Duration and Data Management

The dissolution tests were started in early February 2006. Up to 38 weeks of data are available depending on the parameter. Tests are ongoing. Graphs illustrating concentrations obtained are

provided in Appendix C. This report is based on data collected and checked for quality to the end of October 2006.

Because different reporting limits were used for different cycles and different parameters, the following rules were used to plot data and allow trends to be apparent:

- If the parameter was not determined, the result is not plotted. This is the case for alkalinity and acidity which are only determined if the pH is above or below (respectively) specified values.
- If the result is undergoing quality control re-check, the result is not plotted.
- If the parameter is determined by the same method for each analysis, values below the reporting limit values are plotted as 50% of the reporting limit.
- Because the reporting limits for ICP-MS are below the reporting limit for ICP-ES:
 - If the result was determined by ICP-MS and was below the reporting limit, the value on the graph is 50% of the reporting limit. If the value is at or above the reporting limit, the value is plotted.
 - If the result was determined by ICP-ES and was determined to be below the reporting limit, no value is plotted.
 - If the result was determined by ICP-ES and was determined to be above the reporting limit, the value is plotted.
 - These rules can result in four cycles between plotted results if the parameter is not detected by ICP-ES (e.g. molybdenum in shake flask leachates).

Occasionally, “sawtooth” trends are apparent in which values alternate between high and low for the ICP-ES and ICP-MS analyses. This results from analytical “noise” around the ICP-ES reporting limit when reported values are slightly above the reporting limit. Aluminum is a particular example that commonly shows reported values above the ICP-ES reporting limit of 0.05 mg/L.

Many graphs are plotted on logarithmic axes to allow data spanning a wide range of concentrations to be compared.

4.2.3 Quality Assurance/Quality Control

In addition to Quality Assurance/Quality Control (QA/QC) of leachate chemistry performed by the analytical laboratory, QA/QC on the dissolution test procedure and overall leachate chemistry included blanks, duplicates, leachate ion balances and visual trend analysis to identify severe outliers. These measures were designed mainly in conjunction with the waste rock characterization plan, the results of which are described in RS42.

Quality assurance review for the waste rock and tailings programs identified two specific issues with respect to pH measurements and antimony leaching that affected the subsequent interpretation of the results. These issues also applied to the residue program and are discussed in the following paragraphs.

Trend analysis of pH measurements indicated a “sawtooth” trend in which values alternated between higher and lower values every other week. The reason for the pattern was that pH measurements were performed on filtered and unfiltered leachates on alternate weeks depending on whether samples were being collected for metals analysis. This was consistent with the analytical method. Because vacuum filtration potentially causes weakly buffered leachates to respond to changes in pressure by taking up or releasing carbon dioxide, determination of pH of filtered leachates was discontinued when the concern was identified. For results prior to this point in the test program, pH measurements on filtered leachates were discarded. Where pH results were needed for interpretation of other chemical parameters, the two nearby results were averaged (i.e. assuming the results could be interpolated linearly).

Review of antimony data indicated that test apparatus components of humidity cell tests constructed from polyvinyl chloride (PVC) were leaching antimony due to the use of antimony oxide in manufacturing. Antimony results from humidity cell results were therefore discarded.

4.2.4 Interpretation Methods

Results were interpreted using three methods:

- Leachate chemistry trends were examined as a function of time.
- All leachate results were combined and evaluated with respect to pH as the primary control on concentrations.
- Selected leachate results were input into a thermodynamic chemical equilibrium model to evaluate chemical saturation.

5 Results

5.1 Solids Characteristics

Table 5-1 provides quantitative mineralogy determined by Rietveld x-ray diffraction. Results are expressed as weight percentage of crystalline phases. If amorphous phases are present, the quantities of the indicated crystalline phases will be lower than indicated.

Table 5-2 provides elemental composition of the residues.

Table 5-3 provides sulfur forms from analysis and mineralogy, neutralization potential, carbonate analyses and acid-base accounts. The distribution of sulfate indicated by mineralogy was calculated as follows:

- The proportions indicated by mineralogy for natrojarosite, gypsum and bassanite were used to calculate the quantity of sulfate indicated by mineralogy using the formula weights of these minerals.
- The total sulfate indicated by mineralogy was calculated and compared to the analyzed sulfate. As shown in Table 5-3, there is a strong correspondence between the analytical and mineralogical sulfate amounts.
- The proportion of the analytical sulfate as gypsum and bassanite was calculated based on the proportion of these minerals indicated by mineralogy.

Acid potential (AP) in Table 5-3 was calculated based on sulfur not occurring as calcium sulfate based on the assumption that sulfur as natrojarosite is the source of acid. The factor for converting sulfur as natrojarosite to AP is 23.44 compared to 31.25 for sulfur as iron sulfide.

Table 5-1: Mineralogy of Residues

Mineral	Unit	Leach, no CuSO ₄	Leach, with CuSO ₄	Gypsum	Raffinate Neutralization	Fe/Al	Mg	Combined	Combined no Gypsum
Quartz	%	2.1	3	0.2	0.3	0.3	0.2	2.2	3.4
Plagioclase	%	25.6	5.8						2.2
Gypsum	%	8.1	6.9	99.8	96.3	98.9	76.8	73.4	53.3
Calcite	%							2.9	
Bassanite	%				3.4				
Siderite	%							1.2	
Actinolite	%	1.3							
Talc	%	4.3	3.9					3.2	3.2
Natrojarosite	%	34	63					9.6	29.3
Hematite	%	24.6	17.4					6	8.6
Goethite	%					0.8			
Butlerite	%							1.5	
Brucite	%						22.2		
Halite	%						0.8		

Leach Residues

The leach residues remain from the concentrate following pressure leaching. It was expected that this product would consist of both secondary minerals and resistant primary minerals (silicates).

Leach residues from processing of concentrates produced by sulfide flotation with and without copper sulfate were tested. The XRD results implied differences in the residual silicate component of the residues. The concentrate produced without copper sulfate had 26% residual plagioclase compared to 6% for the concentrate produced with copper sulfate. The oxidation products produced by the process are shown as mainly natrojarosite, which was also confirmed by the sodium content of the samples (Table 5-2). Hematite (iron oxide) and talc (basic magnesium silicate) were also present.

The residual metal content of the leach residues was significantly lower when the feed concentrate was generated using copper sulfate. Nickel, cobalt and zinc were an order-of-magnitude lower.

As expected, the leach residues were acidic and contained residual acidity shown by negative NP. In addition, the presence of natrojarosite resulted in higher acid potential than the other residues (111 and 199 kg CaCO₃/t).

