

Characterization of Arsenic in a Tailings Impoundment Under Post Depositional Conditions

by

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**We accept this thesis as conforming
to the required standard**

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Abstract

Arsenic is found naturally in the gold ores extracted from the Red Lake Mine in Balmertown, Ontario. Milling of ores produced arsenic-rich tailings that have been disposed of in different locations around the site through the over 50 years of mine operations. The composition of the tailings depended upon the mineral processing methods (cyanidation, sulphide flotation, and roasting) used at the time. The primary objective of this thesis was to characterize the forms, stability, and mobility of arsenic in the different wastes located around the mine site. In addition, a potential method to reduce arsenic transport from tailings pond sediments into the overlying pond waters was investigated. Whole rock analysis, Scanning Electron Microscopy (SEM), Rietveld refined powder X-ray diffraction, sequential extractions, and X-ray Absorption Near Edge Structure (XANES) using a Synchrotron light source were used to mineralogically characterize the various tailings types. Experiments were conducted to investigate the behaviour of arsenic in several tailings types under various conditions with the objective of determining if arsenic could be stabilized under reducing conditions, ideally in the form of arsenopyrite or arsenian pyrite.

High aqueous arsenic concentrations were found to be associated with oxidized arsenic bearing mineral phases (i.e. arsenic bearing iron oxyhydroxides contained in historical roaster-derived tailings and tailings pond sediments). Mobilization of a significant fraction of the arsenic contained within these wastes is likely to continue as a result of the reducing conditions that these wastes are stored under. Arsenic is found at relatively low concentrations in the freshly produced tailings, primarily in the form of arsenopyrite, and is likely to remain immobile as long as saturated conditions exist. In order to minimize arsenic mobilization from solid wastes, oxidized arsenic bearing phases (e.g. arsenic bearing iron oxyhydroxides) should be kept dry and dissolved organic carbon influxes should be limited. Reduced arsenic bearing mineral phases (e.g. arsenopyrite, arsenian pyrite), however, should be maintained under saturated conditions. During field and laboratory experiments it appears as if arsenic was immobilized as a reduced sulphide phase under strongly reducing conditions, however further work is required to determine the mechanism and stability of the produced phase.

Table of Contents

1.0	Introduction	1
2.0	Background Information	3
2.1	Historic Operation and Tailings Deposition	3
2.2	Historical Surface Water Chemistry	10
2.3	Historical Groundwater Information	13
3.0	Literature Review	17
4.0	Solids Identification	26
4.1	Sample Collection and Preparation	26
4.1.1	Sample Collection	26
4.1.2	Sample Preparation	31
4.2	Analytical Methods Performed on Samples	32
4.2.1	Whole Rock Analysis	32
4.2.2	Scanning Electron Microscopy	32
4.2.3	Rietveld Refined X-Ray Powder Diffraction	33
4.2.4	Sequential Extractions	34
4.2.5	X-ray Absorption Near Edge Structure	36
4.3	Results and Discussion	40
4.3.1	Whole Rock Analysis	40
4.3.2	Rietveld Refinement	41
4.3.3	Scanning Electron Microscopy	42
4.3.4	Sequential Extractions	61
4.3.5	Synchrotron X-Ray Absorption Spectroscopy	70
4.4	Conclusions	78
5.0	In situ and Laboratory Experiments	82
5.1	In situ Column Experiment	83
5.1.1	Methods	85
5.1.2	Column Experiment Results	88
5.2	Designed Laboratory Experiments	96
5.2.1	Methods	99
5.2.2	Results	103
5.3	Conclusions	121
6.0	Conclusions	123
7.0	Recommendations	128
8.0	References	132
	Appendix I: Historical Surface Water Data	137
	Appendix II: Whole Rock Analysis Results	147
	Appendix III: Rietveld Refinement Reports	149
	Appendix IV: Sequential Extraction Data and Calculations	168
	Appendix V: Column Experiment Results	172
	Appendix VI: Designed Laboratory Experiment Results	188
	Appendix VII: Design Ease Results	193

List of Tables

Table 1: Summary of Whole Rock Analysis Results.....	41
Table 2: Rietveld Refinement Results (wt %)	42
Table 3: Sequential Extraction Data	62
Table 4: Percent of Total Arsenic Removed in Each Extraction Step.....	63
Table 5: Amount of Arsenic Removed in Each Extraction Step.....	64
Table 6: Percent of Total Iron Removed in Each Extraction Step.....	68
Table 7: Amount of Iron Removed in Each Extraction Step	68
Table 8: Semi-quantitative Arsenic Distribution (+/- 10%). Calculated from linear least-squares fitting of the As K-edge Synchrotron XANES spectra. ...	71
Table 9: Design Matrix for Laboratory Experiments	101
Table 10: Average Sulphate Concentration (mg/L) for Each Tailings Type.....	105
Table 11: Average Dissolved Organic Carbon Concentration (mg/L) for Each Tailings Type	106

List of Figures

Figure 1: Tailings Deposition History	6
Figure 2: Time Series Arsenic Data for Primary Pond Discharge	11
Figure 3: Time Series Arsenic Data for Secondary Pond Discharge.....	11
Figure 4: Groundwater Well and Tailings Sampling Locations in Active TMA..	114
Figure 5: Groundwater Well and Tailings Sampling Locations in Inactive TMA	115
Figure 6: Backscattered Electron Image for RLM-1. Particle (a) is pyrrhotite, particles (b) and (c) are iron oxide, and particle (d) is arsenopyrite.	44
Figure 7: X-Ray Spectrum for RLM-1, showing pyrrhotite pattern.....	45
Figure 8: X-Ray Spectrum for RLM-1, showing iron oxide pattern	45
Figure 9: X-Ray Spectrum for RLM-1, showing arsenopyrite pattern.....	46
Figure 10: Backscattered electron image for RLM-2-1.....	47
Figure 11: Backscattered Electron Image for RLM-2-2.	48
Figure 12: Backscattered Electron Image for RLM-3-1.....	49
Figure 13: Backscattered Electron Image for RLM-3-2.	50
Figure 14: X-Ray Spectrum for RLM-3-2	51
Figure 15: Backscattered Electron Image for RLM-4	53
Figure 16: Backscattered Electron Image for RLM-5	54
Figure 17: X-Ray Spectrum for RLM-5, showing arsenic precipitate.....	54
Figure 18: Backscattered Electron Image for RLM-6-1	55
Figure 19: Backscattered Electron Image for RLM-6-1	56
Figure 20: Backscattered Electron Image for RLM-6-2	57

