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Memo

To:	Jim Scott, PolyMet	**Date:**	June 18, 2008
cc:	John Chapman, SRK Aus	**From:**	Stephen Day
Subject:	RS46 Agency Work Plan Request for Section 4.1 DRAFT	**Project #:**	1UP005.001

This memorandum responds to five requests in Section 4.1 of the RS46 workplan:

1. Is the 0.2 wt% S derived from the latest (as of July 2007) humidity cell data reasonable?
2. What do current data predict (i.e., are there any changes since July 2007)?
3. Have the NET acid-producing and acid-consuming reaction rates reached steady state (i.e., individual rates are all still changing and the NET rate must also be changing because pH is still going down) Is there a point at which the predicted critical S% will be very different?
4. The sometimes-very-significant (5 to 45%) adjustment required in the silicate weathering rate to obtain agreement between predicted and observed alkalinity and pH is bothersome. Why is the adjustment necessary and why does it vary so much?
5. LTV Tailings. SRK will provide backup writeup to address arsenic issue with LTV tailings. SRK will model PolyMet tailings pH to evaluate effects on LTV tailings and release of constituents.

The requests are addressed in a logical order. Updated leachate chemistry data were requested in this section and were provided previously.

1   Silicate Weathering Rate Adjustment and Calculation Method

1.1   Silicate Weathering Rate

RS46 described how the weathering rates input into the modeling were adjusted to reflect the difference between alkalinity indicated by analysis of leachates and that provided in the output from React (Geochemist's Workbench). It was found that alkalinity indicated by the model was greater than in the leachates and therefore the quantity of minerals allowed to react was adjusted downward to make the model alkalinity fit the observed alkalinity.

Further inspection of the output from React found that the model was calculating alkalinity from the carbon concentration using a factor of 100/12 rather than 50/12. Rockware confirmed this was a programming error in version 6 of the software. For subsequent modeling, pending receipt of the corrected code, the dissolved carbon was used.

Comparison of modeled dissolved carbon with dissolved carbon in the leachates showed the React model sometimes predicts carbon concentrations and pHs that are lower than observed in the actual leachates. In extreme cases, for example, React predicted a pH of 4.6 for cycle 104 of the P2 +100 mesh compared to observed leachate pH of 6.8. In most cases, the differences were less than 1 pH unit.

The most likely explanation for the difference is that the leachates do not fully reflect silicate weathering reactions in the humidity cells due to retention of leachates and incomplete dissolution of secondary minerals formed during weathering.

As a result of this finding, the revised calculation calibrated the model to produce comparable pH and dissolved carbon by increasing the quantity of silicate minerals reacting in the model.

1.2   Calculation Method

The review workplan requested a sample of the calculation. The attached spreadsheet shows the method used to re-calculate the critical values using recent data for the -100 mesh samples (Cycle 104).

Rows 174 to 176 show the input data for the calculation. Concentrations of Al, Sb, As, Mn and K are not used in the calculation.

The initial step is to model the measured leachate chemistry. The concentrations of sulfate, Ca, Mg and Na are used to calculate pyrrhotite[1], anorthite, forsterite and albite leached in millimoles using their formulae. For example, Ca concentrations were converted to anorthite (in units of mmol/kg) using the volume of water output (V_{output} in L), mass of the sample (M = 1 kg) and the mole weight of calcium (40 mg/mmol):

$$\frac{[Ca].V_{Output}}{M} \cdot \left(\frac{1}{40}\right)$$

Fayalite was calculated based on the composition of olivine indicated by microprobe.

These minerals were reacted with a dilute water of volume V_{output} with fixed carbon dioxide and oxygen partial pressures ($10^{-3.5}$ and 0.2, respectively). Concentrations Ca, Mg and Na of indicated by React were compared with the analyzed concentrations in the leachate to confirm correct data entry. The resulting pH, and TIC are recorded in the spreadsheet in row 181 for sample P2. The amount of silicates reacting was then increased to improve the fit of pH and TIC. In the case of P2, it was found that the initial concentrations resulted in an acidic solution and then increase in the silicates reacting by a factor of 25% resulted in a better fit. Possible explanations for the difference were described in the previous section.

The reacting amount of silicates required to fit the observed data was then used as input into calculation of the titration curve. Rows 190 to 202 show how pyrrhotite reacting (mmol/kg/week) was varied and React was used to predict pH and TIC. The resulting "oxidation rates" are then converted back to sulfate release in mg/kg/week using the molecular weight of sulfate (mg/kg/week). The regression relationship between sulfate and sulfide content was then used to calculate the equivalent sulfur concentration:

$S_{sulfide}(\%) = 0.013.SO_4$ (mg/kg/week) + 0.029.

Since the resulting sulfide concentration reflects data obtained at week 104, the concentration was back-calculated to the initial concentration using the oxidation rate and the time elapsed (104 weeks). This under-estimates the initial sulfur concentration because oxidation rates decrease with time.

The final step is to examine the resulting "titration curves" to determine sulfur concentrations when pH is 5.5 and 7. These sulfur concentrations were ratioed to the actual initial sulfur concentration to produce the graph shown as Figure 6-4 in RS46.

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[1] The form of sulfur was assumed to be pyrrhotite based on the visual identification of the mineral by optical methods. Subsequent XRD work by Lakefield on later tailings samples indicated that the sulfide may be pyrite but at the low levels of sulfur XRD is considered unreliable. Practically, the choice of iron sulfide makes no difference to the outcome of the calculation.