Table 5-2: Elemental Composition of Residues

Parameter	Unit	Leach, no CuSO ₄	Leach, with CuSO ₄	Gypsum	Raffinate Neutralization	Fe/Al	Mg	Combined	Combined no Gypsum
Ag	ppm	11.05	23.8	0.23	0.9	0.33	0.12	4.93	11.05
Al	%	2.82	1.97	0.02	0.02	0.46	0.03	0.54	1.01
As	ppm	35.4	56.3	3	6	15	5	110	34
B	ppm	<10	<10	<10	<10	<10	<10	<10	<10
Ba	ppm	40	30	<10	<10	<10	<10	10	20
Be	ppm	0.05	<0.05	<0.05	<0.05	0.28	<0.05	<0.05	<0.05
Bi	ppm	4.89	6.84	0.5	0.8	0.81	0.04	1.94	3.53
Ca	%	1.88	1.41	14.5	17.1	18.8	15.1	16.35	11.3
Cd	ppm	0.66	0.19	0.22	0.73	0.48	0.44	0.29	0.23
Ce	ppm	8.21	5.45	1.71	0.6	0.85	1.6	2.35	2.93
Co	ppm	133.5	17.9	5.1	9.3	105.5	13.6	6.9	23.6
Cr	ppm	112	154	8	11	457	5	59	116
Cs	ppm	0.1	<0.05	<0.05	<0.05	0.09	<0.05	<0.05	<0.05
Cu	ppm	7380	1280	184.5	22.5	2960	26.9	519	945
Fe	%	17.3	26.9	0.05	0.08	1.88	0.05	5.21	11.75
Ga	ppm	6.47	5.06	2.54	0.07	0.57	0.09	1.22	2.43
Ge	ppm	0.41	0.47	<0.05	<0.05	0.08	<0.05	0.11	0.22
Hf	ppm	0.12	0.06	<0.02	<0.02	0.12	<0.02	0.04	0.04
Hg	ppm	0.04	0.02	0.12	0.35	0.07	0.05	0.11	0.03
In	ppm	0.3	0.355	23.3	0.011	1.01	0.083	0.164	0.28
K	%	0.11	0.1	<0.01	<0.01	0.01	0.01	0.02	0.05
La	ppm	3.6	2.5	0.7	0.5	0.5	2.3	1.1	1.6
Li	ppm	1	0.6	0.1	0.1	0.5	0.5	0.2	0.2
Mg	%	0.28	0.25	0.01	0.01	0.14	9.44	0.39	1.47
Mn	ppm	35	<5	<5	5	23	83	<5	<5
Mo	ppm	21.8	28.4	0.47	0.85	42.3	0.38	9.35	18.9
Na	%	1.28	3	0.02	0.04	0.13	1.04	0.58	1.62
Nb	ppm	0.18	0.21	<0.05	0.06	0.46	0.06	0.11	0.17
Ni	ppm	3270	410	99.9	192.5	2710	1230	260	674
P	ppm	290	110	<10	20	160	40	70	90
Pb	ppm	48.5	56.1	8.3	86.1	20.4	12.5	133.5	32
Rb	ppm	1.7	1	0.2	0.3	0.5	0.3	0.4	0.7
Re	ppm	0.012	0.002	0.015	0.022	0.013	<0.001	0.009	0.009
S	%	5.47	9.22	>10.0	>10.0	>10.0	>10.0	>10.0	>10.0
Sb	ppm	1.22	1.81	0.18	1.25	1.47	0.4	3.99	1.14
Sc	ppm	1.3	0.8	0.4	0.4	4.4	0.5	0.8	1.1
Se	ppm	49.8	73.4	0.3	0.4	0.6	0.5	20.4	39.2
Sn	ppm	4.8	6.1	0.2	0.5	1.6	<0.2	2	3.2
Sr	ppm	73.1	63.9	60.6	106	83.7	86.5	77.3	85.2
Ta	ppm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Te	ppm	2.01	2.91	0.01	0.07	0.09	<0.01	0.83	1.48
Th	ppm	1.1	0.9	<0.2	<0.2	0.3	<0.2	0.3	0.4
Ti	%	0.066	0.042	<0.005	<0.005	0.007	<0.005	0.012	0.019
Tl	ppm	0.1	0.34	0.03	0.03	0.24	0.02	0.06	0.19
U	ppm	0.06	<0.05	<0.05	<0.05	0.55	0.1	0.06	0.09
V	ppm	39	41	1	1	16	1	11	21
W	ppm	0.57	0.49	0.09	0.18	1.12	<0.05	0.26	0.45
Y	ppm	3.88	3.29	1.28	1.14	1.06	7.64	2	2.86
Zn	ppm	171	15	30	98	164	23	32	36
Zr	ppm	<0.5	0.7	1.5	4.2	1.2	<0.5	9.8	1.9

Table 5-3: Acid-Base Accounting Results

Parameter	Unit	Leach, no CuSO ₄	Leach, with CuSO ₄	Gypsum	Raffinate Neutralization	Fe/Al	Mg	Combined	Combined no Gypsum
Paste pH	-	2.6	3.3	3.8	5.4	4.6	9.6	-	9.4
Sulphur Forms									
Total S	%	6.24	9.8	19.55	18.95	17.9	14.4	16.5	13.65
S as SO ₄	%, S	6.1	9.3	18.35	18.55	17.3 5	13.6 5	15.9	13.5
Calculated Sulfur Forms From XRD Mineralogy									
S as Gypsum	%, S	1.51	1.28	18.55	17.90	18.3 8	14.2 7	13.64	9.90
S as Natrojarsoite	%, S	4.49	8.32	0.00	0.00	0.00	0.00	1.27	3.87
Total SO ₄	%, S	5.99	9.61	18.55	17.90	18.3 8	14.2 7	14.91	13.78
Calculated Sulfur Not Present as Calcium Sulfate									
Non-Gypsum	%, S	4.73	8.52	1.00	1.05	-0.48	0.13	2.86	3.75
Neutralization Potential									
Fizz Rating	-	1	1	1	1	1	3	1	2
Neutralization Potential (NP)	kg CaCO ₃ /t	-17	-4	0	0	-10	371	10	51
CO ₂	%	-0.2	-0.2	-0.2	-0.2	-0.2	1.8	-0.2	0.3
C	kgCaCO ₃ /t	2	2	2	2	2	40	2	7
Acid Potential (AP)	kg CaCO ₃ /t	111	199	23	25	-11	3	67	88
Acid-Base Accounting									
NP-AP	kg CaCO ₃ /t	-164	-271	-38	-13	-27	348	-51	-72
NP/AP	-	-	-	0.0	0.0	-	124	0.1	0.6

Gypsum Residue

Gypsum residue is the first hydrometallurgical precipitation product. It is produced by limestone addition to the leach solution following recovery of platinum group metals and prior to copper recovery.