Figure 21: X-Ray Spectrum for RLM-6-2	57
Figure 22: Backscattered Electron Image for Primary Pond Sediment.	59
Figure 23: Percent of Total Arsenic Removed in Each Extraction Step	67
Figure 24: mg As/kg Sediment Removed in Each Extraction Step	67
Figure 25: Percent of Total Iron Removed in Each Extraction Step	69
Figure 26: Arsenic K-edge XANES spectra of three different model compounds with different oxidation states.....	71
Figure 27: Arsenic K-edge XANES spectra of RLM-2 series samples	73
Figure 28: Fitted Arsenic K-edge spectrum of RLM 2-1	73
Figure 29: Fitted Arsenic K-edge spectrum of RLM 2-2	74
Figure 30: Fitted Arsenic K-edge spectrum of RLM 2-3	74
Figure 31: Diagram of an installed column.....	86
Figure 32: Dissolved Arsenic Concentration at the Bottom Sampling Port	89
Figure 33: Concentration of Dissolved Iron at the C3 Bottom Sampling Port....	91
Figure 34: Concentration of Dissolved Arsenic at the Middle Sampling Port	92
Figure 35: Concentration of Dissolved Arsenic at the Surface of the Columns.	94
Figure 36: Designed Experiment Laboratory Setup Photograph.....	103
Figure 37: Flask #6 after Day 21	104
Figure 38: Arsenic Results for Flasks Containing Secondary Pond Sediment	107
Figure 39: Arsenic Results for Flasks Containing RLM-2 Tailings	108
Figure 40: Arsenic Results for Flasks Containing RLM-5 Tailings	109
Figure 41: Arsenic Results for Flasks Containing RLM-7 Tailings	110
Figure 42: Set 1 – Day 42 Interaction Graph for AD	113

Figure 43: Set 1 – Day 42 Interaction Graph for AF.....	114
Figure 44: Set 1 – Day 21 Interaction Graph for CE	115
Figure 45: Set 2 – Day 42 Interaction Graph for BE.....	118
Figure 46: Set 2 – Day 42 Interaction Graph for CE	118

1.0 Introduction

The Red Lake Mine, owned and operated by Goldcorp Inc., is located in Northwestern Ontario, near the community of Balmertown. Gold milling operations have been carried out at the Red Lake Mine since the 1940's. Up until 1980 a roaster was used to make the refractory gold (mostly associated with arsenopyrite) amenable to cyanidation. Prior to the 1970's tailings from the process were discharged directly into Balmer Creek and Balmer Lake. After this time a tailings management area (TMA) was constructed for the disposal of the tailings. From 1996 to 2000 operations were suspended due to a labor dispute, during this time a new 600 tpd mill was commissioned, and modifications were made to the TMA.

The current tailings management area at the Red Lake Mine consists of a primary pond, a secondary pond, and Balmer Lake that acts as a tertiary polishing pond. The discharge from Balmer Lake represents the point where compliance with the current certificate of approval, and the Ontario Municipal Industrial Strategy for Abatement (MISA) must be met.

Goldcorp Inc. would like to remove Balmer Lake from the TMA by generating a secondary pond effluent that is consistently compliant with the effluent criteria in effect for the discharge of Balmer Lake. Arsenic and ammonia have been identified as the parameters of greatest concern in achieving this goal. Arsenic levels in the Secondary Pond are commonly greater than 0.5 mg/L (the compliance concentration) and have been found to exceed 3 mg/L on occasion.

Several sources of arsenic to the TMA have been identified including underground waters, mill process waters, subaerial tailings, subaqueous tailings, groundwater, and mine site run-off. It has been estimated that contributions of arsenic from subaqueous tailings represent the largest arsenic source to the Secondary Pond. Tailings derived from the roasting process, used in the past,

are believed to be located on the bottom of the Secondary Pond. Data collected previously suggest that arsenic is released from the tailings sediments via reductive dissolution. This has been hypothesized to occur during the winter when an ice cover limits atmospheric oxygen diffusion into the pond, and during the summer when an increase in sediment oxygen demand occurs as a result of plankton growth and microbial activity.

Historical operations give rise to many issues at the Red Lake Mine that do not exist at newer mines. The long history of the mine and the many changes made to the milling process and tailings management methodologies make it difficult to determine exactly what types of tailings are stored around the property. To effectively manage the various tailings deposits at the Red Lake Mine site, it is necessary to identify the forms of arsenic found in each of the tailings storage areas. Once the forms of arsenic have been identified and quantified the tailings can be managed appropriately to minimize arsenic dissolution into the surrounding pore waters and surface waters.

In this thesis, the fate and transport of arsenic in the tailings impoundment at Goldcorp's Red Lake Mine are investigated. The primary focus of the study is to quantify the form and stability of arsenic in each of the tailings deposits at the Red Lake Mine. This will enable a better understanding of the sources and geochemical processes controlling arsenic behaviour in the tailings and will allow for recommendations to be made on the most effective way to manage each of the tailings areas. The overall goal of the project is to provide Goldcorp Inc. with information that will enable the development of methods to reduce arsenic levels in the water leaving the tailings impoundments, and assist in planning for closure.