2   Steady State Conditions

Figure 1 illustrates recent humidity cell data. These data have been provided to the MDNR and EIS team in a separate submission. The assessment in RS46 used information available up to week 56. Sulfate release has generally decreased as the test has continued and in some cases this trend is continuing. Alkalinity has also followed a generally decreasing trend following sharp decreases that occurred about week 40. For most tests, alkalinity release appears to be stable. The major exception is P3 -200 mesh which continues to show decreasing alkalinity. Decreasing alkalinity release primarily tracks with decreasing calcium. Magnesium and sodium concentrations appear to have stabilized.

The current data appear to represent more stable conditions than those observed in week 56. Given that leaching of elements linked to silicate weathering appears to have stabilized while sulfate release may continue to decrease, it is believed the current conditions represent a condition in which net alkalinity release is lower than that observed in week 56. However net alkalinity will if sulfide oxidation rates continues to decrease. Because the net alkalinity release rate is lower, the current conditions will yield lower critical values than calculated at week 56.

3   Current Predictions

The original prediction method was repeated using data shown in Figure 1 to provide the calculations at two times during the testwork. The analysis as presented in RS46 was performed with data that continued to show a decreasing trend. The more recent data appears to represent more stable conditions for most tests. The titration curves for the same data used for RS46 are shown in Figure 2. Figure 3 shows the curves calculated for the more recent data. Figure 4 shows a graph of the type shown in RS46 as Figure 6-4 re-calculated for the RS46 data set. Figure 5 shows the same graph for the recent data

Figure 4 shows the correlation between the ratio of critical sulfur concentration to initial sulfur concentration and initial sulfur concentration for each sample. The sulfur concentration at a ratio of 1 indicates the initial sulfur concentration for which it is interpreted the pH condition would not be met at some time. The graph shows that the highest critical sulfur concentration (about 0.3%) would be for -200 mesh tailings. Coarse tailings show a lower critical value of between 0.17% and 0.18%. Bulk tailings are between the two extremes at 0.2% but generally showing behavior nearer to that of coarse rather than fine tailings.

In Figure 5, only the sulfur concentrations relative to pH 5.5 are shown because bulk and coarse tailings have generally made the transition to below pH 7 in the more recent data. The fine tailings remain above pH 7. The relationship in Figure 4 is apparent in Figure 5 but has shifted to the left and become less well defined. The critical level for bulk and coarse tailings is not distinguishable and the critical value is between 0.14% and 0.17%. For -200 mesh tailings, the critical level is shown to be between 0.25 and 0.3%.