The elevated calcium and sulfate content of the gypsum residue sample confirmed that it was dominantly hydrated calcium sulfate. XRD showed that it was 99.8% gypsum.

The metal content of this residue was very low. Acid-base accounting indicated that the dominant sulfur form was sulfate. About 1.2% of the sulfur was not accounted for by sulfate analysis, but XRD failed to recognize any other sulfur minerals. It is likely therefore that the difference reflects analytical uncertainties rather than unknown mineral content.

Raffinate Neutralization Residue

This residue is formed by an intermediate neutralization step between copper removal and precipitation of iron and aluminum.

Raffinate neutralization residue was identified as nearly entirely calcium sulfate (gypsum with minor bassanite) by XRD, which was confirmed by the dominance of calcium and sulfate in the sample. Like the gypsum residue, the metal content of this residue was very low and the sulfur forms analysis was consistent with the dominance of sulfate.

Fe/Al Residue

The Fe/Al residue is formed by two limestone addition steps prior to cobalt, nickel and zinc hydroxide recovery. Note that the full scale plant design combines Fe/Al removal with raffinate neutralization which means that the Fe/Al residue will be combined with the raffinate neutralization residue.

Like the raffinate neutralization residue, the Fe/Al residue was mostly gypsum with some iron and aluminum. Goethite was detected by XRD and iron and aluminum were both an order of magnitude higher than the other two dominantly calcium sulfate residues. The Fe/Al residue contained higher concentrations of copper and nickel compared to the gypsum and raffinate neutralization residues.

Magnesium Residue

The magnesium residue is formed following recovery of the mixed hydroxide product and is the result of final addition of lime to the process solutions. The magnesium originates from the original concentrate leaching step (dissolution of olivine), and addition of magnesium oxide to precipitate the mixed hydroxide product.

The crystalline component of this residue was dominated by gypsum as shown by the elevated sulfate and calcium. The XRD scan showed that brucite (magnesium hydroxide) was present and this was supported by the magnesium content of the sample. The sample showed a strong fizz reaction to hydrochloric acid and carbonate content was equivalent to 4% calcium carbonate (40 kg CaCO₃/t). This suggests that the hydroxide was partially converted to carbonate by atmospheric reaction.

Neutralization potential was high at 371 kg CaCO₃/t compared to the other residues; probably reflecting the presence of amorphous magnesium and possibly calcium hydroxide. This residue was alkaline (pH 9.6) and consistent with the hydroxide content.

The dominant trace metal in this residue was nickel (1230 mg/kg).

Combined Residues including Gypsum Residue

The largest component of the combined residue was the gypsum residue, followed by leach residue, raffinate residue, Mg residue and Fe/Al residue. As a result the material was dominantly calcium sulfate from the gypsum residue. The XRD result also showed the presence of calcite and siderite, presumably due to the magnesium residue.

The overall acid-base account for this sample indicated AP of 67 kg CaCO₃/t and NP of 10 kg CaCO₃/t. Because carbonate content was relatively low compared to NP, most NP was present as hydroxide from the magnesium residue. As a result, the residue was predicted to be potentially acid generating (NP/AP of 0.1). The acid generation potential is produced by natrojarosite which yields acidic leachate when dissolved. This process does not require an oxidant.

Combined Residues without Gypsum Residue

Although this combination did not include the gypsum residue, gypsum remained a significant component from the raffinate neutralization, Fe/Al residue and Mg residues. The overall characteristics of this material are similar to the combination of all residues though both AP and NP were higher in this residue due to the higher proportions of leach and magnesium residues respectively. The NP/AP of the residue was calculated to be 0.6.

5.2 Description of Leachate Chemistry

5.2.1 EPA 1311

Results for EPA 1311 (TCLP) are provided in Appendix B. Concentrations for all parameters were below regulated limits. None of the residues (individually or combined or combined without the gypsum residue) are classified as hazardous wastes.

5.2.2 EPA 1312

Results for EPA 1312 (SPLP) are provided in Appendix B. The use of weakly buffered acidic solution resulted in a range of final leachate pHs that reflect the stage of neutralization in the process. The leach residues had the lowest pH (2.79 and 3.38), followed by gypsum (4.1), raffinate neutralization (4.9), Fe/Al (5.0) and magnesium (9.7). The combined residues had pHs of 9.2 (all residues) and 9.4 (no gypsum residue). The variation in pH also resulted in different metal concentrations in solution. The leach residues had the highest metal concentrations. The two gypsum dominated residues had much lower metal concentrations (despite the lower pH). The higher metal content of the Fe/Al residue resulted in higher leachate metal concentrations. The three non-acidic leachates had low metal concentrations.

5.2.3 Price (1997) Method

Results for Price (1997) method are provided in Appendix B. This method uses deionized water as its extractant and a low liquid to solid ratio (3:1) compared to SPLP and TCLP which both use 20:1. The Price (1997) method is closely related to the SPLP method which uses deionized water weakly buffered by sulfuric and nitric acids. Both of these methods are different from the TCLP method which uses acetic acid to buffer pH.

As a result of the low liquid to solid ratio in the Price (1997) method, leachate pHs were lower than for the SPLP for the more acidic residues. The two leach residues had pHs of 2.1 and 2.6, followed by gypsum (3.3) and raffinate neutralization (4.2). For the three non-acidic residues, the pH was slightly lower with the Price (1997) method.

Differences in metal concentrations between the SPLP and Price (1997) methods appear to reflect the different liquid to solid ratios. Both copper and nickel concentrations were 4 to 7 times higher in the Price (1997) method leachates for the leach, gypsum, raffinate neutralization and Fe/Al residues. Concentrations of these elements in leachates from the three non-acidic residues were relatively low which obscured differences between the leachates.

5.3 Description of Kinetic Test Leachate Chemistry

5.3.1 Sequential Shake Flasks

Sequential shake flask charts are provided in Appendix C.1. Data are provided on a CD included in the report pocket.