2.0 Background Information

The Red Lake Mine has a long history of operations since the 1940's. As a result of the past milling and tailings management practices, elevated surface and groundwater arsenic levels have developed around different areas of the mine site. As an initial step to understanding the cause of the elevated arsenic concentrations it is necessary to compile available historical information on the milling process flow sheets that were used over the years. The different milling processes resulted in the production of several types of tailings solids, that were deposited in various areas around the mine site. Information was collected from various reports and from mine personnel in an attempt to gain an understanding of the tailings management practices that have taken place at the mine. In this section the historical milling and tailings management practices are discussed and historical surface and groundwater chemistry data are reviewed. It is shown that there are three primary types of tailings that were produced throughout the operation of the mine: Low sulphide content cyanidation/flotation tailings, high sulphide content cyanidation tailings, and roaster-derived tailings. It is expected that the arsenic in each of the tailings types will be contained in different forms and associated with different minerals. The tailings solids were deposited in two main areas. Initially solids were deposited in the vicinity of Balmer Creek, and at a later date solids were deposited at different locations throughout the currently active tailings management area. Elevated groundwater arsenic concentrations exist in areas where roaster-derived tailings were reported to have been deposited.

2.1 Historic Operation and Tailings Deposition

The Red Lake Mine property was first staked in 1926 as part of the Red Lake Gold Rush. Diamond drilling began in March 1945, and shaft sinking started in 1946. In December of 1948 milling began at Dickenson's Red Lake Mine. Initially 100 tons of ore per day passed through the processing plant, which consisted of grinding in cyanide solution followed by being treated in a cyanide

circuit. Late in 1950 a mineral jig was placed in the grinding circuit and the concentrate from the jig was amalgamated. The tailings produced during this time period are likely to be high sulphide content cyanidation tailings. The milling rate increased to 300 tons per day in early 1951 after another grinding circuit was installed. Flotation equipment and a roaster were also added. In 1951 the flowsheet consisted of grinding the ore in water with free gold recovered with a mineral jig and amalgamated. Following grinding, the slurry passed through a flotation circuit. The flotation concentrate was roasted, and calcine (roaster product) and flotation tailings were subjected to cyanidation.

Milling capacity was increased to 450 tons per day in 1954 by the addition of a standard cone crusher into the circuit. In addition, the grinding was conducted in cyanide, and was converted to two stage grinding. Free gold was recovered following secondary grinding via corduroy blankets and a mineral jig. Concentrate from the blankets and jig was amalgamated, and blanket tailings reported to cyanidation. Gold was recovered from the cyanide solution via precipitation with zinc dust. Cyanide tailings were sent to the flotation circuit, flotation concentrate was roasted and the calcine leached along with the blanket tailings.

In 1956 the processing plant had a capacity of 450 tons per day and the process consisted of crushing, grinding in cyanide, amalgamation of free gold recovered with a mineral jig, cyanidation of the grinding slurry along with calcine residue, and finally flotation of the leach product. Flotation concentrate was roasted. The roaster had a capacity of 16 tons per day. The above information was taken from a memo prepared by M.G. Sveinson, Mill Metallurgist, on September 17th, 1956.

The roaster operated continuously from 1951 until it was shutdown in 1980 for environmental, health and safety reasons. It is speculated that the roaster was shutdown due to new regulations concerning air emissions from roasters that were scheduled to come into effect July 1st, 1980 (Barr, 1983). In 1982 the

milling capacity was increased to 700 tons per day. The flotation circuit continued to operate until November 1990, with concentrate being sold to custom smelters until 1989 and stockpiled after that. During the time period from 1980 – 1990 it is likely that the tailings produced were low sulphide content cyanidation tailings. In 1994 the mill operated at approximately 1000 tons per day (rated capacity was 850 tons/day). In February of 1995 the milling rate was reduced to 680 tons/day in order to facilitate increased exploration costs. Milling ceased operation in June of 1996, the mill was demolished and construction of a new mill was completed in June 2000. High sulphide content cyanidation tailings were likely produced from the time flotation operation ceased (November 1990) until the mill shutdown in 1996.

The new mill consists of a standard crushing/grinding circuit with gravity recovery using a Knelson Concentrator. Knelson concentrate is tabled and refined into bullion on site. Slurry from the grinding circuit passes through a leaching and carbon in pulp (CIP) circuit. The carbon is stripped and reactivated, and the gold is recovered from the pregnant solution by electrowining. CIP tailings pass through a cyanide detoxification circuit and ferric sulphate is added in an attempt to precipitate dissolved arsenic. The CIP tailings then pass through a flotation circuit where refractory sulphides are concentrated. The concentrate is currently stockpiled on site and shipped to a custom smelter for further refining. Flotation tailings are sent to the paste backfill plant. Approximately 50% of the tailings are used underground as backfill and the remainder of the low sulphide content cyanidation/flotation tailings are piped to the tailings management area (TMA).

Throughout the operation of the mine, mill tailings were disposed of in several different areas. Figure 1a shows a schematic of the area prior to operation of the mine. Prior to 1960 there were no control structures in place to attempt to retain the tailings in any way. Tailings were spilled on the ground and flowed into and along Balmer Creek (Figure 1b). Tailings located on both sides of Balmer Creek