In summary, the recent data indicate lower critical values than presented in RS46. The susceptibility of coarse and bulk tailings to pH depression has been shown by the kinetic testwork and incorporated into the water quality predictions. The fine tailings continue to have a higher predicted critical sulfur level.
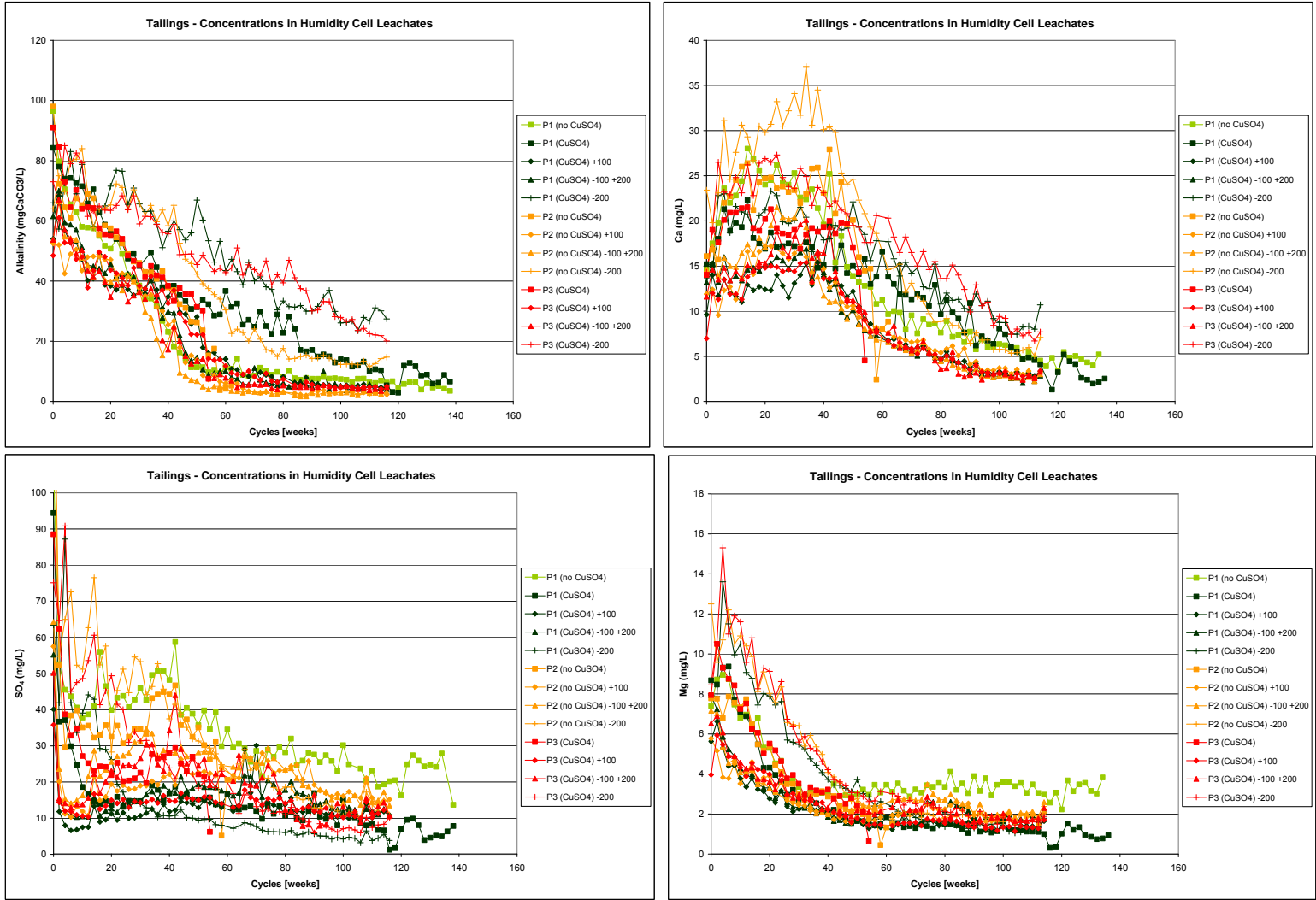
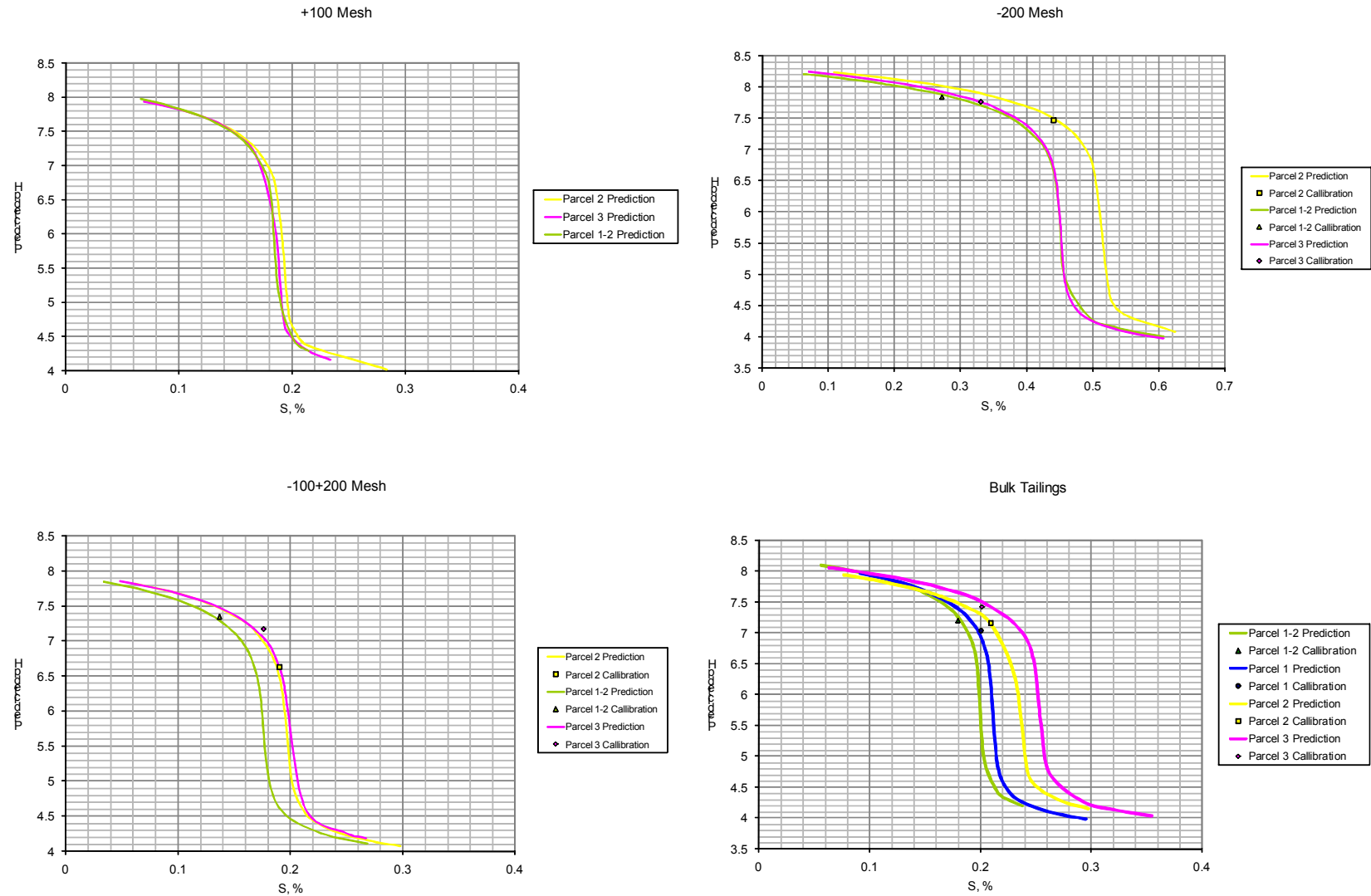**Figure 1. Recent Tailings Humidity Cell Data**

