# CARMACKS COPPER PROJECT CARMACKS, YUKON

# PROCESS WATER TREATABILITY STUDY REPORT NEUTRALIZATION TESTWORK on PROCESS SOLUTIONS

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## TABLE OF CONTENTS

<b>1.0</b> 1.1 1.2	OBJECTIVE	.1
<b>2.0</b> 2.1	EXPERIMENTAL APPROACH	
3.0	RESULTS & DISCUSSION	6
3.1	Feed Sample	.6
3.2	Neutralization Test	.7
3	.2.1 Reagent Requirements	10
3	.2.2 Sludge Generation & Settling Data	11
3.3	90-minute Retention Time	13
3.4	High Iron to Total Metals Ratio	15
3.5	HDS Simulation	18
3.6	LC50 Acute Toxicity Analysis	
4.0	CONCLUSIONS	22

## LIST OF TABLES

Table 1. Feed Characterization (in mg/L)	6
Table 2. Raffinate Neutralization Results Summary (in mg/L)	8
Table 3. PLS Neutralization Results Summary (in mg/L)	9
Table 4. Lime Requirement	11
Table 5. Impact of retention time on effluent quality for Raffinate (in mg/L)	13
Table 6. Impact of retention time on effluent quality for PLS (in mg/L)	14
Table 7. Impact of high iron concentration on effluent quality for Raffinate (in mg/L)	16
Table 8. Impact of high iron concentration on effluent quality for PLS (in mg/L)	17
Table 9. Lime Requirement with high iron concentration	18
Table 10. HDS simulation at pH 9.5 for Raffinate (in mg/L)	19
Table 11. HDS simulation at pH 9.5 for PLS (in mg/L)	20
Table 12. Lime Requirement with Sludge Recycle	21

## LIST OF FIGURES

Figure 1. Raffinate & PLS Settling Test	. 12
Figure 2. Sludge Generation Summary	.12

## LIST OF APPENDICES

- Appendix A. Settling Test data
- Appendix B. EVS-Golder Toxicity Analysis Report
- Appendix C. MAXXAM Analysis Report

## 1.0 OBJECTIVE

The primary objective of this treatability study was to demonstrate the viability of chemical precipitation using lime to treat PLS and Raffinate solution should circumstances require the plant to release excess solution into the water management system. The testing was conducted to determine the effectiveness of chemical precipitation, in particular the High Density Sludge (HDS) process, to meet acceptable discharge targets. Additionally, the results of this testing will be used to estimate reagent requirements and sludge generation rates and provide potential design parameters for a conceptual design. The following report provides detail of that work and the conclusions reached as a result.

## 1.1 The HDS Process

The effective removal of base metals in a chemically stable form in the HDS process is primarily the result of the formation of co-precipitates with iron on the surfaces of the recycled sludge particles. The chemical stability of the precipitate is favorably influenced by a high iron to total metals ratio in the treatment plant feed. Typically, a sludge recycle loop is used to increase this ratio. However, a simple recycle is sometimes not sufficient to change metal ratios and, in extreme examples, iron may have to be added. Otherwise, the storage site for the sludge produced must allow for the possibility of long-term instability. In all cases, the oxidation of ferrous iron to ferric iron is the principal oxygen-consuming reaction, and oxygen transfer into solution may well be controlling the reaction and hence the reactor tank sizing.

Design plant throughput is also influenced by the volume of water to be treated. For example, seasonal changes will determine variations in run-off, much of which may have to be treated. Increased flow may be accompanied by a dilution of contaminants, both acid and metal, and the resulting plant influent may require reduced oxidation and/or residence time, thus compensating for the increased flow.

The near-complete precipitation of the metals as hydroxides in the neutralization process proceeds according to the following reactions:

 $M^{++} + SO_4^{=} + Ca^{++} + 2(OH)^{-} + 2H_2O \rightarrow M(OH)_2 + CaSO_4 \bullet 2H_2O$  $2M^{+++} + 3(SO_4)^{=} + 3Ca^{++} + 6(OH)^{-} + 6H_2O \rightarrow 2M(OH)_3 + 3CaSO_4 \bullet 2H_2O$ 

As implied by the equations above, the products of these reactions are metal hydroxide precipitates and calcium sulfate (gypsum). If the sulfate concentration of the wastewater is high enough, there will be sufficient gypsum produced to exceed its solubility and it will precipitate with the sludge.

The main features of the HDS process can be summarized as follows: Lime  $[Ca(OH)_2]$  and recycled sludge are added to the lime-sludge mix tank at the head of the process, providing the main neutralization agent. This mixture is discharged to the rapid mix tank where it is mixed with influent, thereby achieving neutralization. This mixture is fed to the main lime reactor where a combination of aggressive aeration and high shear agitation ensures optimum process chemistry and subsequent clarifier performance. The discharge from the lime reactor is treated with flocculant in the flocculation tank. In the final step, the clarifier separates the treated effluent from the sludge, a portion of which is recycled to the head of the process.

The HDS process is normally operated at a pH between 9.0 and 9.5, as most metals encountered will precipitate at or below this concentration of hydroxide ions. Oxidation of ferrous to ferric iron takes place rapidly at this pH, with air being the most common oxidizing agent.

For efficiency, the process relies on sludge recycle from the treated effluent. In most plants this is achieved in a thickener-style clarifier, which provides pumpable sludge in the underflow as the separated solids product. Recycling sludge from a settling pond or from filters are alternatives but they may present handling problems.

### 1.2 Advantages of the HDS Process

The HDS process has many advantages over other lime precipitation systems. The most important of these is a substantial reduction in sludge volume resulting from an increase in sludge density. An increase from 5 percent solids to 40 percent solids is typical of HDS systems; this reduces the volume of sludge produced by over 95 percent. The resulting reduction in sludge disposal costs increases the cost effectiveness of the process. In addition to reduced sludge volume and superior sludge density, there is an increase in sludge stability, both chemically and physically. Within a few days of deposition, the sludge can drain to in excess of 65 percent solids and possesses enough physical stability to support the heavy equipment on the surface of the impoundment area. Chemically the sludge has shown

excellent stability characteristics at mining sites in British Columbia, Canada and at numerous other sites. Following twenty-five years of impoundment at one facility, there has been no contamination of the surrounding groundwater or any other evidence of metal reversion.

Other advantages of the HDS process include:

- A high quality effluent is produced,
- The process is easily automated,
- HDS is a proven technology, and
- Operating plants consist of standard equipment available from many competitive manufacturers, which reduces the need for large spare parts inventories,
- Lower neutralization costs than conventional lime treatment.

## 2.0 EXPERIMENTAL APPROACH

Two containers (approximately 15 liters each) containing samples of PLS and Raffinate were shipped to CEMI in January 2007 for bench-scale neutralization testing. The samples were obtained from ongoing large column leach testwork being conducted at PRA laboratory on ore samples from the Carmacks Copper Project in Yukon. A 250 mL aliquot of each solution was taken for head analysis. The samples were filtered through a 0.45 micron membrane filter and analyzed for pH, conductivity and sulfate at CEMI while total metals, total sulfur and total dissolved solids (TDS) analysis were analyzed at Maxxam Analytics located in Vancouver, BC.