Figure 1: Tailings Deposition History

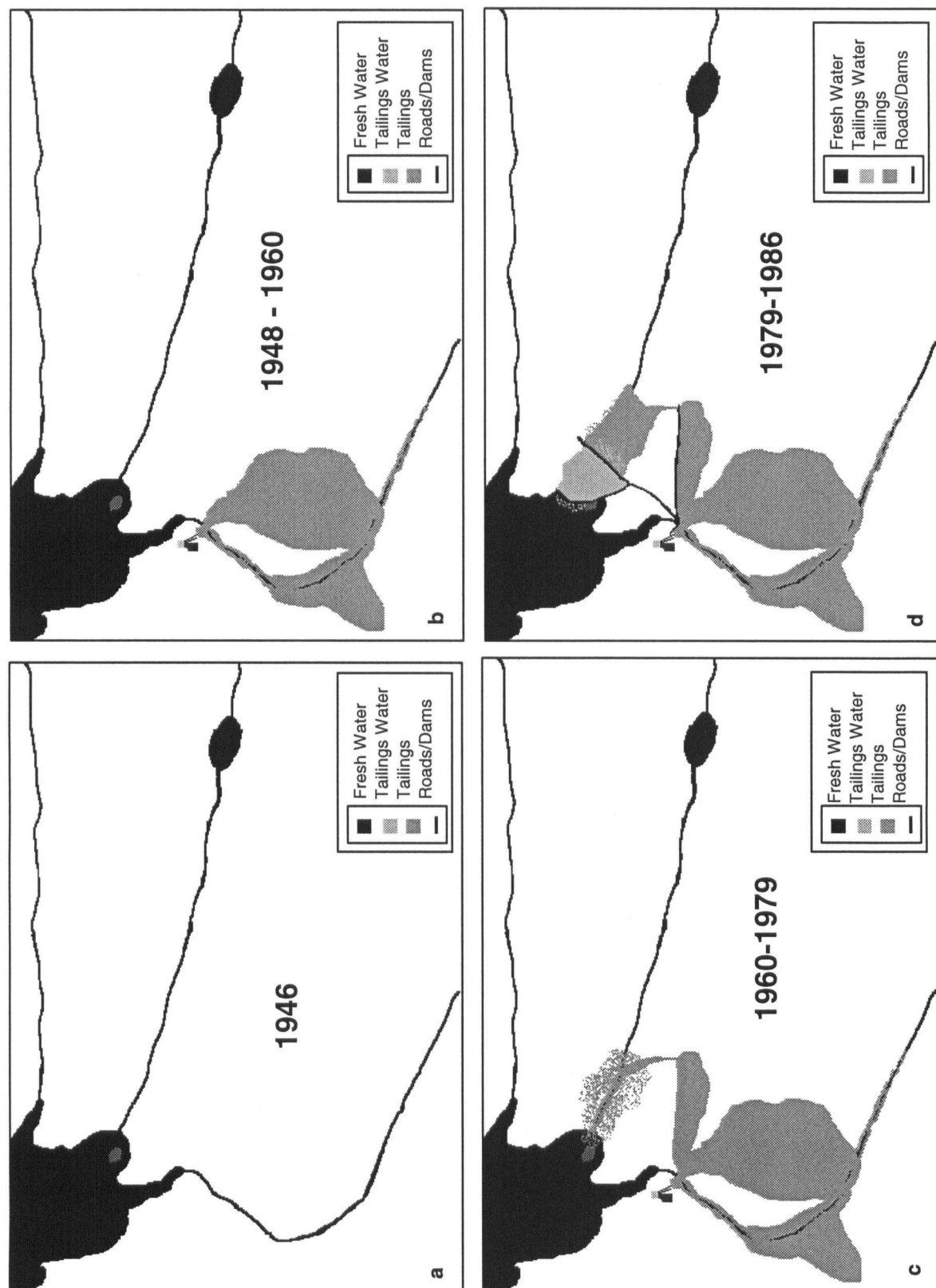
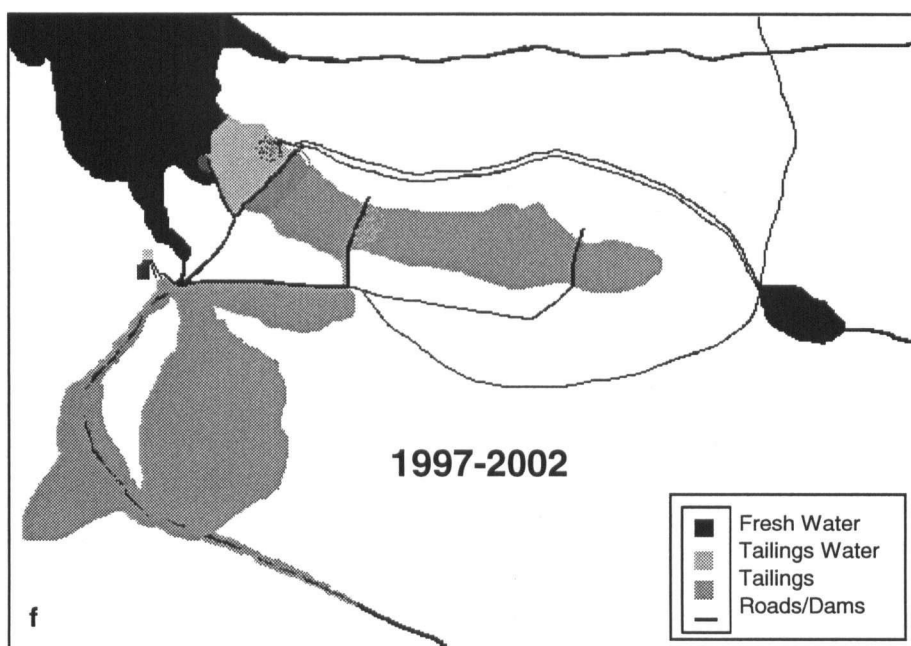
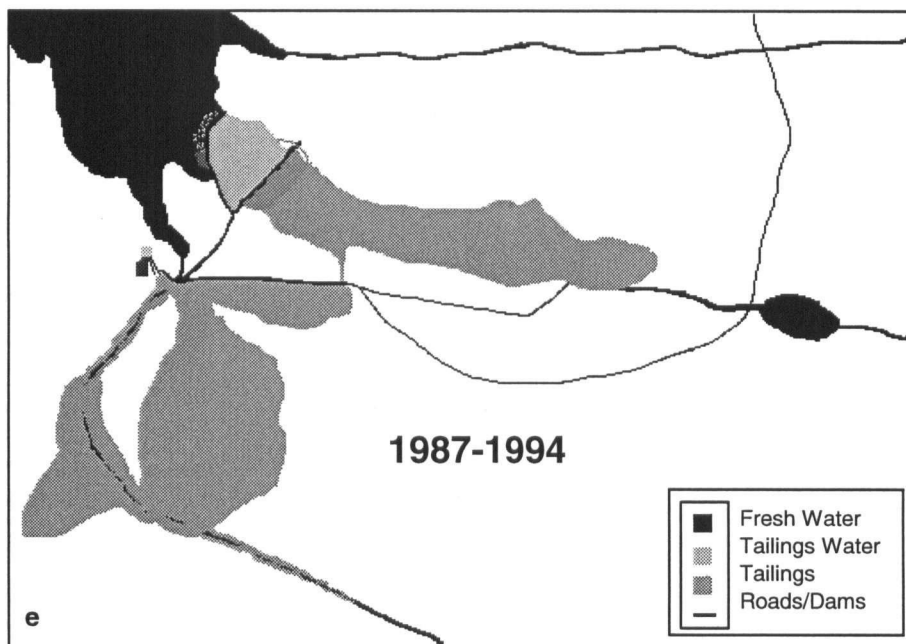