+100 Mesh

-200 Mesh

-100+200 Mesh

Bulk Tailings

Figure 2. Titration Curves - Data in RS46

+100 Mesh
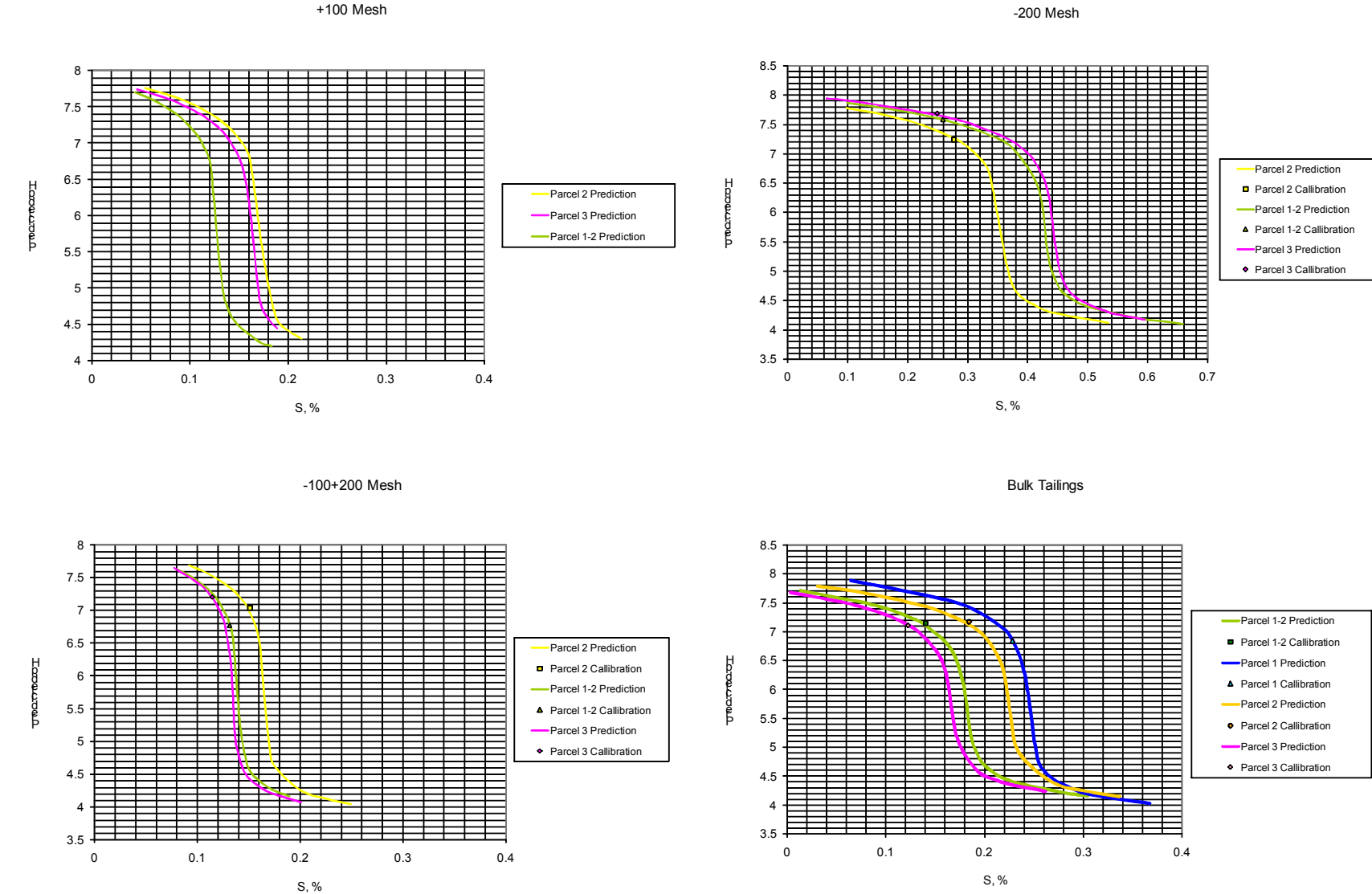
-200 Mesh

-100+200 Mesh

Bulk Tailings

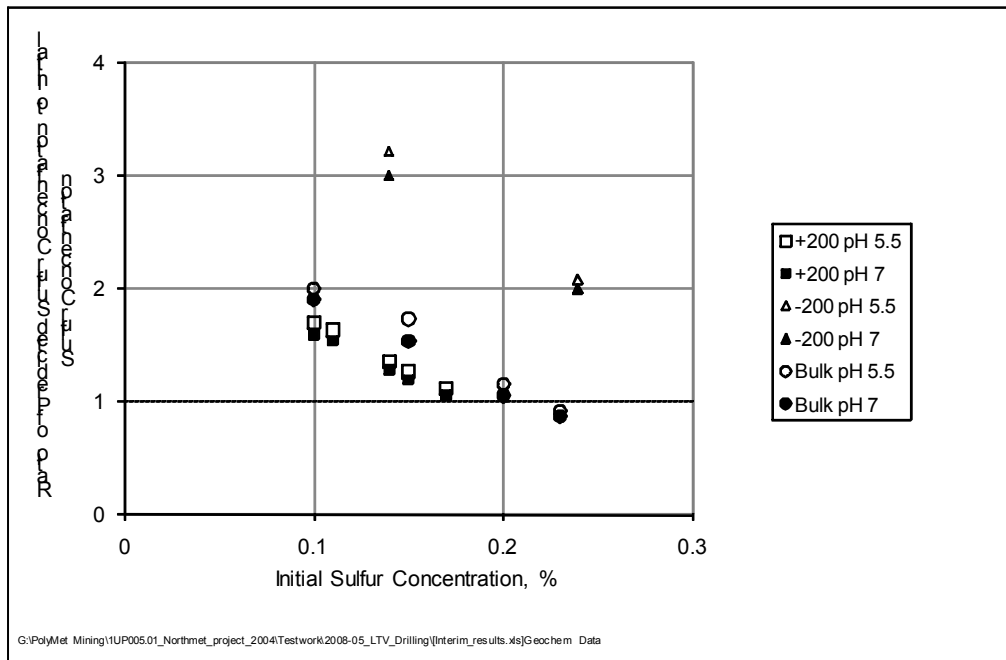**Figure 3. Titration Curves - Recent Data**