## 2.1 Testing Program

The testing program consisted of four steps. The first step consisted of a preliminary screening procedure to evaluate lime dosage rates. Aliquots of 1500 mL of the feed water were added to four 1-liter beakers. Lime was added in different dosages to yield a final pH ranging from 8.0 to 9.5 (in 0.5 pH increments). Rapid mixing was used and pH was maintained at the desired level with addition of lime. After 60 minutes of high agitation allowing time for oxidation, solution was transferred into a 1-liter graduated cylinder and flocculant was added to determine the settling rate. During the rapid mixing, samples were collected for metal analysis after 15 minutes, 30 minutes and 60 minutes to determine the appropriate residence time for oxidation. At the conclusion of the settling period, the solution was filtered through a 0.45 micron membrane filter, filter cake was dried and weighed to determine solids generation and the filtrate was sent to Maxxam Analytics in Vancouver, Canada for metal, total sulphur and TDS analysis.

In the second step of the test program, the pH that provided the best effluent quality in the first step was used and retention time was increased from 60 minutes to 90 minutes in order to determine the affect of longer reaction time on effluent water quality. At the completion of the tests, the solution was filtered and submitted for metal analysis as described in step one.

In the third step of the test program, iron in the form of ferrous sulphate was added to the feed solution to determine the affect of high iron concentration on effluent quality. Iron is a common ingredient which aids in heavy metals removal by co-precipitation and generally results in lower metals concentration in the effluent than otherwise.

Once results of all three steps were available, a large batch of water was treated using the best combination of pH, iron addition and retention time that provided the best effluent quality with lowest mass of sludge. The treatment was carried out in the following manner:

A 500 mL sample of the contaminated water was neutralized to the pH selected in the initial screening tests with lime slurry, followed by flocculant addition, settling, and decanting the overflow in order to recycle sludge. The required amount of lime was then added to the settled sludge and the sludge/lime mixture was well mixed followed by another 500 mL of the contaminated water being added to this mixture. The slurry was agitated for reaction time determined in the initial tests. This procedure was repeated 10 times. The overflow from the final cycle was filtered and submitted for chemical analysis.

Once all the results were available and reviewed by WCC, another 3.0L of the sample was neutralized to the optimum pH and retention time. After neutralization, the slurry was filtered and the pH was adjusted to 8.0 by sparging the solution with CO<sub>2</sub>. The filtrate was then sent to EVS Golder in North Vancouver, BC for LC50 tests using Daphnia Magna.

## 3.0 RESULTS & DISCUSSION

## 3.1 Feed Sample

The table below summarizes the metals contained in the feed water.

	MMER Limit	Raffinate	PLS
pН		1.98	3.55
Aluminum (Al)		5680	5180
Antimony (Sb)		<0.005	<0.005
Arsenic (As)	0.50	0.024	<0.005
Barium (Ba)		0.02	0.02
Beryllium (Be)		0.247	0.233
Bismuth (Bi)		<0.5	<0.5
Boron (B)		<0.08	<0.08
Cadmium (Cd)		0.965	0.873
Calcium (Ca)		492	456
Chromium (Cr)		2.24	2.22
Cobalt (Co)		18	17.6
Copper (Cu)	0.30	4.88	1470
Iron (Fe)		22.4	20.1
Lead (Pb)	0.20	0.017	0.004
Lithium (Li)		1.08	1.08
Magnesium (Mg)		5890	5340
Manganese (Mn)		688	643
Molybdenum (Mo)		0.37	0.28
Nickel (Ni)	0.50	14.1	12.7
Phosphorus (P)		5	5
Potassium (K)		15	30
Selenium (Se)		0.202	0.205
Silicon (Si)		102	101
Silver (Ag)		0.157	0.149
Sodium (Na)		79.5	77.8
Strontium (Sr)		0.35	0.34
Thallium (TI)		<0.0005	<0.0005
Tin (Sn)		<20	<0.2
Titanium (Ti)		<0.03	<0.03
Uranium (U)		0.451	0.461
Vanadium (V)		<0.05	<0.05
Zinc (Zn)	0.50	72	68.4
Zirconium (Zr)		<0.05	<0.05
Sulphur (S)		19200	19400
Total Dissolved Solids		81900	83200
Notes:			

 Table 1. Feed Characterization (in mg/L)

Bold - Exceeds MMER discharge target

As indicated in the above table, the primary metals of concern are aluminum, copper, manganese, nickel, selenium and zinc.

## 3.2 Neutralization Test

The feed sample was neutralized to pH 7.5, 8.0, 8.5 and 9.5 using hydrated lime with the lime being added as a 20% slurry. For each test, a 1500 mL sample was neutralized to the selected pH while being vigorously agitated. The neutralized sample was agitated for 60 minutes while maintaining the selected pH by adding additional lime when necessary. Samples were taken after 15 minutes, 30 minutes and 60 minutes of reaction time. After 60 minutes, solution was transferred into a graduated cylinder, flocculant (Percol E10 was selected based on flocculant scoping tests) was added, and the slurry was allowed to settle. The interfacial height between the slurry and the overflow was recorded every minute for the first 10 minutes, and after regular intervals up to 180 minutes. After the settling test, the sample was filtered and the filter cake was dried and weighed to determine the sludge generation. The following table summarizes the results of the neutralization tests.

	MMER	Raffinate	pH 7.5	pH 8.0	pH 8.5	рН 9.5
	Limit		(60min)	(60min)	(60min)	(60min)
pН		1.98	7.61	8.01	8.43	9.40
Aluminum (Al)		5680	0.241	0.678	1.02	1.17
Antimony (Sb)		<0.005	<0.005	<0.005	<0.005	<0.001
Arsenic (As)	0.50	0.024	0.006	0.006	<0.005	0.003
Barium (Ba)		0.02	0.02	<0.01	<0.01	0.009
Beryllium (Be)		0.247	<0.002	<0.002	<0.002	<0.0002
Bismuth (Bi)		<0.5	<0.5	<0.5	<0.5	<0.05
Boron (B)		<0.08	<0.08	<0.08	<0.08	<0.008
Cadmium (Cd)		0.965	0.0239	0.0083	0.0043	0.0007
Calcium (Ca)		492	445	431	449	480
Chromium (Cr)		2.24	<0.005	<0.005	<0.005	<0.001
Cobalt (Co)		18	0.222	0.064	0.014	0.0019
Copper (Cu)	0.30	4.88	0.334	0.218	0.142	0.069
Iron (Fe)		22.4	<0.05	<0.05	<0.05	<0.005
Lead (Pb)	0.20	0.017	0.068	<0.003	<0.003	<0.0005
Lithium (Li)		1.08	0.771	0.637	0.455	0.036
Magnesium (Mg)		5890	4610	4120	3520	340
Manganese (Mn)		688	123	64.3	28.6	0.546
Molybdenum (Mo)		0.37	0.1	0.15	0.14	0.141
Nickel (Ni)	0.50	14.1	<0.08	<0.08	<0.08	<0.008
Phosphorus (P)		5	<1	<1	<1	<0.1
Potassium (K)		15	20	12	15	23
Selenium (Se)		0.202	0.139	0.126	0.117	0.071
Silicon (Si)		102	0.6	<0.5	<0.5	0.22
Silver (Ag)		0.157	0.109	0.11	0.0869	0.0558
Sodium (Na)		79.5	67.6	65.9	64.6	61.6
Strontium (Sr)		0.35	3.39	3.37	2.54	2.56
Thallium (TI)		<0.0005	<0.0005	<0.0005	<0.0005	0.0001
Tin (Sn)		<20	<0.2	<0.2	<0.2	<1
Titanium (Ti)		< 0.03	< 0.03	<0.03	<0.03	<0.003
Uranium (U)		0.451	0.0064	0.0072	0.0053	0.0008
Vanadium (V)		<0.05	<0.05	<0.05	<0.05	<0.005
Zinc (Zn)	0.50	72	< 0.05	<0.05	<0.05	<0.005
Zirconium (Zr)		<0.05	<0.05	<0.05	<0.05	<0.005
Sulphur (S)		19200	6130	5500	4760	973
Total Dissolved Solids		81900	28200	25600	21900	4320