Samples of leach residues, gypsum residue, raffinate neutralization residue and Fe/Al residue consistently produced acidic leachate but pH steadily increased for all residues except for the leach residue from processing of concentrate produced using copper sulfate. The raffinate neutralization residue showed erratic increase in pH reaching high values above 7. Leachates were dominated by calcium and sulfate. Sulfate concentrations were lowest for the leach residues (60 and 200 mg/L in most recent samples) but stable at about 1600 mg/L for the other acidic residues. Trends for other parameters included:

- Aluminum concentrations were greatest for the leach residues and slowly increased up to 3.4 mg/L for the residue produced from concentrate using copper sulfate. Other tests showed declining and low concentrations.
- Cobalt, copper, nickel and zinc concentrations were greatest for the Fe/Al residue as the test proceeded (0.003 mg Co/L, 1.4 mg Cu/L, 0.2 mg Ni/L and 0.02 mg Zn/L in most recent leachate) and steadily declined in all cases.
- Iron concentrations were greatest but declining for the gypsum residue (1.7 mg/L in a recent leachate).
- Lead concentrations were greatest and declining for the raffinate neutralization residue (0.01 mg/L in latest sample).
- Sodium concentrations were greatest for the leach residues and slightly increasing (7 mg/L in recent leachate).

Magnesium residues showed declining pH from 9.6 initially to 6.4 in recent leachates. Leachates were dominated by sulfate concentrations at higher levels than other residues (2,500 to 7,900 mg/L)

and magnesium rather than calcium as the dominant cation. Sodium and chloride concentrations were initially elevated (both above 1000 mg/L) then near to 1 mg/L. Concentrations of metal ions were very low and stable or declining. The exception was boron, which showed increasing concentrations reaching 0.16 mg/L in recent leachates.

Combined residues showed stable or very slightly declining pH reaching about 7. Leachate chemistry was dominated by calcium and sulfate at narrowly constrained stable concentrations. Alkalinity leaching declined but appeared to stabilize at about 30 mg CaCO₃/L. Major element chemistry reflected mixing of waters from the individual residues. Metal concentrations were generally low. The following exceptions were apparent:

- Arsenic leaching from both residues was greater than other residues and appeared to be stable. Greatest concentrations were 0.003 mg/L.
- Molybdenum leaching in these residues was greater than other residues. Maximum concentrations were 0.03 mg/L in both combined residues, but these concentrations declined. The combined residue without gypsum showed higher concentrations than the combined residue.
- Selenium concentrations were also greatest for these residues and showed a stable trend following decreases. The combined residue without gypsum showed higher concentrations (maximum of 0.019 mg/L). Concentrations in most recent samples were 0.007 mg/L.

5.3.2 Humidity Cells

Humidity cell results charts are provided in Appendix C.2.

Samples of leach residues, gypsum residue, raffinate neutralization residue and Fe/Al residue consistently produced acidic leachate but pH steadily increased for all residues, except for the leach residue from processing of concentrate produced using copper sulfate. The raffinate neutralization residue showed the greatest increase in pH (from 3.3 to 4.6, except for one point at 6.0). Leachates were dominated by calcium and sulfate. Sulfate concentrations rapidly stabilized between 1600 and 1900 mg/L, becoming 1600 mg/L as the test proceeded. Concentrations of other parameters either remained stable or decreased, for example:

- Aluminum concentrations were greatest for the most acidic leach residues (up to 14 mg/L following an initial flush) but remained relatively stable.
- Cobalt, copper, nickel and zinc concentrations were greatest for the Fe/Al residue as the test proceeded (0.03 mg Co/L, 10 mg Cu/L, 2.8 mg Ni/L and 0.25 mg Zn/L in most recent leachate) and steadily declined in all cases.
- Iron concentrations were greatest and relatively stable for the gypsum residue (1.7 mg/L in a recent leachate).
- Lead concentrations were greatest and declining for the raffinate neutralization residue (0.05 mg/L in latest sample).

- Sodium concentrations were greatest for the leach residues and stable or slightly decreasing.

Acidity of these leachates was stable or slowly declining for the leach residues at near 100 mg CaCO₃/L, and declining at lower levels for the gypsum dominated residues.

Magnesium residues showed declining pH from 9.4 initially to 7.4. Leachates were dominated by sulfate concentrations at higher levels than other residues (5,000 to 10,000 mg/L) and magnesium rather than calcium as the dominant cation. Sodium and chloride concentrations were initially elevated (both above 1000 mg/L) then declined to less than 10 mg/L. Concentrations of metal ions were very low and stable or declining.

Combined residues showed stable or very slightly declining pH near 7 after about 20 weeks. Leachate chemistry was dominated by calcium and sulfate. Alkalinity leached at low levels (about 23 mg CaCO₃/L in recent leachates). Major element chemistry reflected mixing of waters from the individual residues. For example, chloride leaching initially followed the same trend as the magnesium residue for the combined residue without gypsum. Metal concentrations were generally low. The following exceptions were apparent:

- Arsenic leaching from both residues showed an increasing trend though at low levels. The combined residue showed the greatest concentration in any residue leachate (0.007 mg/L).
- Molybdenum leaching in these residues was greater than any other residue. Maximum concentrations were 0.14 mg/L in the combined residue, but these concentrations declined. The combined residue without gypsum showed stable concentrations between 0.03 and 0.09 mg/L.
- Selenium concentrations were also greatest for these residues and showed a slowly increasing trend for the combined residue without gypsum. Concentrations in most recent samples were 0.03 mg/L.

5.3.3 MDNR Reactors

MDNR reactor results charts are provided in Appendix C.3.

Samples of leach residues, gypsum residue, raffinate neutralization residue and Fe/Al residue consistently produced acidic leachate but pH steadily increased for all residues except for the leach residue from processing of concentrate produced using copper sulfate. Like other tests, the raffinate neutralization residue showed the greatest increase in pH (from 3.3 to 4.6). Leachates were dominated by calcium and sulfate. Like the sequential shake flask results, sulfate concentrations were lowest for the leach residues (90 and 200 mg/L in most recent samples) but stable between 1400 and 1600 mg/L for the other acidic residues. Concentrations of other parameters either remained stable or decreased, for example:

- Aluminum concentrations were greatest for the most acidic leach residues (up to 2.8 mg/L following an initial flush) but remained relatively stable.

- Cobalt, copper and nickel concentrations were greatest for the Fe/Al residue as the test proceeded (0.006 mg Co/L, 3.1 mg Cu/L, and 0.5 mg Ni/L in most recent leachate) and steadily declined in all cases.
- Zinc concentrations were comparable in Fe/Al residue and raffinate neutralization residue as the test proceeded. Zinc concentrations in most recent leachates were about 0.04 mg/L.
- Iron concentrations were similar and relatively stable after about 20 weeks for the leach residue (copper sulfate used for concentrate), gypsum residue and raffinate neutralization residues (highest concentrations of about 0.2 mg/L).
- Lead concentrations were greatest and declining for the raffinate neutralization residue (0.02 mg/L in latest sample).
- Sodium concentrations were greatest for the leach residues and stable or slightly decreasing.