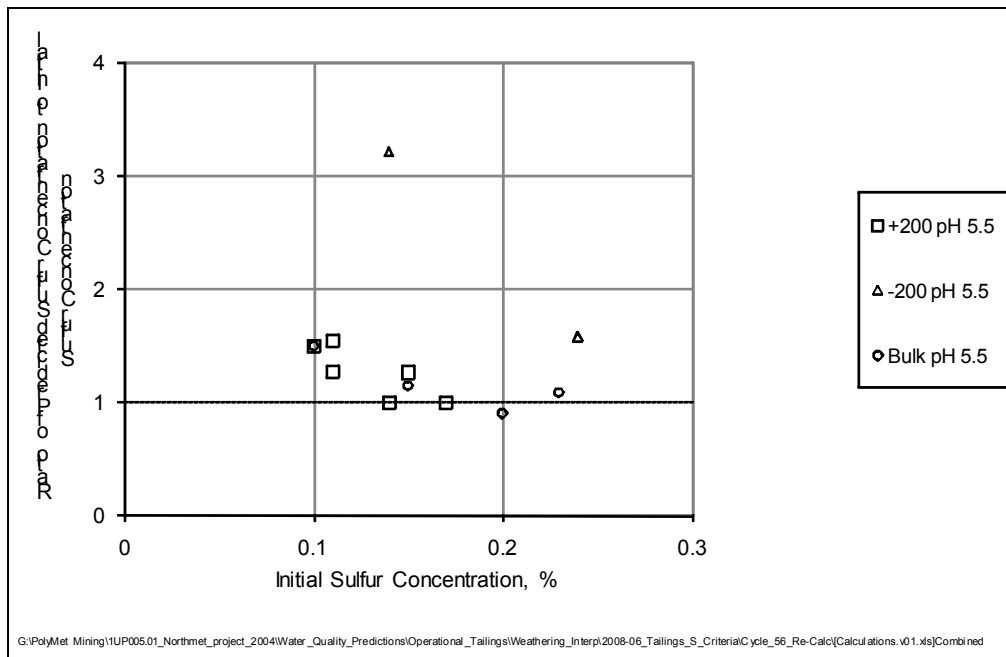**Figure 4. Critical Sulfur Values for RS46 Dataset**

Figure 5. Critical Sulfur Values for Recent Data

4 LTV Tailings Effects
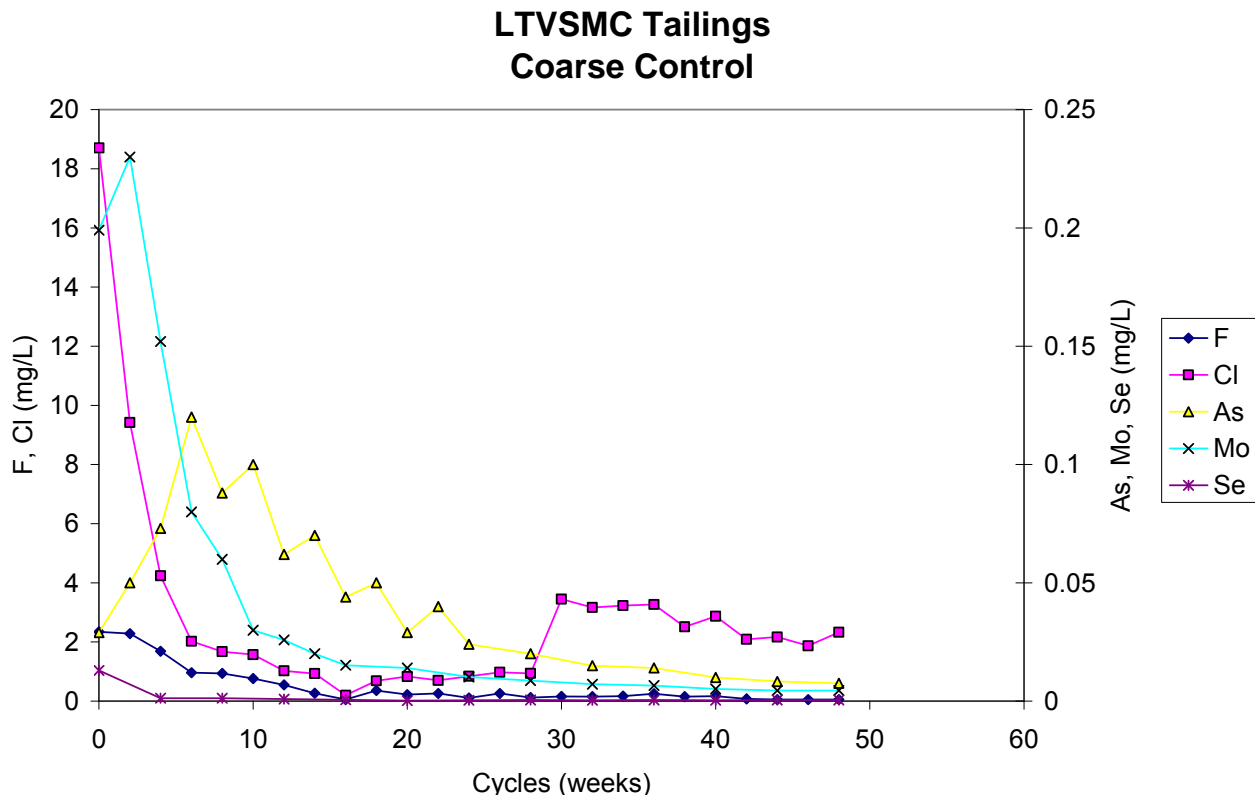
4.1 Arsenic Leaching

4.1.1 Background

Column leach test data for LTV tailings presented in RS46 showed unusual leaching of arsenic from LTV tailings compared to observed concentrations in waters at the tailings basin. As requested, this section provides additional discussion of this observation. Also new data are introduced for the coarse LTV tailings.