Table 2. Raffinate Neutralization Results Summary (in mg/L)

Notes:

Bold – Exceeds process water quality target

	MMER	PLS	pH 7.5	pH 8.0	pH 8.5	рН 9.5
	Limit		(60min)	(60min)	(60min)	(60min)
pН		3.55	7.60	8.04	8.49	9.45
Aluminum (Al)		5180	0.213	0.41	0.616	6.06
Antimony (Sb)		<0.005	<0.005	<0.005	<0.005	<0.001
Arsenic (As)	0.50	<0.005	0.006	0.007	<0.005	0.002
Barium (Ba)		0.02	0.01	0.01	0.01	0.011
Beryllium (Be)		0.233	<0.002	<0.002	<0.002	< 0.0002
Bismuth (Bi)		<0.5	<0.5	<0.5	<0.5	< 0.05
Boron (B)		<0.08	<0.08	<0.08	<0.08	<0.008
Cadmium (Cd)		0.873	0.0169	0.0089	0.0048	0.0001
Calcium (Ca)		456	419	409	411	535
Chromium (Cr)		2.22	<0.005	<0.005	<0.005	<0.001
Cobalt (Co)		17.6	0.045	0.011	0.004	<0.0005
Copper (Cu)	0.30	1470	0.159	0.124	0.101	0.0416
Iron (Fe)		20.1	<0.05	<0.05	<0.05	0.009
Lead (Pb)	0.20	0.004	<0.003	<0.003	<0.003	<0.0005
Lithium (Li)		1.08	0.151	0.162	0.274	0.005
Magnesium (Mg)		5340	4090	3620	2960	7.1
Manganese (Mn)		643	92.7	41.1	20.9	0.033
Molybdenum (Mo)		0.28	0.07	0.05	0.08	0.038
Nickel (Ni)	0.50	12.7	<0.08	<0.08	<0.08	<0.008
Phosphorus (P)		5	<1	<1	<1	<0.1
Potassium (K)		30	17	15	12	23
Selenium (Se)		0.205	0.131	0.128	0.105	0.039
Silicon (Si)		101	0.7	0.6	<0.5	0.13
Silver (Ag)		0.149	0.0971	0.0998	0.0842	0.0187
Sodium (Na)		77.8	66.6	64.5	60.9	59.5
Strontium (Sr)		0.34	3.55	3.85	3.29	2.55
Thallium (TI)		<0.0005	<0.0005	<0.0005	<0.0005	0.0001
Tin (Sn)		<0.2	<0.2	<0.2	<0.2	<1
Titanium (Ti)		<0.03	<0.03	<0.03	<0.03	<0.003
Uranium (U)		0.461	0.0047	0.0042	0.0021	0.0001
Vanadium (V)		<0.05	<0.05	<0.05	<0.05	<0.005
Zinc (Zn)	0.50	68.4	<0.05	<0.05	<0.05	0.018
Zirconium (Zr)		<0.05	<0.05	<0.05	<0.05	<0.005
Sulphur (S)		10400	E 470	4070	4000	FOO
Sulphur (S)	 	19400	5470	4870	4090	500
Total Dissolved Solids		83200	26500	22600	19200	2420

**Table 3.** PLS Neutralization Results Summary (in mg/L)

Notes:

**Bold** – Exceeds process water quality target

Based on the test data summarized in Table 2 and Table 3 above, it was determined that neutralization at pH 9.5 would be required due to high TDS and sulphur concentration at lower pH as well as lower manganese, copper and other metals concentrations at pH 9.5. Furthermore, as illustrated in Figure 1 below, as the operating pH increases aluminum is

dissociated back into solution while manganese and copper concentrations decrease in solution.

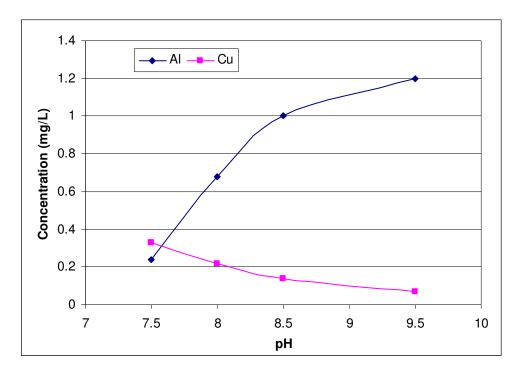


Figure 1. Aluminum & Copper Concentration with increasing pH

It may seem that a two stage system may be required to remove manganese and aluminum; however, all HDS plants that are currently operating in a single stage system are effectively able to remove aluminum and manganese. The sulfate concentration which remained high (above 2500 mg/L) is possibly due to lack of crystal seed formation to enhance the precipitation of gypsum and possibly, the low amount of recycled sludge. The expected sulfate in the industrial plant should be in the range of 1800 to 2000 mg/L.

## 3.2.1 Reagent Requirements

The lime usage in the bench-scale testing is summarized in Table 3. Lab grade calcium hydroxide prepared as a 20% slurry was used for testing under optimal temperature and agitation; therefore, the results may vary from the field consumption.

Test	Initial pH	Sample	Target	Test	20% Lime	Lime Consumption
#	initial pri	Vol. (mL)	pН	pН	(mL)	(g/L)
PLS 1		1500	7.5	7.7	244	32.5
PLS 2	3.55	1500	8.0	8.04	247	32.9
PLS 3		1500	8.5	8.46	286	38.1
PLS 4		1500	9.5	9.45	354	47.2
RAFF 1		1500	7.5	7.61	244	32.5
RAFF 2	1.98	1500	8.0	8.01	271	36.1
RAFF 3		1500	8.5	8.43	305	40.7
RAFF 4		1500	9.5	9.4	386	51.5

 Table 4. Lime Requirement

## 3.2.2 Sludge Generation & Settling Data

As shown in Figure 2 below, the sludge generated during the neutralization was observed to be white in colour (due to high aluminum content) and increased with pH. The sludge generation is summarized in Figure 2 below and detailed settling test results are provided in Appendix A.