Magnesium residues showed declining pH from 9.8 initially to 7.4. Leachates were dominated by sulfate concentrations generally at higher levels than other residues (up to 5,000 mg/L) and magnesium rather than calcium as the dominant cation. Sodium and chloride concentrations were initially elevated (both above 200 mg/L) then declined to near or less than 1 mg/L. Concentrations of metal ions were very low and stable or declining.

Combined residues showed stable or very slightly declining pH between 7 and 7.4 after about 9 weeks. Leachate chemistry was dominated by calcium and sulfate. Alkalinity leached at low levels (about 23 mg CaCO₃/L in recent leachates). Major element chemistry reflected mixing of waters from the individual residues. For example, chloride leaching initially followed the same trend as the magnesium residue for the combined residue without gypsum. Metal concentrations were generally low. The following exceptions were apparent:

- Arsenic leaching from both residues was greater than other residues and appeared to be stable. Greatest concentrations were 0.002 mg/L.
- Boron leaching from the combined residue showed an increasing trend reaching a maximum concentration of 0.27 mg/L.
- Molybdenum leaching in these residues was greater than any other residue at first but then decreased and showed similar concentrations to the Fe/Al Residue. Maximum concentrations were 0.06 mg/L in the residue without gypsum, but these concentrations declined.
- Selenium concentrations were also greatest for these residues and showed a stable trend with maximum concentrations of 0.008 mg/L.

6 Interpretation of Dissolution Testwork

6.1 General Interpretation of Leachate Chemistry

6.1.1 Saturation Indices

In order to interpret the testwork chemistry, selected leachate chemistry data from all tests were input into Geochemists' Workbench (Bethke 2005) to evaluate whether the leachates were in equilibrium with any of the known mineral components of the residues. As shown in the foregoing descriptions, the humidity cells yielded the highest concentrations of metals. This is consistent with the low applied liquid to solid ratio in these tests (0.5 mL/g) compared to the sequential shake flasks (3 mL/g) and MDNR Reactors (2.7 mL/g). The humidity cells are therefore most likely to show chemical saturation. Table 6-1 shows saturation indices for minerals identified by XRD and other minerals that may control solubility. Color coding shows leachates that are close to chemical saturation (green shading for $-0.5 < SI < 0.5$) and well over-saturated (amber for $SI > 0.5$). Saturation indices were calculated for the initial release and chemistry after 28 weeks following the decrease that typically occurred in the early weeks.

Leachate from leach residues appeared to be constrained by dissolution of silica and gypsum both initially and as the test proceeded. While it is likely that natrojarosite is dissolving releasing ferric iron, the low pH of the leachates means that the solubility of natrojarosite is not limited and ferric hydroxide does not precipitate. The gypsum and raffinate neutralization residues show much the same result though it appears that under initial conditions fluorite was also dissolving or forming in the raffinate neutralization residue as shown by SI above 1. Fluoride concentrations were 42 mg/L initially. In the higher pH Fe/Al residues, gypsum continued to be an important overall chemistry control, but ferric hydroxide was indicated as at saturation meaning that iron oxides were probably controlling solution chemistry. Also, the SI for tenorite was -1.2 compared to lower than -4.4 for the more acidic residues. For the magnesium residue, brucite and carbonates were near or well saturated consistent with the mineralogy of the samples. This effect was most apparent in the early weeks but diminished in week 28.

For the combined residues, the effect of gypsum dissolution was again apparent for the entire testwork period. In the first week, dissolution of natrojarosite to form ferric hydroxide appeared to be occurring as shown by the SI values. Week 28 showed the same effect but in reality iron was not detected so the SI's are maximum values and do not confirm that ferric hydroxide formed. Tenorite was over-saturated in the first week but not subsequently. Dissolution of carbonates also appeared to be an important effect.

In summary, the evaluation of saturation indices indicates that leachates were consistently in equilibrium with silica and gypsum and in the early stages of testing were probably also in equilibrium with iron and copper oxides. The interpretation did not provide any indication of possible constraints on the solubility of other potential contaminants such as cobalt, nickel and zinc. As a result, metal concentrations were compared to pH for all tests to evaluate pH control on metal concentrations.