Figure 1 (Continued): Tailings Deposition History



consist of material subjected to cyanidation alone (1948 – 1951), and material subjected to cyanidation, flotation, and roasting (1951 – 1960). In 1960 a dyke was constructed and the tailings discharge point was moved in an attempt to divert tailings from directly entering Balmer Creek. The tailings flowed into a horseshoe – shaped depression, flowing through a road culvert making their way through a small creek to Balmer Lake (Figure 1c). It was reported that retention time in the horseshoe – shaped area was minimal, allowing tailings solids to reach Balmer Lake. In 1962, classification of the tailings began and 65% by weight of the tailings (coarse fraction) were used as fill underground, with the remaining material being pumped to the horseshoe – shaped area. In 1979 a certificate of approval was issued, giving permission to build two Dams, #1 and #2. Dam #1 was constructed to separate a primary pond from a secondary pond, and Dam #2 was constructed to separate the secondary pond from Balmer Lake. Both Dams were constructed to be permeable, allowing water to flow relatively unimpeded through them but retaining solids behind them. The bottoms of the newly created Primary and Secondary Ponds contained tailings subjected to cyanidation, flotation and roasting (Figure 1d). In 1984 the Primary Dam (Dam #1) was raised and clay was placed on the upstream side to make the dam relatively watertight. A spillway was constructed with a Gabion weir to discharge water from the Primary Pond to the Secondary Pond.

In April of 1985 a 600-foot long section of the Primary Dam failed, resulting in the release of solids and solution into the Secondary Pond. This breach in turn caused a fifty-foot section of the Secondary Dam to fail resulting in the release of tailings slurry into Balmer Lake. Consequently, some non-roaster tailings were deposited in the Secondary Pond. In 1986 wick drains were installed in the Primary Dam in an attempt to stabilize the dam. In 1986 a flow control weir was completed at Balmer Creek (L2). In 1987 the tailings pipeline was extended to its now current discharge location, approximately 5000 ft upstream of the Primary Dam (Figure 1e). In addition, the crests of both the Primary and Secondary Dams were raised approximately 1.5 feet. In 1988, the crest of the Primary Dam

was raised by an additional 1-2 feet. The Secondary Dam failed again on April 23rd, 1990. High water levels in the Secondary pond overtopped the dam, washing out a 150 foot section. An emergency spillway was installed in the dam to prevent an additional washout from occurring in the future.

Around 1994 two splitter dykes, constructed out of waste rock, were placed in the Primary Pond. Splitter Dyke #1 was constructed just downstream of the tailings discharge point, and Splitter Dyke #2 was built approximately 1000 ft upstream of the Primary Dam (Figure 1f). The dykes were built in an attempt to retain more solids further back in the tailings system and to increase the residence time in the Primary Pond. The dykes function reasonably well, with the majority of the solids being retained upstream of Splitter Dyke #2. Improvements were made to the permeable rock fill dams in the Secondary Pond during 1995 and 1996. Filter layers were added to the upstream side of the Dams to turn them into water retaining embankments. An engineered stop log weir was constructed to allow for controlled release of water from the pond. In May of 1997 a Diversion Channel was completed that carried water from the Beaver Pond (upstream of the tailings management area) around the tailings management area, discharging into the Secondary Pond downstream of the Primary Pond Spillway. This water acts as a significant source of dilution in the Secondary Pond. Figure 1 (a-f) depicts the historical evolution of the tailings management areas at the Red Lake Mine.

2.2 Historical Surface Water Chemistry

Water chemistry data for the Primary Pond, and G1 (effluent of Secondary Pond) is available since 1991. Grab samples were collected from the Primary Pond and G1 and were analyzed at a number of laboratories throughout the years (since 2000 all samples for environmental compliance have been analyzed at Envirotest Laboratories Inc. in Thunder Bay Ontario – a CAEAL certified lab). Complete tabulated data can be found in Appendix I. Figures 2 and 3 show the time series of arsenic data for the Primary Pond, and for G1, respectively. The time series can be broken down in to three segments: Before shutdown (Jan-91 - April-96), shutdown (May-96 – Oct-00), and after shutdown (Nov-00 – present).