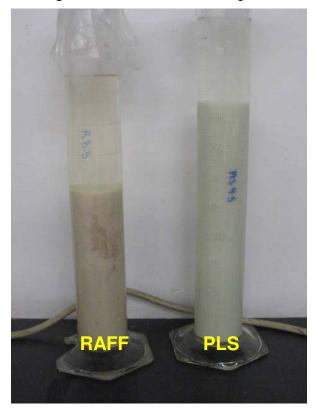
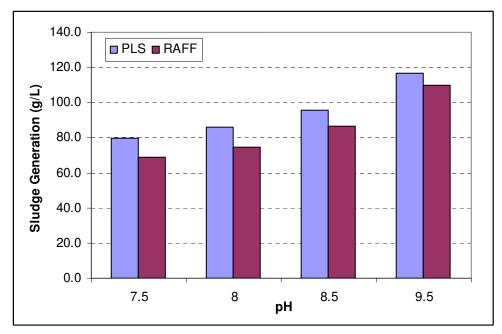


Figure 2. Raffinate & PLS Settling Test





## 3.3 90-minute Retention Time

Altering of retention time was evaluated to understand the impact of retention time on the effluent quality. This phase of the testing program was conducted at pH 9.5 based on the results of the first phase of the work, which showed a pH of 9.5 was necessary to achieve low concentrations of manganese and copper.

	MMER	Raffinate	рН 9.5	pH 9.5
	Limit	naiiiiale	(60min)	(90min)
pН		1.98	9.40	9.49
Aluminum (Al)		5680	1.17	8.06
Antimony (Sb)		<0.005	<0.001	<0.001
Arsenic (As)	0.50	0.024	0.003	0.001
Barium (Ba)		0.02	0.009	0.009
Beryllium (Be)		0.247	<0.0002	<0.0002
Bismuth (Bi)		<0.5	<0.05	<0.05
Boron (B)		<0.08	<0.008	0.039
Cadmium (Cd)		0.965	0.0007	0.0002
Calcium (Ca)		492	480	603
Chromium (Cr)		2.24	<0.001	<0.001
Cobalt (Co)		18	0.0019	<0.0005
Copper (Cu)	0.30	4.88	0.069	0.0219
Iron (Fe)		22.4	<0.005	0.009
Lead (Pb)	0.20	0.017	< 0.0005	<0.0005
Lithium (Li)		1.08	0.036	0.014
Magnesium (Mg)		5890	340	22.9
Manganese (Mn)		688	0.546	0.045
Molybdenum (Mo)		0.37	0.141	0.106
Nickel (Ni)	0.50	14.1	<0.008	<0.008
Phosphorus (P)		5	<0.1	<0.1
Potassium (K)		15	23	23
Selenium (Se)		0.202	0.071	0.023
Silicon (Si)		102	0.22	0.12
Silver (Ag)		0.157	0.0558	0.0128
Sodium (Na)		79.5	61.6	60.5
Strontium (Sr)		0.35	2.56	2.86
Thallium (TI)		<0.0005	0.0001	<0.0001
Tin (Sn)		<20	<1	<0.2
Titanium (Ti)		<0.03	<0.003	<0.003
Uranium (U)		0.451	0.0008	0.0001
Vanadium (V)		<0.05	<0.005	<0.005
Zinc (Zn)	0.50	72	<0.005	<0.005
Zirconium (Zr)		<0.05	<0.005	<0.005
Sulphur (S)		19200	973	514
Total Dissolved Solids		81900	4320	2460

Table 5. Impact of retention time on effluent quality for Raffinate (in mg/L)

	MMER	PLS	pH 9.5	pH 9.5
- 1.1	Limit	0.55	(60min)	(90min)
pH		3.55	9.45	9.38
Aluminum (Al)		5180	6.06	20.1
Antimony (Sb)	0.50	< 0.005	< 0.001	< 0.001
Arsenic (As)	0.50	< 0.005	0.002	0.001
Barium (Ba)		0.02	0.011	0.007
Beryllium (Be)		0.233	<0.0002	< 0.0002
Bismuth (Bi)		<0.5	< 0.05	< 0.05
Boron (B)		<0.08	<0.008	<0.008
Cadmium (Cd)		0.873	0.0001	<0.0001
Calcium (Ca)		456	535	619
Chromium (Cr)		2.22	<0.001	<0.001
Cobalt (Co)		17.6	<0.0005	<0.0005
Copper (Cu)	0.30	1470	0.0416	0.0306
Iron (Fe)		20.1	0.009	0.03
Lead (Pb)	0.20	0.004	<0.0005	<0.0005
Lithium (Li)		1.08	0.005	0.006
Magnesium (Mg)		5340	7.1	3.85
Manganese (Mn)		643	0.033	0.028
Molybdenum (Mo)		0.28	0.038	0.041
Nickel (Ni)	0.50	12.7	<0.008	<0.008
Phosphorus (P)		5	<0.1	<0.1
Potassium (K)		30	23	23
Selenium (Se)		0.205	0.039	0.027
Silicon (Si)		101	0.13	0.14
Silver (Ag)		0.149	0.0187	0.0023
Sodium (Na)		77.8	59.5	59.6
Strontium (Sr)		0.34	2.55	2.3
Thallium (TI)		<0.0005	0.0001	<0.0001
Tin (Sn)		<0.2	<1	<0.2
Titanium (Ti)		< 0.03	< 0.003	< 0.003
Uranium (U)		0.461	0.0001	0.0002
Vanadium (V)		<0.05	< 0.005	<0.005
Zinc (Zn)	0.50	68.4	0.018	0.012
Zirconium (Zr)		< 0.05	<0.005	<0.005
· · · · ·				
Sulphur (S)		19400	500	503
Total Dissolved Solids		83200	2420	2440

Table 6. Impact of retention time on effluent quality for PLS (in mg/L)

Notes:

Bold – Exceeds process water quality target

The results summarized in Table 5 and Table 6 show that a retention time of 60 minutes to 90 minutes provides very similar effluent quality for PLS solution; however, a significant improvement in total sulphur and TDS is observed with 90 minute retention time for Raffinate solution. Therefore, a retention time of 90 minutes may be sufficient for design purposes due to

lower TDS and sulphur concentration. However, as indicated in the above table, the concentration of aluminum increased slightly with a longer reaction time. As a result, a pH adjustment following solid/liquid separation may be required to meet aluminum discharge target.

## 3.4 High Iron to Total Metals Ratio

Iron concentration in the feed is expected to be much higher than the 20 mg/L present in the feed solution samples provided; therefore, it was decided to add iron as ferrous sulphate to determine impact of higher iron concentration on the effluent quality. Iron is a common ingredient which aids in heavy metals removal by co-precipitation and generally results in lower metals concentration in the effluent than otherwise. Iron was added to the feed as ferrous sulphate and the neutralization tests were conducted at pH 9.5 based on the results of the first phase of the work.