Table 6-1: Saturation Indices for Humidity Cell Leachates

Mineral	Initial Release (week 1)								Release at Week 28							
	Leach Residue, no CuSO ₄	Leach Residue	Gypsum	Raffinate Neutralization Residue	Fe /Al	Mg Residue	Combined Residue	Comb. Residue, no Gypsum	Leach Residue, no CuSO ₄	Leach Residue	Gypsum	Raffinate Neutralization Residue	Fe /Al	Mg Residue	Combined Residue	Comb. Residue, no Gypsum
Hematite	2.7	2.7	5.2	6.9	10.0	13.4	13.6	13.5	3.3	2.4	5.9	7.2	8.2	10.4	10.4	10.4
Quartz	0.3	0.8	0.5	0.8	0.8	-0.7	0.8	-0.1	1.0	0.8	-0.3	-0.1	0.8	-1.5	1.2	1.1
Fluorite	-6.3	-3.2	-4.4	0.6	0.6	-0.2	-0.2	-0.5	-6.3	-6.6	-1.6	-1.5	-1.7	-0.9	-1.4	-1.4
Chalcedony	0.0	0.5	0.2	0.6	0.5	-0.9	0.5	-0.3	0.8	0.5	-0.5	-0.4	0.5	-1.8	0.9	0.9
Barite	-0.5	-0.7	-0.8	0.2	-0.5	0.0	-0.6	-0.3	-1.0	-1.2	-0.3	-0.1	-0.9	-0.8	-0.9	-1.1
Jarosite-K	-1.0	-0.9	-0.4	0.1	2.5	-5.4	-3.6	-4.3	-7.4	-6.6	-6.1	-4.7	-4.4	-7.9	-7.7	-7.6
Gypsum	-0.4	-0.3	-0.2	-0.2	-0.1	-0.1	-0.2	-0.2	-0.2	-0.2	-0.1	-0.2	-0.1	-0.1	-0.2	-0.1
Anhydrite	-0.6	-0.4	-0.4	-0.4	-0.3	-0.3	-0.3	-0.3	-0.3	-0.4	-0.3	-0.3	-0.3	-0.3	-0.3	-0.3
Amorphous Silica	-1.0	-0.5	-0.8	-0.4	-0.5	-1.9	-0.5	-1.3	-0.2	-0.5	-1.5	-1.4	-0.5	-2.8	-0.1	-0.1
Bassanite	-1.2	-1.1	-1.0	-1.0	-0.9	-0.9	-1.0	-1.0	-1.0	-1.0	-0.9	-1.0	-1.0	-0.9	-1.0	-0.9
Fe(OH)3(ppd)	-3.5	-3.5	-2.3	-1.4	0.1	1.8	1.9	1.9	-3.2	-3.7	-1.9	-1.3	-0.8	0.3	0.3	0.3
Jarosite-Na	-1.9	-2.5	-2.4	-2.0	0.8	-7.2	-5.2	-5.9	-9.4	-8.9	-8.8	-7.1	-8.3	-10.2	-9.8	-9.8
Epsomite	-2.2	-1.9	-3.5	-3.3	-1.9	-2.1	-2.1	-1.9	-5.4	-5.4	-6.6	-6.6	-6.4	-2.1	-4.1	-3.7
Tenorite	-5.7	-6.1	-5.0	-4.4	-1.2	1.1	0.7	0.9	-5.6	-6.7	-5.0	-5.4	-1.0	-1.3	-1.4	-2.0
Gibbsite	-6.4	-6.9	-4.7	-6.0	-3.3	-1.2	-0.5	-0.8	-1.5	-3.0	-3.2	-2.8	0.2	-1.0	-0.6	-0.7
Halite	-4.8	-3.9	-6.7	-6.6	-4.5	-4.3	-5.4	-4.4	-9.8	-9.5	-11.0	-10.5	-11.2	-9.7	-10.2	-10.0
Ni(OH)2(s)	-11.3	-11.7	-10.5	-8.5	-5.4	-1.6	-2.3	-2.5	-11.1	-12.3	-10.6	-10.2	-6.8	-5.4	-6.1	-5.7
Kaolinite	-11.8	-11.8	-7.9	-9.7	-4.6	-3.2	1.0	-1.3	-0.5	-3.9	-6.5	-5.3	2.4	-4.5	1.6	1.4
Brucite	-14.9	-13.7	-14.1	-12.3	-8.9	-0.3	-1.6	-0.8	-13.9	-14.9	-13.8	-13.3	-11.8	-3.2	-5.5	-5.0
Alunite	-10.2	-11.4	-8.0	-13.9	-8.2	-14.8	-11.4	-12.9	-2.6	-4.8	-10.3	-9.5	-1.8	-12.2	-10.7	-11.0
Cuprite	-20.9	-21.7	-19.2	-17.6	-12.3	-14.2	-14.9	-14.3	-15.7	-19.0	-12.0	-17.9	-11.1	-9.9	-13.1	-15.6
Talc	-31.9	-26.4	-28.5	-21.8	-11.9	8.3	10.3	9.1	-25.8	-30.0	-30.7	-28.4	-20.6	-4.1	-0.2	1.3
Dolomite ²	-	-	-	-	-8.8	3.5	2.5	2.9	-	-	-16.3	-	-12.4	-0.2	-1.5	-1.4
Dolomite-ord ²	-	-	-	-	-8.8	3.5	2.5	2.9	-	-	-16.3	-	-12.4	-0.2	-1.5	-1.4
Dolomite-dis ²	-	-	-	-	-10.3	1.9	0.9	1.4	-	-	-17.9	-	-14.0	-1.8	-3.1	-2.9
Calcite ²	-	-	-	-	-5.3	0.9	0.4	0.5	-	-	-6.7	-	-4.8	-0.9	-0.6	-0.7

Notes:

1. Green shading indicates saturation indices between -0.5 and 0.5. Amber shading indicates saturation indices greater than 0.5.
2. Carbonate not reported in leachates at low pH. Saturation indices for carbonate minerals not calculated.

6.1.2 pH Control on Metal Concentrations

The overall assumption in evaluating these plots is that if similar concentrations are indicated by tests operating at different liquid to solid ratios, and there is a relationship with pH that is consistent with first principles, it can be concluded that a solubility control is operating. If tests operating at low liquid to solid ratios yield higher concentrations than tests operating at high ratios, and the difference in concentrations can be accounted for by the ratio, it is more likely that the availability of soluble components is limited. The following bullets indicate observations for individual parameters.

Graphs are provided in Appendix D.

- **Aluminum.** A strong relationship between pH and Al concentration was defined mainly by humidity cell leachates but also by some MDNR reactor and shake flask leachates for the low pH samples. A strong control at neutral to basic pH was indicated by all test types.
- **Arsenic.** The leachate data indicated a pH relationship in which there was a pH minimum at about 6. Concentrations were comparable at both higher and lower pHs. At low pH, the relationship was defined by humidity cells. Lower concentrations were indicated for shake flask and MDNR reactor leachates. It is likely that solubility at acidic pHs is greater than indicated by the testwork. At pH greater than 6, arsenic concentrations were positively correlated to pH and the relationship was defined by all test types. The data are a good indication of arsenic constraints under these conditions.
- **Cadmium.** The results showed that cadmium was much more soluble under acidic conditions than neutral to basic conditions. The Fe/Al residues showed greatest solubility of cadmium at lowest pHs. Cadmium is probably more soluble at acidic pH than indicated by testwork. The presence of non-detectable cadmium at neutral to basic pH indicates that the detection limit is a reasonable indication of cadmium concentrations under these conditions.
- **Cobalt.** A strong relationship was shown for pH and cobalt concentrations. The bulk of the data describe increasing cobalt concentrations spanning several orders of magnitude as pH decreases from 9 to 3. The Fe/Al residues show a distinctive group at higher concentrations than the other residues. This group was defined by all three types of tests and implies a common solubility control for cobalt which is probably co-precipitated cobalt associated with iron oxides in this residue. Because this residue is also present in the combined residues and concentrations at neutral to basic pH are similar for all three tests, the data are a reliable indication of cobalt concentrations at neutral and moderately acidic pH when the Fe/Al residue is being leached.
- **Chromium.** Chromium results defined a strong pH relationship with all types of tests. Chromium concentrations showed a minimum at about pH 6 and higher concentrations for lower and higher pHs.