4.1.2 Observations

Column Tests

Testing of LTV tailings intended to evaluate the interaction between leachates from NorthMet tailings and LTV tailings was described in RS46. In summary, the tests were designed to evaluate possible effects on the LTV tailings caused by burial of LTV tailings beneath NorthMet Project tailings. Details of the experiment were provided in RS46.

All experiments showed elevated peak leaching of arsenic early in the test (6 weeks) at concentrations between 0.10 and 0.15 mg/L (e.g. Figure 6) from LTV tailings. Similar results were obtained for LTV control columns (no NorthMet tailings) and the LTV columns receiving leachates from the NorthMet tailings. The results indicated that the effect was not caused by the NorthMet tailings but was a characteristic of the LTV tailings.

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Figure 6. Leaching Trends for Coarse LTV Tailings Control.

The peak coincided with similar early peaks for a number of parameters including sulfate, fluoride, chloride, boron, molybdenum and selenium (Figure 6). While concentrations of fluoride, boron and molybdenum close to the observed peak levels from the control columns have been documented in groundwater and seeps at the LTV basin (Table 4-1, RS46), concentrations of sulfate and arsenic in the testwork were above maximum concentrations in groundwater. The peak arsenic concentrations were more than an order-of-magnitude above maximum concentrations in seeps and groundwater (maximum 0.0053 mg/L). Maximum sulfate concentrations in the testwork leachates were 899 mg/L compared to maximum of 530 mg/L in groundwater.

Characterization of Coarse LTV Tailings for Alternative Tailings Management

To support development of plans to use coarse LTV tailings for construction of the NorthMet Project tailings dams, samples of LTV tailings were collected from ten locations in four potential borrow areas (Figure 6) in May 2008. Borings were advanced until fine tailings were encountered.

Figure 7. Locations of Coarse LTV Tailings Sampling. Depths of borings are shown.

Thirty-three samples were tested for sulfur concentrations, an element scan (by aqua regia and four acid digestion) and water leachable components. The latter was performed as a shake flask type test (24 hour agitation) but with the lowest practical water to solid ratio (see attached data) in order to minimize dilution of leachates and detection of trace elements. Analytical results are attached.

Total sulfur concentrations varied from undetected to 0.09% with a median value of 0.02%. ICP sulfur concentrations were slightly higher (maximum 0.11%, median 0.04%). Sulfate sulfur was undetected (<0.01%) in all but two samples reported as 0.01% sulfur indicating that sulfur was dominated by sulfide (likely as pyrite). Shake flask leachates were basic (pH between 8.1 and 8.6) and dominated by bicarbonate, calcium and magnesium. Sulfate concentrations varied from 1 to 158 mg/L. The more significant leachable

trace elements included boron, fluoride and molybdenum (maxima of 0.23 mg/L, 2.56 mg/L, 0.28 mg/L, respectively). Maximum arsenic concentrations were 0.009 mg/L which is slightly greater than maximum concentrations in seepage.

Conversion of leachable sulfate and arsenic from concentrations in solution (mg/L) to solid (mg/kg) revealed a positive correlation (Figure 8). The leach ratio for these experiments was comparable to those observed in the column tests (As/S $\approx 10^{-4}$ on a molar basis).

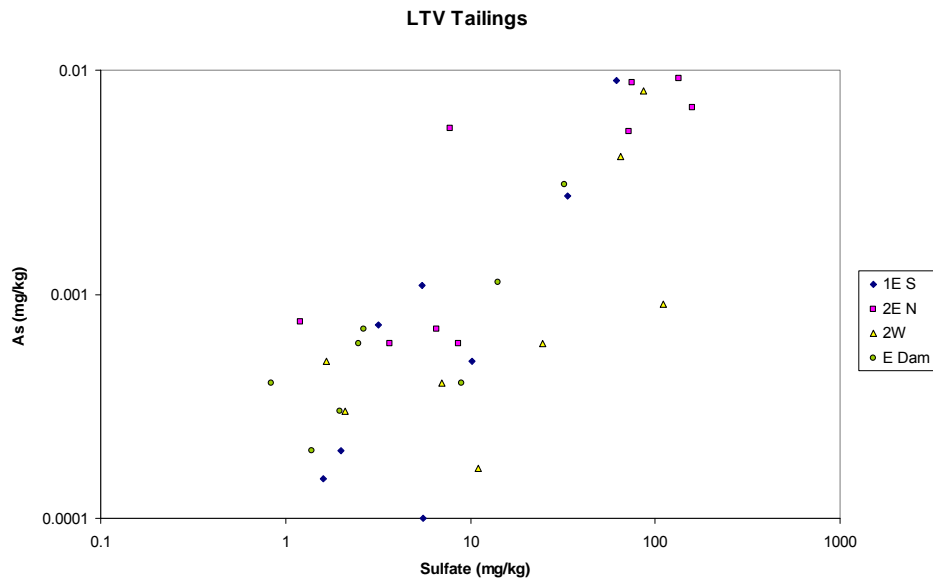Leachable sulfate and arsenic also increased with depth in tailings.

G:\PolyMet Mining\1UP005.01_Northmet_project_2004\Testwork\2008-05_LTV_Drilling\[Interim_results.xls]

Figure 8. Comparison of Leachable Arsenic and Sulfate for Coarse LTV Tailings Samples.