	MMER Limit	Raffinate Feed	No Fe Addition	0.7g/L Iron	1.0g/L Iron	1.5g/L Iron	4.0g/L Iron
pН		1.98	9.40	9.48	9.54	9.60	9.54
Aluminum (Al)		5680	1.17	2.78	6.92	9.04	8.29
Antimony (Sb)		<0.005	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Arsenic (As)	0.50	0.024	0.003	0.002	0.001	0.001	< 0.001
Barium (Ba)		0.02	0.009	0.01	0.007	0.007	0.007
Beryllium (Be)		0.247	<0.0002	<0.0002	< 0.0002	< 0.0002	< 0.0002
Bismuth (Bi)		<0.5	<0.05	< 0.05	<0.05	<0.05	<0.05
Boron (B)		<0.08	<0.008	<0.008	<0.008	<0.008	0.009
Cadmium (Cd)		0.965	0.0007	0.0005	0.0002	0.0002	0.0003
Calcium (Ca)		492	480	469	587	568	618
Chromium (Cr)		2.24	<0.001	<0.001	< 0.001	<0.001	<0.001
Cobalt (Co)		18	0.0019	0.0026	<0.0005	< 0.0005	0.0006
Copper (Cu)	0.30	4.88	0.069	0.0398	0.0357	0.0319	0.0908
Iron (Fe)		22.4	<0.005	0.193	0.026	0.05	0.274
Lead (Pb)	0.20	0.017	< 0.0005	0.0007	0.002	< 0.0005	< 0.0005
Lithium (Li)		1.08	0.036	0.084	0.018	0.013	0.028
Magnesium (Mg)		5890	340	147	36.2	21.1	26.5
Manganese (Mn)		688	0.546	0.328	0.078	0.059	0.089
Molybdenum (Mo)		0.37	0.141	0.078	0.096	0.086	0.075
Nickel (Ni)	0.50	14.1	<0.008	<0.008	<0.008	<0.008	<0.008
Phosphorus (P)		5	<0.1	<0.1	<0.1	<0.1	<0.1
Potassium (K)		15	23	19	20	20	21
Selenium (Se)		0.202	0.071	0.033	0.031	0.023	0.008
Silicon (Si)		102	0.22	0.26	0.16	0.33	0.14
Silver (Ag)		0.157	0.0558	0.0282	0.0239	0.0203	0.0037
Sodium (Na)		79.5	61.6	51	52.5	53.1	54.5
Strontium (Sr)		0.35	2.56	1.68	2.03	1.95	2.6
Thallium (TI)		< 0.0005	0.0001	<0.0001	<0.0001	< 0.0001	< 0.0001
Tin (Sn)		<20	<1	< 0.02	<0.2	<0.2	<0.02
Titanium (Ti)		< 0.03	<0.003	<0.003	<0.003	< 0.003	<0.003
Uranium (U)		0.451	0.0008	0.0004	0.0004	0.0003	0.0005
Vanadium (V)		<0.05	<0.005	<0.005	<0.005	<0.005	<0.005
Zinc (Zn)	0.50	72	<0.005	0.02	0.013	0.014	0.008
Zirconium (Zr)		<0.05	<0.005	<0.005	< 0.005	<0.005	<0.005
Sulphur (S)		19200	973	593	518	481	523
Total Dissolved Solids		81900	4320	3280	2650	2560	2600

Notes:

Bold – Exceeds process water quality target

	MMER Limit	PLS Feed	No Fe Addition	0.7g/L Iron	1.0g/L Iron	1.5g/L Iron	4.0g/L Iron
рН	Linin	3.55	9.45	9.39	9.44	9.51	9.58
Aluminum (Al)		5180	6.06	5.48	13.2	12	21
Antimony (Sb)		< 0.005	< 0.001	< 0.001	<0.001	<0.001	<0.001
Arsenic (As)	0.50	< 0.005	0.002	0.001	0.001	< 0.001	<0.001
Barium (Ba)	0.00	0.02	0.011	0.009	0.007	0.007	0.005
Beryllium (Be)		0.02	< 0.0002	<0.0002	<0.0002	< 0.0002	<0.0002
Bismuth (Bi)		<0.235	<0.05	<0.05	<0.05	<0.05	<0.05
Boron (B)		<0.08	<0.03	0.016	<0.008	<0.08	0.008
Cadmium (Cd)		0.873	0.0001	0.0002	<0.0001	<0.0001	0.0002
Calcium (Ca)		456	535	554	612	612	624
Chromium (Cr)		2.22	< 0.001	< 0.001	<0.001	< 0.001	<0.001
Cobalt (Co)		17.6	< 0.0005	0.0005	< 0.0005	< 0.0005	< 0.0005
Copper (Cu)	0.30	1470	0.0416	0.1	0.041	0.0373	0.0217
Iron (Fe)		20.1	0.009	0.082	0.011	0.021	0.045
Lead (Pb)	0.20	0.004	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.0005
Lithium (Li)		1.08	0.005	0.04	0.007	0.007	0.007
Magnesium (Mg)		5340	7.1	48	7.5	7.33	3.33
Manganese (Mn)		643	0.033	0.083	0.034	0.029	0.031
Molybdenum (Mo)		0.28	0.038	0.046	0.031	0.038	0.067
Nickel (Ni)	0.50	12.7	<0.008	<0.008	<0.008	<0.008	<0.008
Phosphorus (P)		5	<0.1	<0.1	<0.1	<0.1	<0.1
Potassium (K)		30	23	21	22	23	21
Selenium (Se)		0.205	0.039	0.033	0.029	0.028	0.006
Silicon (Si)		101	0.13	0.15	0.1	0.11	0.18
Silver (Ag)		0.149	0.0187	0.0205	0.0115	0.0114	0.0015
Sodium (Na)		77.8	59.5	53.1	56.5	58.3	53.9
Strontium (Sr)		0.34	2.55	2.32	2.23	2.27	2.48
Thallium (TI)		<0.0005	0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Tin (Sn)		<0.2	<1	<0.2	<0.2	<0.2	<0.2
Titanium (Ti)		<0.03	<0.003	<0.003	<0.003	< 0.003	<0.003
Uranium (U)		0.461	0.0001	0.0004	0.0003	0.0003	0.0002
Vanadium (V)		<0.05	<0.005	<0.005	<0.005	<0.005	<0.005
Zinc (Zn)	0.50	68.4	0.018	0.01	<0.005	0.005	0.007
Zirconium (Zr)		<0.05	<0.005	<0.005	<0.005	<0.005	<0.005
Sulphur (S)		19400	500	518	513	501	505
Total Dissolved Solids		83200	2420	2630	2540	2450	2550
Notes:		00200	2420	2000	2040	2400	2000

Table 8 Im	nact of high	iron concentration	on effluent a	uality for PLS	(in ma/l)
	ipact of high		on childent qu		$(\Pi \Pi \Pi \mathfrak{g} / \mathbf{L})$

**Bold** – Exceeds process water quality target

The results summarized in Table 7 and Table 8 show that a high iron to dissolved metals concentration provides very similar effluent quality; however, a significant improvement in selenium precipitation was observed as selenium concentration decreased considerably from 71 ug/L with no iron addition to 6 ug/L with high iron concentration for Raffinate and 39 ug/L to 8 ug/L for PLS. However, similar to previous tests, the concentration of aluminum increased slightly with higher iron concentration. Furthermore, as expected, the lime consumption, summarized in Table 9 below, increased with iron concentration. The higher lime requirement will have an operational as well as capital cost impact as the lime loop and the pumping

requirements will be higher.

Test	Initial pH	Sample	20% Lime	Lime Consumption
#	initial pri	Vol. (mL)	(mL)	(g/L)
PLS - 0.7 g/L Fe		600	145	48.3
PLS - 1.0 g/L Fe	3.55	600	151	50.3
PLS - 1.5 g/L Fe	5.55	600	157	52.3
PLS - 4.0 g/L Fe		600	170	56.7
RAFF - 0.7 g/L Fe		600	157	52.3
RAFF - 1.0 g/L Fe	1.98	600	161	53.7
RAFF - 1.5 g/L Fe		600	166	55.2
RAFF - 4.0 g/L Fe		600	177	59.0

## 3.5 HDS Simulation

From previous testing results, it was decided to conduct the HDS simulation with 60 minute retention time at pH 9.5 and using 500 mL feed sample.