- **Copper.** The relationship for copper was similar to cobalt. At low pH, the Fe/Al residues showed the greatest concentrations in all test types. At higher pHs, copper concentrations were consistent for different residues. It appears likely that a copper oxide, co-precipitated with the iron oxide solids in the Fe/Al residue will control copper concentrations.
- **Iron.** Iron concentrations were mostly negatively correlated with pH except at the highest pH for which iron concentrations increased. Iron concentrations are higher than the ideal solubility of ferric hydroxide for pH greater than 4. This implies that ferric hydroxide was forming but that it formed as colloids which passed through the filter.
- **Manganese.** A strong negative correlation was apparent. Like Co and Cu, the Fe/Al residues showed the highest concentrations at lower pH implying that these residues were a source of co-precipitate. Because the relationship is indicated by all test types, the data appears to be a reliable indicator of manganese concentrations.
- **Molybdenum.** A positive relationship between molybdenum and pH was indicated for combined residues, Fe/Al residues and gypsum residues. The relationship at higher pHs was indicated by MDNR reactors and humidity cell samples.
- **Nickel.** The relationship for nickel was very similar to copper. The Fe/Al residues showed higher leachable nickel than other test types at acidic pH indicating that these residues with their elevated nickel concentrations probably contained co-precipitated nickel. Some leachates from the magnesium residues appeared to contain higher nickel concentrations than the combined residues possibly indicating a different solubility control (such as nickel hydroxide). The data for the combined residues which reflects the effect of leaching of Fe/Al residues imply lower nickel leaching from this control.
- **Lead.** Leaching of lead was apparent under acidic conditions but not neutral to basic conditions. Highest lead concentrations were apparent for the raffinate neutralization residue. The source of lead is unknown though this material contained the second highest lead concentration of any residue. Similar elevated lead concentrations were indicated for shake flasks and MDNR reactors but not for humidity cells.
- **Selenium.** Data for selenium showed that selenium leaching was greatest at higher pH and that concentrations were correlated with pH. The neutral to basic relationship was defined by all test types whereas under acidic conditions, greatest concentrations were shown by humidity cells implying that selenium was more soluble under these conditions than shown by the testwork.
- **Thallium.** In general, the relationship resembled nickel. The Fe/Al residue appeared to be the main source of leachable thallium and the relationship between pH and thallium concentration at neutral to basic pH was indicated by humidity cell and MDNR reactor leachates.
- **Zinc.** Like many other elements, the relationship for zinc appeared to be controlled by leaching of the Fe/Al residue as a source of co-precipitated zinc. Zinc concentrations at neutral to basic pH were consistently indicated by several different types of testwork.

Evaluation of metal concentrations with respect to pH indicates that under pH neutral to basic conditions, the concentrations indicated by humidity cells in combined residues are a reliable indicator of expected near equilibrium leaching. Maximum concentrations indicated in humidity cell leachates on combined residues (with gypsum) at neutral pH are shown in Table 6-2.

Leaching under acidic conditions is well-defined for the Fe/Al residue because solubility appears to be limited by the dissolution of iron oxides containing co-precipitated metal oxides of elements such as cadmium, cobalt, copper, manganese, nickel and zinc. For the acidic leach residue, upper limit solubility was not defined by the testwork; however, separate disposal of this waste is not contemplated.

Table 6-2: Summary of Maximum Concentrations Observed in Humidity Cell Leachates

Parameter	Concentration (mg/L)	Test Type
pH Range	6.6 to 8.5	All
SO ₄	7347	Humidity Cell
Al	0.18	Shake flask
As ¹	0.004	Humidity Cell
Cd	0.0004	Humidity Cell
Co	0.005	Humidity Cell
Cr	0.05	Humidity Cell
Cu	0.015	Humidity Cell
Fe	0.4	Humidity Cell
Mn	0.0023	Humidity Cell
Mo	0.14	Humidity Cell
Ni	0.098	Humidity Cell
Pb	0.0005	Humidity Cell
Se	0.054	Humidity Cell
Tl	0.0002	Humidity Cell
Zn	0.01	Humidity Cell

Notes:

1. Arsenic concentrations increased to 0.0075 mg/L as the test proceeded. The arsenic concentrations shown are for initial leachates for which maxima occurred for other parameters.

6.2 Trend Evaluation

6.2.1 Trends in Leachate Chemistry Shown by Testwork

As discussed in Section 5.3, various trends in leach chemistry have been observed. These include:

- pH which has trended steadily upward for most acidic residues and steadily downward for most non-acidic residues.

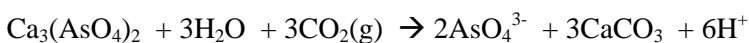
- Parameters showing general stable trends without apparent increases or decreases, for example sulfate and calcium for most test materials using all three test protocols. Some metals have also shown stable leaching.
- Parameters showing steady downward trends in concentrations, which include most metals.
- Parameters showing steady upward trends in concentrations, for example, arsenic in humidity cell leachates and boron in sequential shake flask and MDNR reactor tests.
- Undetectable trends due to concentrations below detection limits.

The main factors expected to contribute to trends in leachate chemistry are the presence of process solutions that presumably equilibrated with the solids prior to testing, the progressive dissolution of the solids by weekly additions of deionized water and removal of the leachate, and interaction between parameters that affect solubility (mainly pH).

The initial flushing of process waters typically yielded water containing high concentrations of sulphate, chloride, magnesium and sodium. Calcium concentrations were relatively low in the humidity cell leachates during this phase. Subsequent stable concentrations of some parameters can indicate that the solution is in chemical equilibrium with the solid(s) that are the source of the parameter, but also may indicate that the quantity available for dissolution during the leaching cycle is the same each week. The latter is not a chemical equilibrium. Sulfate is controlled by the dissolution of gypsum and SI's indicate that the solutions are in chemical equilibrium with gypsum in most cases. The exception is shown by the MDNR reactors and sequential shake flask tests on leach residues which yielded sulfate concentrations below the level expected for gypsum. This is probably a result of the lower concentrations of gypsum in this material.

General declining trends in metal concentrations may be due to shifts in pH (both downward and upward) and declining availability of readily leachable solids. Dissolution is controlled by available surface area which is expected to decline as the tests proceeded. In addition, as oxides age they become more crystalline trapping the co-precipitated metals and making the metals less leachable.

The upward trend in arsenic concentrations leaching from humidity cells containing combined residues occurs at low concentrations but appears to be related to the presence or absence of gypsum. The trend could be a result of breakdown of calcium arsenate which occurs as it equilibrates with carbon dioxide in the atmosphere:

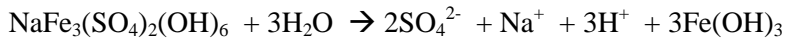


Calcium arsenate is not known to occur in the residues but arsenic concentrations are too low to allow detection of the compound directly.

6.2.2 Trends Beyond Testwork Time Frame

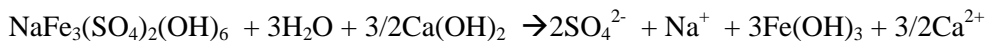
The proposed final disposal method will involve combination of all residues. The following discussion considers the long term pore water chemistry expected for the combined residues.

In the time frame of the tests, the combined residues were non-acidic because buffering capacity from brucite and possibly also calcite were present to offset the acidity produced by dissolution of natrojarosite:



Eventually, it is expected that acid buffering minerals will be exhausted and the residues will become acidic unless additional buffering capacity is added. This conclusion was confirmed by modeling the complete dissolution of all the mineralogical components of the residues in any of the proportions shown in Table 4-1 using React (Bethke 2005). As pH drops, metal mobility can also be expected to increase due to accelerated dissolution of the Fe/Al residue. Because the leach residue is dominantly natrojarosite and it is also the major component of the residue it is expected that acidification will result from dissolution of only a small proportion of the natrojarosite. However, under field conditions, dissolution of natrojarosite will be slow due to the slow movement of water through the residue mass.