Before Shutdown

Prior to the shutdown, Primary Pond waters were characterized by high concentrations of arsenic and cyanide. The average concentrations of total arsenic and total cyanide were 1.58 mg/L and 24 mg/L respectively. The arsenic concentration was consistently above 0.5 mg/L and a trend of increasing arsenic concentrations before the shutdown was observed. The total cyanide concentration never fell below 2 mg/L. In addition, the total suspended solids concentration was 52 mg/L, and the Cu, Ni, Zn, and Fe concentrations were also elevated, averaging 2.92, 1.65, 1.35, and 6.1 mg/L, respectively. The average ammonia concentration was relatively low at 4.8 mg/L, and the average pH was 8.3. The concentration of arsenic at G1 was consistently above 0.5 mg/L before the shutdown with concentration peaks occurring predominately in late summer (Aug – Sep) and early winter (Dec). The average concentrations of total arsenic, total iron and total cyanide for this time period were 1.2 mg/L, 3.27 mg/L and 5.79 mg/L, respectively. The total iron and cyanide concentrations were consistently above 1.0 mg/L and 0.5 mg/L, respectively. The pH of G1 water averaged 7.95, the total suspended solids concentration was 25 mg/L, and the average ammonia

Figure 2: Time Series Arsenic Data for Primary Pond Discharge

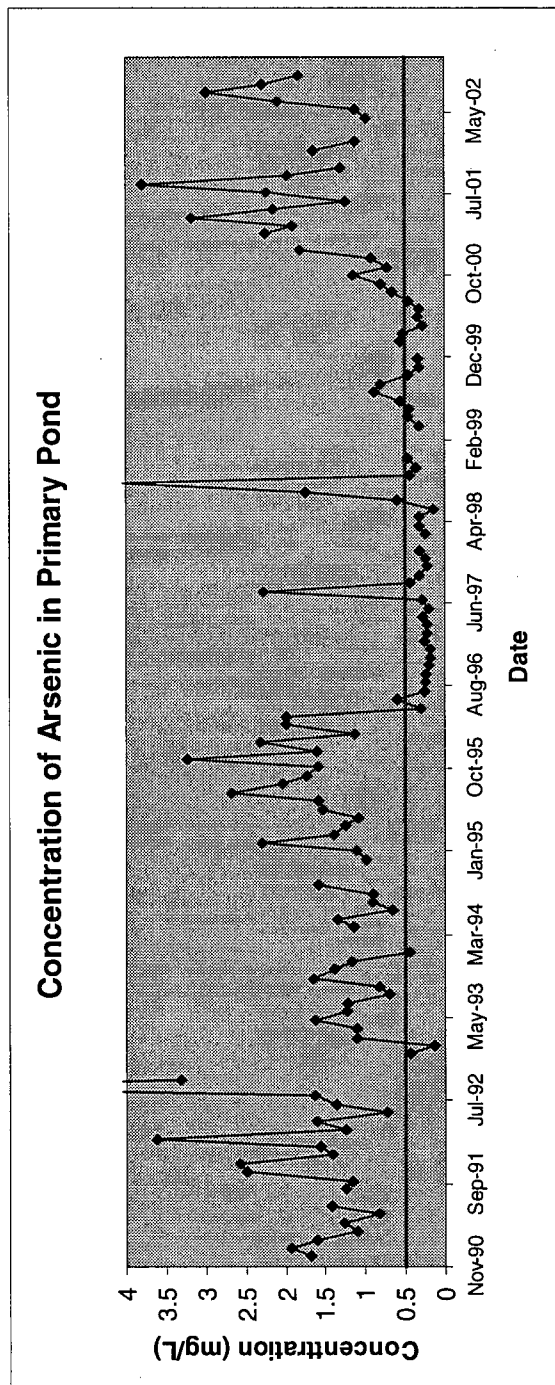
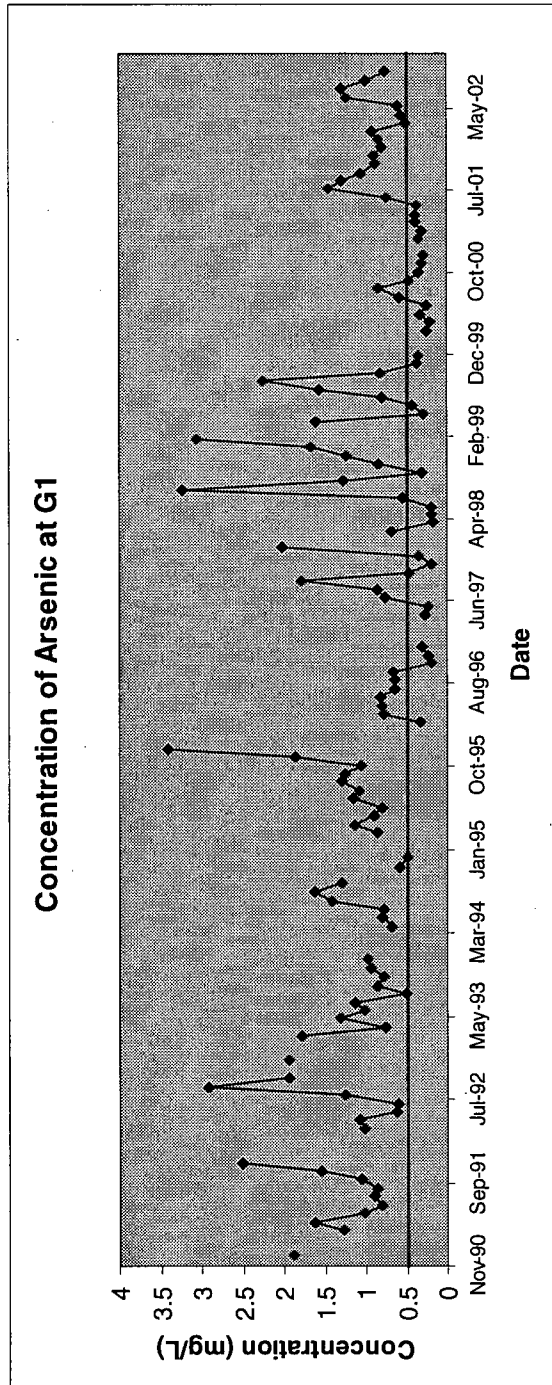


Figure 3: Time Series Arsenic Data for Secondary Pond Discharge (G1)



concentration was 6.86 mg/L. In addition, Cu, Ni, and Zn concentrations averaged 1.26, 0.87, and 0.4 mg/L, respectively.