The following table provides the results of the bench scale HDS simulations at the pH 9.5. The individual neutralization tests and the HDS simulations only provide an indication of effluent quality that can be achieved with a proper HDS process where the recycle solids significantly improves precipitation kinetics through catalysed reactions.

	MMER Limit	Raffinate	No Recycle	HDS Simulation Cycle 10
рН		1.98	9.40	9.51
Aluminum (Al)		5680	1.17	11.5
Antimony (Sb)		<0.005	<0.001	<0.001
Arsenic (As)	0.50	0.024	0.003	0.003
Barium (Ba)		0.02	0.009	0.016
Beryllium (Be)		0.247	<0.0002	<0.0002
Bismuth (Bi)		<0.5	<0.05	<0.05
Boron (B)		<0.08	<0.008	<0.008
Cadmium (Cd)		0.965	0.0007	<0.0001
Calcium (Ca)		492	480	609
Chromium (Cr)		2.24	<0.001	<0.001
Cobalt (Co)		18	0.0019	<0.0005
Copper (Cu)	0.30	4.88	0.069	0.0208
Iron (Fe)		1500	<0.005	0.011
Lead (Pb)	0.20	0.017	<0.0005	<0.0005
Lithium (Li)		1.08	0.036	0.032
Magnesium (Mg)		5890	340	3.56
Manganese (Mn)		688	0.546	0.011
Molybdenum (Mo)		0.37	0.141	0.025
Nickel (Ni)	0.50	14.1	<0.008	<0.008
Phosphorus (P)		5	<0.1	<0.1
Potassium (K)		15	23	24
Selenium (Se)		0.202	0.071	0.03
Silicon (Si)		102	0.22	0.2
Silver (Ag)		0.157	0.0558	0.0079
Sodium (Na)		79.5	61.6	57.9
Strontium (Sr)		0.35	2.56	5.64
Thallium (TI)		<0.0005	0.0001	<0.0001
Tin (Sn)		<20	<1	<1
Titanium (Ti)		< 0.03	<0.003	<0.003
Uranium (U)		0.451	0.0008	<0.0001
Vanadium (V)		< 0.05	<0.005	<0.005
Zinc (Zn)	0.50	72	<0.005	0.01
Zirconium (Zr)		<0.05	<0.005	<0.005
Sulphur (S)		19200	973	491
Total Dissolved Solids		81900	4320	2410

Table 10. HDS simulation at pH 9.5 for Raffinate (in mg/L)

	MMER Limit	PLS	No Recycle	HDS Simulation Cycle 10
pН		3.55	9.45	9.44
Aluminum (Al)		5180	6.06	30.3
Antimony (Sb)		< 0.005	< 0.001	<0.001
Arsenic (As)	0.50	<0.005	0.002	0.001
Barium (Ba)		0.02	0.011	0.008
Beryllium (Be)		0.233	<0.0002	<0.0002
Bismuth (Bi)		<0.5	<0.05	<0.05
Boron (B)		<0.08	<0.008	<0.008
Cadmium (Cd)		0.873	0.0001	<0.0001
Calcium (Ca)		456	535	652
Chromium (Cr)		2.22	<0.001	<0.001
Cobalt (Co)		17.6	<0.0005	<0.0005
Copper (Cu)	0.30	1470	0.0416	0.0361
Iron (Fe)		1500	0.009	0.005
Lead (Pb)	0.20	0.004	<0.0005	<0.0005
Lithium (Li)		1.08	0.005	0.004
Magnesium (Mg)		5340	7.1	2.23
Manganese (Mn)		643	0.033	0.012
Molybdenum (Mo)		0.28	0.038	0.01
Nickel (Ni)	0.50	12.7	<0.008	<0.008
Phosphorus (P)		5	<0.1	<0.1
Potassium (K)		30	23	27
Selenium (Se)		0.205	0.039	0.031
Silicon (Si)		101	0.13	0.08
Silver (Ag)		0.149	0.0187	0.0139
Sodium (Na)		77.8	59.5	63.9
Strontium (Sr)		0.34	2.55	2.05
Thallium (TI)		<0.0005	0.0001	<0.0001
Tin (Sn)		<0.2	<1	<1
Titanium (Ti)		<0.03	<0.003	<0.003
Uranium (U)		0.461	0.0001	<0.0001
Vanadium (V)		<0.05	<0.005	<0.005
Zinc (Zn)	0.50	68.4	0.018	<0.005
Zirconium (Zr)		<0.05	<0.005	<0.005
Sulphur (S)		19400	500	510
Total Dissolved Solids		83200	2420	2360

Table 11. HDS simulation at pH 9.5 for PLS (in mg/L)

The results summarized in Table 10 and Table 11 above show that there was slight improvement in effluent quality after HDS simulation. A comparison of these results to the previous tables suggests that the metal removal efficiency for all metals, including selenium was slightly improved with the use of sludge recycle. Furthermore, as indicated in Table 12 below, the lime consumption was lower with sludge recycle.

Test	Initial pH	Sample	20% Lime	Lime Consumption
#		Vol. (mL)	(mL)	(g/L)
PLS - Cycle 1-10	3.55	500	120.22	48.1
RAFF - Cycle 1-10	1.98	500	133.67	53.5
KAI I - Cycle I-10	1.98	300	133.07	55.5

Table 12. Lime Requirement with Sludge Recycle

## 3.6 LC50 Acute Toxicity Analysis

After reviewing results for previous tests, it was decided to neutralize another 3.0 L feed solution to pH 9.5 for 90 minutes. Iron was added as ferrous sulphate to the feed in order to increase iron concentration from 20 mg/L to 1500 mg/L. After neutralization, the slurry was filtered and pH was adjusted to 8.0 with CO<sub>2</sub>.

The samples were then tested with 48-h Daphnia magna (LC50), performed to the Environment Canada protocol for conducting acute toxicity tests using Daphnia magna (EPS 1/RM/14, Second Edition, 2000). Details of the results are provided in Appendix B. The solution was not assayed as it is expected to be similar to the HDS simulation results provided in Table 10 and Table 11. The results of the acute toxicity tests indicate that all acceptability criteria specified by the protocol were met.

## 4.0 CONCLUSIONS

This study was a preliminary bench-scale investigation of the potential water treatment needs for the Carmacks Copper Project. Process water (PLS and Raffinate) was treated using conventional chemical precipitation (lime neutralization – High Density Sludge Process) treatment. The results presented in this report are representative of the samples received at the Canadian Environmental and Metallurgical Inc. laboratory.

Based on the test data presented in this report, the following conclusions can be made:

- Metals of concern can be removed using chemical precipitation with lime, specifically High Density Sludge (HDS) process.
- Neutralization at pH 9.5 with 90 minute retention time is required to meet the discharge criteria. Although 60 minute retention time is sufficient to meet all metals discharge target, lower TDS and total sulfur concentrations were achieved with longer retention time.
- Effluent quality improved with high iron concentration and recycle of solids.
- All acceptability criteria specified by the protocol for acute toxicity tests using Daphnia Magna were met.