PolyMet has proposed to add additional limestone or lime to the combined residues to ensure that they do not become acidic. The theoretical quantities of alkaline material needed can be calculated assuming the complete dissolution of natrojarosite balanced by calcium carbonate or hydroxide:



Using these reactions, the quantities of limestone or lime required are 6.2 and 2.3 g/kg per percent natrojarosite, respectively. This does not consider the effect of buffering by brucite from the Mg residue, which would reduce the requirement. These calculations assume the complete dissolution of natrojarosite. In reality, the process will not proceed to this endpoint because the conversion to ferric hydroxide will result in a decrease in volume and formation of iron hardpan. The latter will act as a barrier to water movement and dissolution of the residues.

6.3 Comparison of Results with Other Testwork Programs

As indicated in Section 2.2.1, other hydrometallurgical processes exist for recovery of metals from copper sulfide concentrates but none are directly comparable to the process proposed for the NorthMet Project. No comparisons with other testwork programs can be made.

6.4 Effect of Process Variations

The main process variation expected to occur is in the proportion of the various residues and the mineralogical composition of the residues. Changes in the proportion of leach and magnesium residues will result in a need to adjust the amount of basic material (i.e. limestone or lime) to be added. The magnesium residue would need to constitute about 50% of the combined residue to eliminate the need for additional basic material.

6.5 Conclusions

Characterization of hydrometallurgical residues has shown:

- Four of the residues (leach, gypsum, raffinate neutralization and Fe/Al) are expected to be acidic. The magnesium residue will be basic.
- The dominant mineral in the leach residue is jarosite, which generates acidic water when dissolved. Leach residue is the dominant component of the combined residues.
- The other residues (including magnesium) are mainly gypsum. The gypsum and raffinate neutralization residues are nearly entirely calcium sulfate. The Fe/Al residue also contains goethite, and the magnesium residue contains brucite.
- The Fe/Al residue also contains iron probably in amorphous form that contains co-precipitated metals.
- None of the residues were classified as hazardous wastes using the EPA 1311 protocol.
- Kinetic leach tests using three different protocols showed very similar results. Dissolution effects generally decreased with time though dissolution of gypsum exerted a very strong effect.
- Neutral to basic leachates produced by combined residues are believed to represent chemical saturation conditions suitable for prediction of pore water chemistry.
- The combined residue produced non-acidic leachate during the test but is expected to become acidic in the future unless additional basic material is added. PolyMet has proposed to add additional basic material as required to offset the acid potential of natrojarosite.

7 Pore Water Chemistry Prediction

7.1 Operational Model

7.1.1 Explanation of Modeling Approach

Because humidity cell test leachates had equilibrated with the residues, the testwork leachates are assumed to be an analogue for the residue pore water chemistry. No adjustment to the water chemistry is assumed to scale-up from test to site conditions.

7.1.2 Inputs to Water Quality Model

The main variable that could cause variations in water chemistry is inflow rate. However, because the concentrations in testwork leachates were found to be in equilibrium with the solids, concentrations will be independent of flow rate.

7.1.3 Results

Table 6-2 indicates predicted maximum expected concentrations in pore waters provided that pore waters remain non-acidic due to the addition of additional basic material to offset acidity produced by long term dissolution of natrojarosite. It is proposed that these are maximum values because they were produced by initial contact of leachates with the residues.

Leachate chemistry is expected to be dominated by the dissolution of gypsum, which will result in elevated sulfate concentrations. The presence of magnesium due to the dissolution of brucite ($\text{Mg}(\text{OH})_2$) will support higher sulfate concentrations than occurs for dissolution of pure gypsum.

The performance of combine residue without the gypsum residue is expected to be similar to combined residue with gypsum.

7.1.4 Conclusions

The chemistry of leachates in contact with combined residues in testwork has been estimated using results from leaching experiments.

7.2 Closure and Post-Closure Model

A separate prediction was not performed for closure conditions. Leachate chemistry as shown in Table 6-2 is expected to persist to closure. Slow movement of water through the residues is not expected to result in significant long term depletion of residues.

8 Conclusions

This report provides predicted pore water chemistry for the proposed disposal of combined residues in the hydrometallurgical residue cells. The results will be used to assess the requirement for treatment of residue leachates drained from cells at cell closure and the potential water quality impacts of leakage from the cells.

This report “**1UP005.01 – RS33/RS65 – Hydrometallurgical Residue Characterization and Water Quality Model – NorthMet Project - DRAFT**”, has been prepared by SRK Consulting (Canada) Inc.

Stephen Day, M.Sc., P.Geo. (British Columbia)
Principal Geochemist

9 References

- Allison, J.D., Brown, D.S., and Novo-Gradac, K.J. (1991). MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual, EPA/600/3-91/021. U.S. Environmental Protection Agency, Environ. Res. Lab., Athens, Ga.
- Barr Engineering. 2006. Environmental Sampling and Analysis Hydrometallurgical Process Liquids and Solids Sampling Results Pilot Test – NorthMet Deposit. Draft-02. May 15, 2006.
- Barr Engineering. 2007. RS28T - Hydrometallurgical Residue and Flotation Tailings Cell Design and Location. Draft-02. February 16, 2007.
- Bethke, C. 2005. The Geochemist's Workbench. A User's Guide to Rxn, Act 2, Tact, React, and Gtplot. Hydrogeology Program, University of Illinois. 184 pp.
- Ootokumpu 2006. HydroCopper™. <http://www.outokumputechnology.com/>.
- Parkhurst, D.L., and Appelo, C.A.J., 1999. User's guide to PHREEQC (Version 2)--a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.
- PolyMet Mining, 2007. Detailed Project Description. January 22, 2007.
- Price, W. 1997. Draft Guidelines and Recommended Methods for the Prediction of Metal Leaching and Acid Rock Drainage at Minesites in British Columbia. Reclamation Section, British Columbia Ministry of Energy and Mines. April 1997.
- SRK Consulting, 2005. Flotation Tailings and Hydrometallurgical Residue Geochemical Characterization Plan, NorthMet Project, Minnesota. Prepared for PolyMet Mining Inc. September 2005.
- TeckCominco, Undated. The CESL Process. Hydrometallurgical refinement of sulphide concentrates. http://www.cesl.com/downloads/cesl_brochure_english_2005.pdf.