4.1.3   Possible Explanations for Difference Between Site Monitoring Data and Test Results

In general, column leach and shake flask tests are expected to yield similar to much lower concentrations compared to field waters provided that the field monitoring sites are unaffected by mixing with dilute background waters. Similar concentrations for laboratory and field may be produced if the leachate in the test equilibrates with minerals which limit solubility. This may be the case for fluoride which was near saturated with respect to fluorite in the column test leachates (Table 6-5, RS46). Lower concentrations in testwork are expected where the short flow path length and high solution volume to solid ratio results in limited contact time and dilution. This is particularly relevant for the shake flask leachates. For the column tests where concentrations of some parameters were comparable to field observations, it appears that contact time in the test was sufficient to equilibrate with some minerals and that groundwater maximums are not diluted to a major degree. The presence of testwork maximum concentrations in the column tests that were considerably above field observed maximum values implies that different weathering and leaching mechanisms occurred in the laboratory and field setting.

Three possible explanations for elevated arsenic concentrations were considered:

- The early "flush" phenomenon in the columns was partly due to weathering of the samples in storage prior to testing.
- De-sorption of arsenic sorbed during the taconite process.
- The effect of arsenic leaching from LTV tailings is not reflected in site monitoring data.

Pre-Test Weathering

The samples for column testing were collected in October 2005 and immediately tested for solids composition and mineralogy. The samples were then stored at room temperature in plastic bags for 6 months before being loaded into the columns for leach testing. XRD analyses showed that the tailings contained small amounts of pyrite (Table 5-1, RS46) which was reflected as low but detectable sulfur concentrations between 0.02 and 0.04%.

Sulfur leached from the columns was consistent with these concentrations indicating that pyrite was probably oxidized in storage and rapidly flushed at the beginning of the procedure. This mechanism indicates that pyrite was fully oxidized prior to the test and held as soluble sulfates. As the test started, the sulfate was immediately dissolved and highest concentrations were observed in the first leachates. Because sulfate is highly soluble and concentrations were below mineral saturation levels, the majority of the load was quickly flushed within a few cycles. Long term concentrations remain very low relative to the flush. Using this concept, any chalcophile (sulfur-preferring) elements contained in the pyrite would also be held as oxidation products until leaching started. The chalcophile elements include arsenic and selenium, as well as copper and zinc[2]. The rate of leaching of these oxidation products depends on the secondary minerals that they form when pyrite is oxidized.

Arsenic leaching was observed to lag behind sulfate by about 6 weeks (Figure 6). Possible explanations include a solubility control that depended on another parameter, and a lag effect due to sorption at high concentrations in pore water and desorption as leaching concentrations decreased.

It was concluded that the leaching of arsenic could reflect the rapid dissolution of oxidation products generated in storage prior to testing.

De-Sorption of Arsenic Sorbed During the Taconite Process

Berndt et al (1999) concluded that arsenic was sorbed to the tailings during processing of taconite ores because modeling showed that within the pH range expected in the tailings, arsenic is expected to be quantitatively fully adsorbed. This conclusion was supported by their observation that arsenic does not accumulate in process water compared to molybdenum and fluoride.

The sorption explanation for the delay in the arsenic peak (compared to sulfate) confirms that arsenic is sorbed but that de-sorption can occur. As arsenic is expected to be present as a negatively-charged species (oxyanion), desorption of existing sorbed arsenic could occur if pH of the leachate increased. However, the pH of the process water tended to be above 8 and approaching 9 (Berndt et al. 1999) and early leachates from the columns had pH below 8. Therefore, the decrease in pH would not encourage de-sorption of arsenic adsorbed during the process. In fact, the reverse would be expected. Sorbed arsenic at pH above 8 would be expected to be protected from de-sorption at pHs below 8.

The explanation of the observed delay in column tests of the arsenic flush produced by leaching of accumulated weathering products does not require a pH change but rather that the source of soluble arsenic decreases. The results are consistent with the tailings' capability to adsorb arsenic but indicate that the model finding of Berndt et al (1999) did not fully reflect the sorption behavior of arsenic on the LTV tailings.

Leaching Effect Not Reflected in Monitoring Data

This explanation would conclude that oxidation of the pyrite in tailings is leaching sulfate (as observed in seepage and groundwater) but that monitoring of seepage and groundwater has not detected peak leaching of arsenic because the peak has either not yet arrived or has passed.

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[2] The full element list is Ag, As, Bi, Cd, Cu, Ga, Ge, Hg, In, Pb, Po, S, Sb, Se, Sn, Te, Tl and Zn.

The recent sampling of the coarse LTV tailings showed they contain leachable sulfate and arsenic which is consistent with oxidation of the contained pyrite. The latter was leached at much lower concentrations than the column tests, but at slightly higher concentrations than observed under site conditions.

Leached amounts in the extraction tests were converted to estimated pore water concentrations (Table 1) using measurements of the moisture content from previous near surface characterization of the coarse LTV tailings (2.2 to 7.3%, 4.8% used, which translates to 9.9% saturation), porosity (0.48), and bulk density (1.6 t/m^3). A higher saturation level of 38% indicated by modeling of the PolyMet coarse tailings was also used to provide a second estimate. The low saturation levels are influenced by dry surface conditions and therefore concentrations are considered to be an upper bound. The higher saturation levels are considered to represent a lower bound because the saturation level is expected to be lower than 38%.