# **APPENDIX A**

Settling Test Data

#### **CLIENT**

WCC - Carmack Project Bench Scale Neutralization *Test Date:* 18-Jan-07 *Tested By:* RD *Test I.D.:* PLS 7.5

#### **1. INITIAL CONDITIONS**

**SAMPLE** 1L PLS Sample Neutralized to pH 7.5

#### 2. TEST CONDITIONS

FLOCCULANT Type: 3008 M Concentration: 0.5 g/L Addition (mL): 20.0

#### Settling vessel size (mL/cm): 29 Undecanted slurry vol. (mL): 950.0 Slurry weight (g): 1014.2 Dry Solids weight (g): 79.9 Final interface Height (mL): 540

#### 3. COMMENTS

Time (min)	Volume (mL)	Height (mm)	Pulp Density
0	950	328	7.9
1	880	303	8.5
5	790	272	9.4
10	720	248	10.2
15	670	231	10.9
25	640	221	11.3
50	590	203	12.2
60	580	200	12.4
120	560	193	12.8
180	540	186	13.2
240	540	186	13.2

#### 4. SETTLING DATA AND CALCULATIONS

#### **CLIENT**

WCC - Carmack Project Bench Scale Neutralization *Test Date:* 18-Jan-07 *Tested By:* RD *Test I.D.:* PLS 8.0

#### **1. INITIAL CONDITIONS**

SAMPLE

1L PLS Sample Neutralized to pH 8.0

#### 2. TEST CONDITIONS

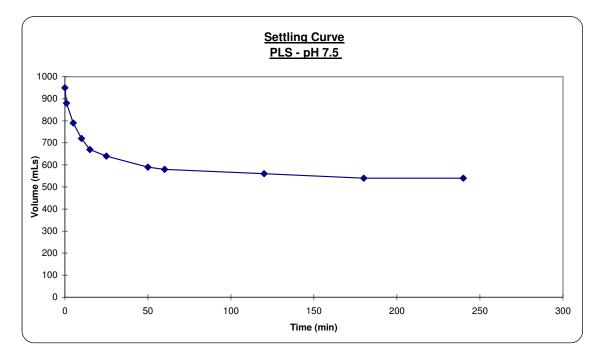
FLOCCULANT Type: 3008M Concentration: 0.5 g/L Addition (mL): 20

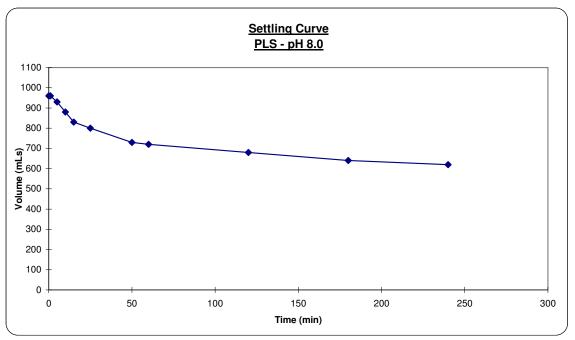
#### Settling vessel size (mL/cm): 29 Undecanted slurry vol. (mL): 960.0 Slurry weight (g): 1033.35 Dry Solids weight (g): 86.1 Final interface Height (mL): 620

#### 3. COMMENTS

Time (min)	Volume (mL)	Height (mm)	Pulp Density
0	960	331	7.8
1	960	331	7.8
5	930	321	8.0
10	880	303	8.5
15	830	286	8.9
25	800	276	9.2
50	730	252	10.1
60	720	248	10.2
120	680	234	10.7
180	640	221	11.3
240	620	214	11.7

#### 4. SETTLING DATA AND CALCULATIONS





#### **CLIENT**

WCC - Carmack Project Bench Scale Neutralization *Test Date:* 18-Jan-07 *Tested By:* RD *Test I.D.:* PLS 8.5

#### **1. INITIAL CONDITIONS**

**<u>SAMPLE</u>** PLS solution neutralized to pH 8.5

#### 2. TEST CONDITIONS

FLOCCULANT Type: 3008 M Concentration: 0.5 g/L Addition (mL): 20

#### Settling vessel size (mL/cm): 29 Undecanted slurry vol. (mL): 1000.0 Slurry weight (g): 1077.60 Dry Solids weight (g): 95.35 Final interface Height (mL): 640

#### 3. COMMENTS

Time					
(min)	Volume (mL)	Height (mm)	Pulp Density		
0	1000	345	7.5		
5	960	331	7.8		
10	920	317	8.1		
15	880	303	8.5		
22	850	293	8.7		
25	840	290	8.8		
30	820	283	9.0		
60.0	780	269	9.5		
120	720	248	10.2		
180	680	234	10.7		
240	670	231	10.9		
300	660	228	11.0		
360	650	224	11.2		
420	640	221	11.3		

#### 4. SETTLING DATA AND CALCULATIONS

#### **CLIENT**

WCC - Carmack Project Bench Scale Neutralization *Test Date:* 18-Jan-07 *Tested By:* RD *Test I.D.:* PLS pH 9.5

#### **1. INITIAL CONDITIONS**

**SAMPLE** PLS Solution Neutralized to pH 9.5

#### 2. TEST CONDITIONS

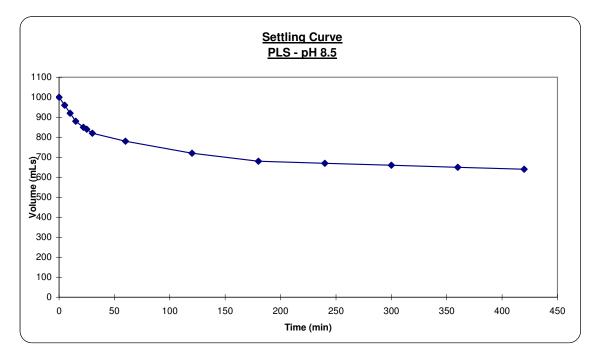
FLOCCULANT Type: 3008M Concentration: 0.5 g/L Addition (mL): 20

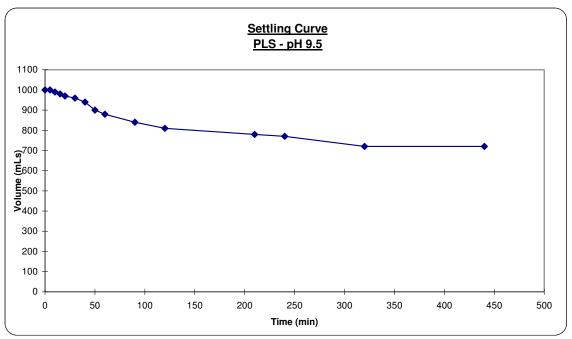
#### Settling vessel size (mL/cm): 29 Undecanted slurry vol. (mL): 1000.0 Slurry weight (g): 1061.43 Dry Solids weight (g): 116.6 Final interface Height (mL): 720

#### 3. COMMENTS

Time (min)	Volume (mL)	Height (mm)	Pulp Density
0	1000	345	7.5
5	1000	345	7.5
10	990	341	7.6
15	980	338	7.7
20	970	334	7.7
30	960	331	7.8
40	940	324	8.0
50	900	310	8.3
60	880	303	8.5
90	840	290	8.8
120	810	279	9.1
210	780	269	9.5
240	770	266	9.6
320	720	248	10.2
440	720	248	10.2

#### 4. SETTLING DATA AND CALCULATIONS





#### **CLIENT**

WCC - Carmack Project Bench Scale Neutralization *Test Date:* 18-Jan-07 *Tested By:* RD *Test I.D.:* RAFF 7.5