During Shutdown

During the shutdown all contaminant concentrations dropped dramatically in the Primary Pond. The average arsenic concentration during the shutdown was calculated to be 0.54 mg/L. In general, peaks in the arsenic concentration were seen in August. Outside of the summer peaks, the arsenic concentration was for the most part below 0.5 mg/L, with a trend of increasing arsenic concentration observed as time progressed. The average Cu, Ni, and Zn were low at 0.06, 0.07, and 0.02 mg/L, respectively, and the iron concentration decreased significantly to 0.66 mg/L. The average total cyanide concentration during the shutdown was 0.36 mg/L. The average total suspended solids concentration was <15 mg/L, the pH averaged 7.8, and the ammonia concentration dropped to 1.53 mg/L.

Significant peaks in the arsenic concentration at G1 during Aug/Sep and Jan/Feb occurred throughout the shutdown. For the first time, arsenic concentrations below 0.5 mg/L were seen. The diversion channel, completed in May 1997, added dilution to the Secondary Pond, which likely aided in reducing arsenic concentrations. The average concentrations of arsenic, iron and cyanide during the shutdown were 0.72 mg/L, 0.66 mg/L and 0.07 mg/L, respectively. The average pH was 7.63, while the average total suspended solids and ammonia concentrations decreased to <10 mg/L, and 0.43 mg/L, respectively.

After Shutdown

Under the new mill operation (after the shutdown) the average arsenic concentration in the Primary Pond was calculated to be 1.84 mg/L, with peaks observed in august of 2001 and 2002. The concentration of arsenic usually

exceeded 1 mg/L. The introduction of an INCO-SO₂ cyanide destruction process in the mill greatly reduced the cyanide concentration in the Primary Pond. The average cyanide concentration after the shutdown was 2.27 mg/L, with the lowest concentrations being observed in the summer months. The ammonia concentration, however, increased dramatically, averaging 27.7 mg/L. Cu, Ni, Zn, and Fe concentrations were significantly lower than before the shutdown averaging 0.12, 0.019, 0.013, and 0.36 mg/L, respectively. The average total suspended solids concentration was 5 mg/L, and the pH averaged 7.9.

Since July 2001, the arsenic concentration at G1 has not dropped below 0.5 mg/L, peaks in arsenic concentration occurred in August of 2001 and 2002, and the average concentration was determined to be 0.736 mg/L. The average concentrations of cyanide and ammonia at G1 after the shutdown were 0.09 mg/L, and 7.96 mg/L respectively. The cyanide concentration rose since the shutdown ended, however the concentration was almost always below 0.2 mg/L. Cu, Ni, Zn, and Fe concentrations remained much lower than before the shutdown, averaging 0.03, 0.02, 0.01, and 0.47 mg/L, respectively. The average total suspended solids and pH were 5.84 mg/L and 7.7.

2.3 Historical Groundwater Information

Initial groundwater work was conducted at the site in 1993. Wells were installed in the active TMA, the inactive TMA, and the Mill/Headframe area. As of 2002 only 5 of the eleven wells were still functional. Twelve additional groundwater monitoring wells were installed in March of 2002 and all operational wells were sampled in 2002. Figures 4 and 5 show the groundwater well locations in the active and inactive TMA's, respectively.

Elevated arsenic concentrations are seen in all of the tailings deposits surrounding the Red Lake Mine site. The highest arsenic concentrations occur in

Figure 4: Groundwater Well and Tailings Sampling Locations in Active Tailings Management Area