Table 1. Estimated Pore Water Sulfate and Arsenic Concentrations

Statistic	Observed Near Surface Saturation		PolyMet Coarse Tailings Modeled Saturation	
	Sulfate mg/L	Arsenic mg/L	Sulfate mg/L	Arsenic mg/L
Median	260	0.024	68	0.0061
95th Percentile	4000	0.3	1000	0.078
Maximum	5300	0.31	1400	0.081

As indicated above, leachable concentrations generally increased as depth increased, therefore, the 95th percentile and maximum concentrations possibly indicate pore water concentrations at depth in the coarse tailings. The calculations indicate pore water concentrations of both sulfate and arsenic exceeding concentrations observed in seepage. Upper bound sulfate concentrations are about an order-of-magnitude above observed sulfate confirming that the saturation level is probably greater than used in the calculation. The lower bound sulfate is within the same order as observed (i.e. about two times). The upper bound arsenic concentrations are greater than would be expected in pore waters but the lower bound is an order-of-magnitude above observed.

The lack of detection of arsenic concentrations at the expected levels in seepage may reflect the frequency of monitoring or a delay in arsenic appearance in seeps due to attenuation.

Conclusions and Implications

Weathering of the LTV tailings samples in storage prior to testing appears to be a plausible explanation for the observed flushing of sulfate and arsenic at the beginning of the column tests. However, this process is probably occurring in the unsaturated zone of the coarse LTV tailings, albeit at a much lower rate leading to the observed elevated sulfate concentrations in seepage. It is suspected but not demonstrated that arsenic concentrations above those observed in seepage occur in the basin pore waters but these are not yet expressed in seepage due to attenuation by iron oxides in the LTV tailings.

It is concluded that arsenic concentrations may increase in seepage at some time in the future regardless of whether the basin is used for disposal of PolyMet tailings.

In terms of the alternate plan for use of coarse LTV tailings, the flush of soluble load from the tailings will be included in the water quality predictions in addition to the ongoing effect of oxidation of the pyrite.

4.2   pH of PolyMet Pore Waters

4.2.1   Background

The workplan requested a prediction of the pH of the porewaters in the PolyMet tailings.

4.2.2   Observations
Key observations from water quality analyses and kinetic tests are as follows:

- The process water pH indicated by pilot plant testing in 2005 ranged from 8.1 to 8.75 (from a source water with a pH of 7.99), with a median value of 8.56.

- The pH of the leachates from most samples tested in the MDNR reactors commenced within the range of about 7.0 to 8.0, but rapidly converged to a range of about 7 to 7.5. Thereafter, typically after 30 weeks of testing, a decrease to within the pH range of 6.5 to 7.0 was observed. In the later stages of the tests (> ~60 cycles for whole samples), the pH again increased marginally to a relatively narrow range centred ranging from about 6.7 to 7.2.

- The pH of the leachates from the ASTM humidity cells commenced at a slightly more alkaline pH, ranging from about 7.6 to 8.4, but rapidly converged to a pH range to 7.8 to 8.0. Thereafter, the pH values decreased variously to as low as 6.5 but generally remained in the pH range of about 6.5 to 7.5. In the later stages (> 70 weeks) of the tests on the whole samples the leachate pH values generally were within the range of 6.9 to 7.5. (Note that the leachate to solid contact ratio for the MDNR cells was about five times higher than for the ASTM cells which will have contributed to the observed pH differences.)

- The particle size distribution may have an impact on the pH range, however there is no well defined correlation with the possible exception that the pH decrease occurred sooner and more rapidly for the coarser fractions

4.2.3   Geochemical Modeling

As discussed above, geochemical modeling completed using Geochemists' Workbench suggests that tailings can be produced which will not generate acid rock drainage if acid neutralization is reliant on carbonic acid weathering of silicate minerals.

Furthermore, as discussed in RS46, modelling of carbon dioxide diffusion into the tailings, together with the 'recycling' as carbon dioxide is released from bicarbonate neutralization of acidity generated at depths in excess of the depth of diffusion will support ongoing neutralization and maintain neutral tailings porewater.

4.2.4   Conclusions

Based on the available data and supporting geochemical modeling it is concluded that:

- While the tailings may be deposited with process water at pH 8.1 to 8.75, the tailings porewater would be expected to remain above pH 7.5 but below about 8 for the duration of operations since repeated flushing and covering of exposed tailings with freshly deposited tailings will negate the effects of extended exposure and oxidation as indicated by the kinetic tests.

- For some time after deposition ceases the tailings pH would be expected to remain above pH 7 but likely below 7.5, corresponding to the pH range for the early stages of ASTM humidity cells and DNR reactor.

- As the oxidation zone develops in the near surface tailings and carbon dioxide diffuses into the system, the porewater pH in the near surface layer (say between 1 and 2 m below surface) would be expected to decrease within the range of 6.5 to 7.0. Below this surface layer, as water percolates down, the pH would however increase to above pH 7 (likely 7 to 7.5) based on the geochemical modeling and supporting calculations.

- As the oxidation reactions lead to the depletion of sulphide minerals within the near surface layer, the pH is likely to rebound in the oxidation zone to about 7, but remain below 7.5 (later stages of kinetic tests). This will lead to a deeper but less aggressive oxidation zone in which the pH will decrease, but likely less markedly than in the more aggressive near surface oxidation zone, so that the pH profile from surface will be at or above 7 then decrease to between 6.5 and 7, and then increase again to about 7. The deeper the oxidation zone, the less the deviation is likely to be from pH 7 (depletion and transition reactions).

- This means that the pH of the bulk of the seepage from the base of the tailings deposit will remain in the range of 7 to 7.5. Locally however it is possible that toe seepage could occur that is between 6.5 and 7 due to short flow paths, near surface effects and so. This would be restricted to zones within the immediate distance of the embankment toe where the benefit of transition and deeper zones reactions would not be available.

In conclusion, the pH of water exiting the NorthMet Project tailings and entering the LTV tailings is expected to be comparable to existing pHs in the LTV tailings. No leaching effects due to differences in pH are expected as the NorthMet Project tailings pore waters come into contact with LTV tailings.