#### **1. INITIAL CONDITIONS**

**SAMPLE** Raffinate solution neutralized to pH 7.5

#### 2. TEST CONDITIONS

FLOCCULANT Type: 3008M Concentration: 0.5 g/L Addition (mL): 20

#### Settling vessel size (mL/cm): 29 Undecanted slurry vol. (mL): 870.0 Slurry weight (g): 913.3 Dry Solids weight (g): 68.88 Final interface Height (mL): 510

#### 3. COMMENTS

Time (min)	Volume (mL)	Height (mm)	Pulp Density
0	870	300	8.6
5	840	290	8.8
10	810	279	9.1
15	780	269	9.5
22	740	255	9.9
25	730	252	10.1
30	720	248	10.2
60	670	231	10.9
120	595	205	12.1
180	560	193	12.8
240	550	190	13.0
300	530	183	13.4
360	520	179	13.7
420	510	176	13.9
460	510	176	13.9

#### 4. SETTLING DATA AND CALCULATIONS

#### **CLIENT**

WCC - Carmack Project Bench Scale Neutralization *Test Date:* 18-Jan-07 *Tested By:* RD *Test I.D.:* RAFF 8.0

#### **1. INITIAL CONDITIONS**

**<u>SAMPLE</u>** Raffinate solution neutralized to pH 8.0

#### 2. TEST CONDITIONS

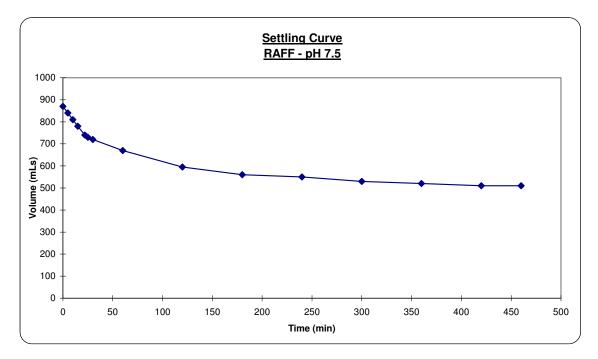
FLOCCULANT Type: 3008M Concentration: 0.5 g/L Addition (mL): 20

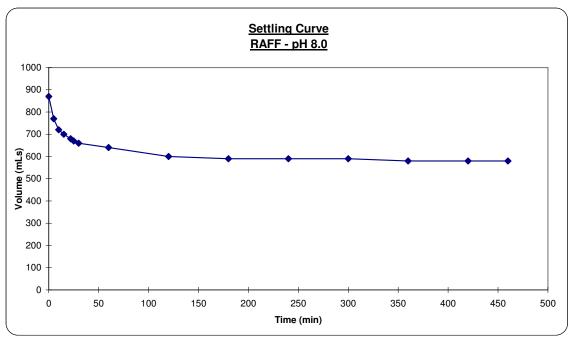
#### Settling vessel size (mL/cm): 29 Undecanted slurry vol. (mL): 870.0 Slurry weight (g): 939.6 Dry Solids weight (g): 74.44 Final interface Height (mL): 580

#### 3. COMMENTS

Time (min)	Volume (mL)	Height (mm)	Pulp Density
0	870	300	8.6
5	770	266	9.6
10	720	248	10.2
15	700	241	10.5
22	680	234	10.7
25	670	231	10.9
30	660	228	11.0
60	640	221	11.3
120	600	207	12.0
180	590	203	12.2
240	590	203	12.2
300	590	203	12.2
360	580	200	12.4
420	580	200	12.4
460	580	200	12.4

#### 4. SETTLING DATA AND CALCULATIONS





#### **CLIENT**

WCC - Carmack Project Bench Scale Neutralization *Test Date:* 18-Jan-07 *Tested By:* RD *Test I.D.:* RAFF 8.5

#### **1. INITIAL CONDITIONS**

**SAMPLE** Raffinate solution neutralized to pH 8.5

#### 2. TEST CONDITIONS

FLOCCULANT Type: 3008M Concentration: 0.5 g/L Addition (mL): 20

#### Settling vessel size (mL/cm): 29 Undecanted slurry vol. (mL): 970.0 Slurry weight (g): 1037.87 Dry Solids weight (g): 86.5 Final interface Height (mL): 600

#### 3. COMMENTS

4. SETTLING DATA AND CALCULATIONS				
Time (min)	Volume (mL)	Height (mm)	Pulp Density	
0	970	334	7.7	
5	840	290	8.8	
10	810	279	9.1	
15	750	259	9.8	
20	730	252	10.1	
40	670	231	10.9	
60	640	221	11.3	
110	610	210	11.9	
240	600	207	12.0	
360	600	207	12.0	
420	600	207	12.0	

#### 4. SETTLING DATA AND CALCULATIONS

#### **CLIENT**

WCC - Carmack Project Bench Scale Neutralization *Test Date:* 18-Jan-07 *Tested By:* RD *Test I.D.:* RAFF 9.5

#### **1. INITIAL CONDITIONS**

**SAMPLE** Raffinate solution neutralized to pH 9.5

#### 2. TEST CONDITIONS

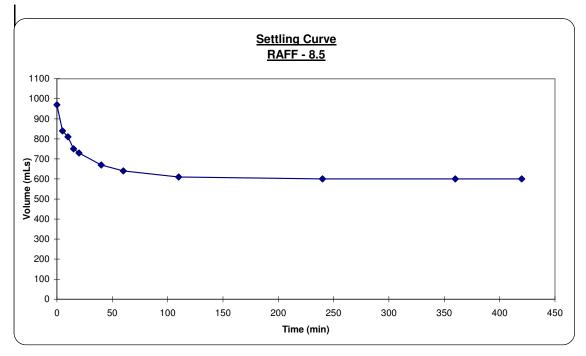
FLOCCULANT Type: 3008M Cocentration: 0.5 g/l Addition (mL): 20

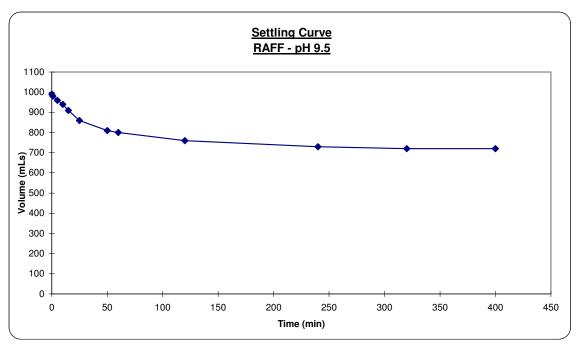
#### Settling vessel size (mL/cm): 29 Undecanted slurry vol. (mL): 990.0 Slurry weight (g): 1067.5 Dry Solids weight (g): 109.7 Final interface Height (mL): 720

#### 3. COMMENTS

4. SETTLING DATA AND CALCULATIONS				
Time (min)	Volume (mL)	Height (mm)	Pulp Density	
0	990	341	7.6	
1	980	338	7.7	
5	960	331	7.8	
10	940	324	8.0	
15	910	314	8.2	
25	860	297	8.6	
50	810	279	9.1	
60	800	276	9.2	
120	760	262	9.7	
240	730	252	10.1	
320	720	248	10.2	
400	720	248	10.2	

#### 4. SETTLING DATA AND CALCULATIONS





# **APPENDIX B**

EVS-Golder Toxicity Analysis Report