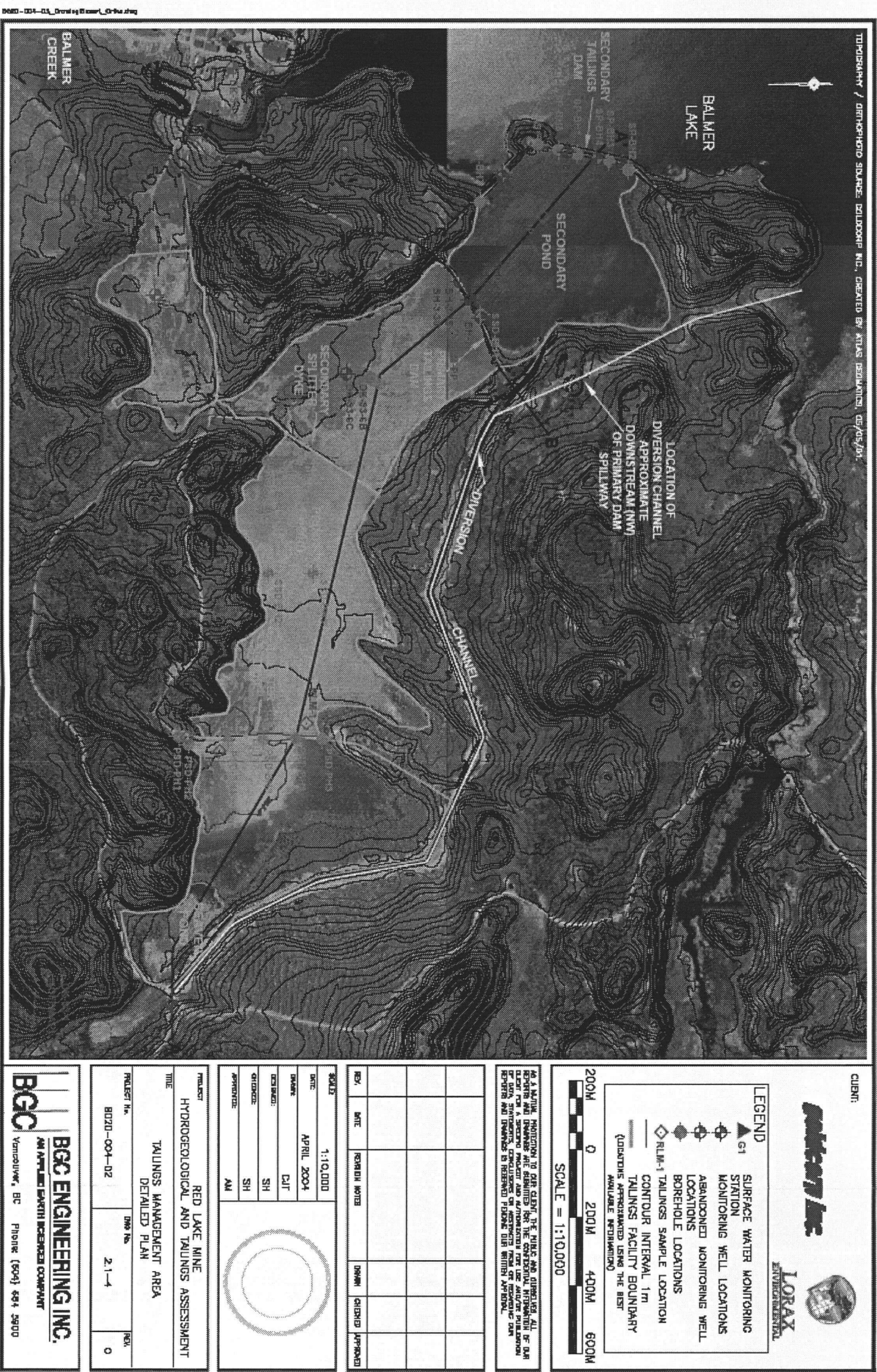
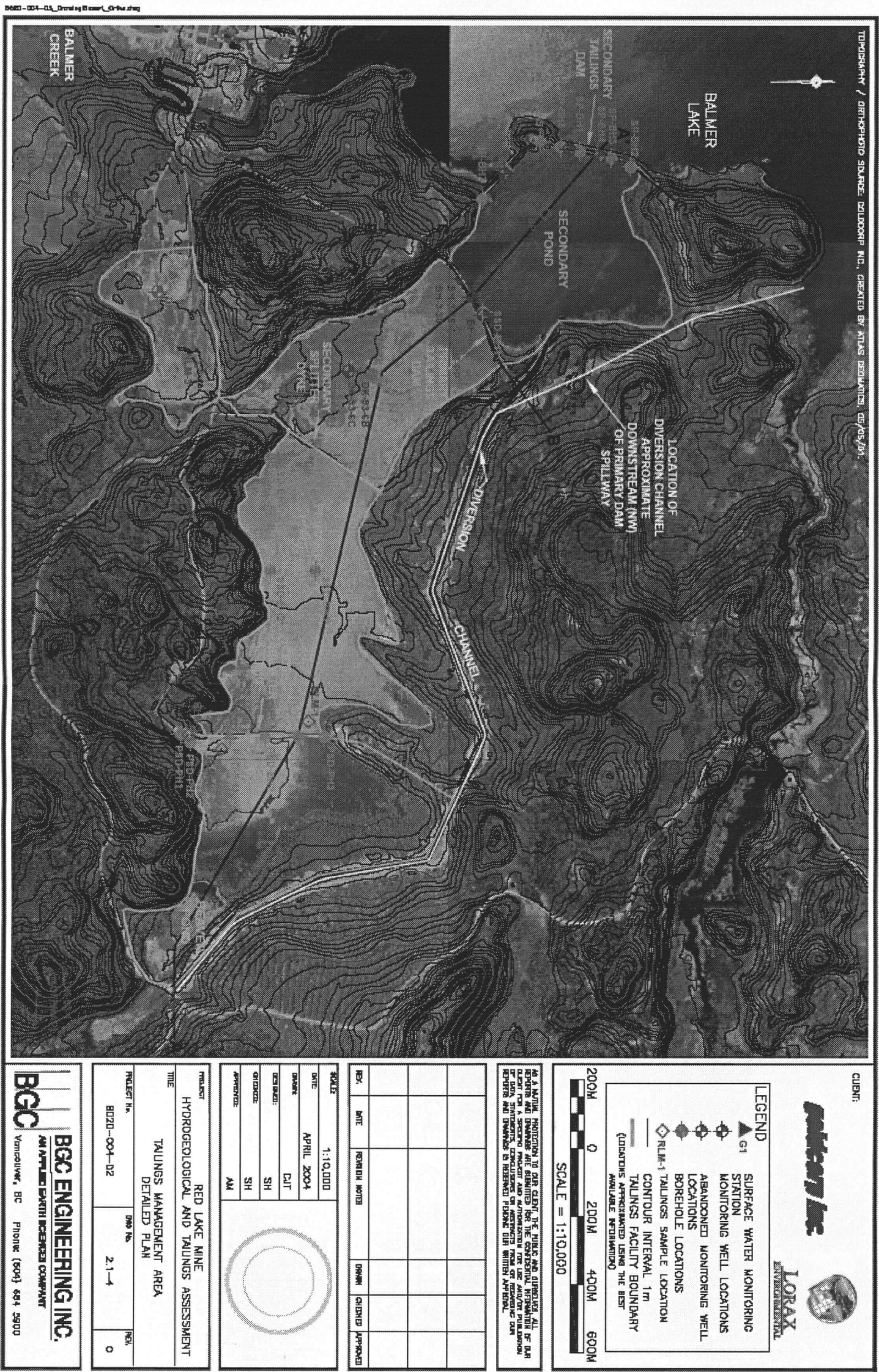


Figure 4: Groundwater Well and Tailings Sampling Locations in Active Tailings Management Area

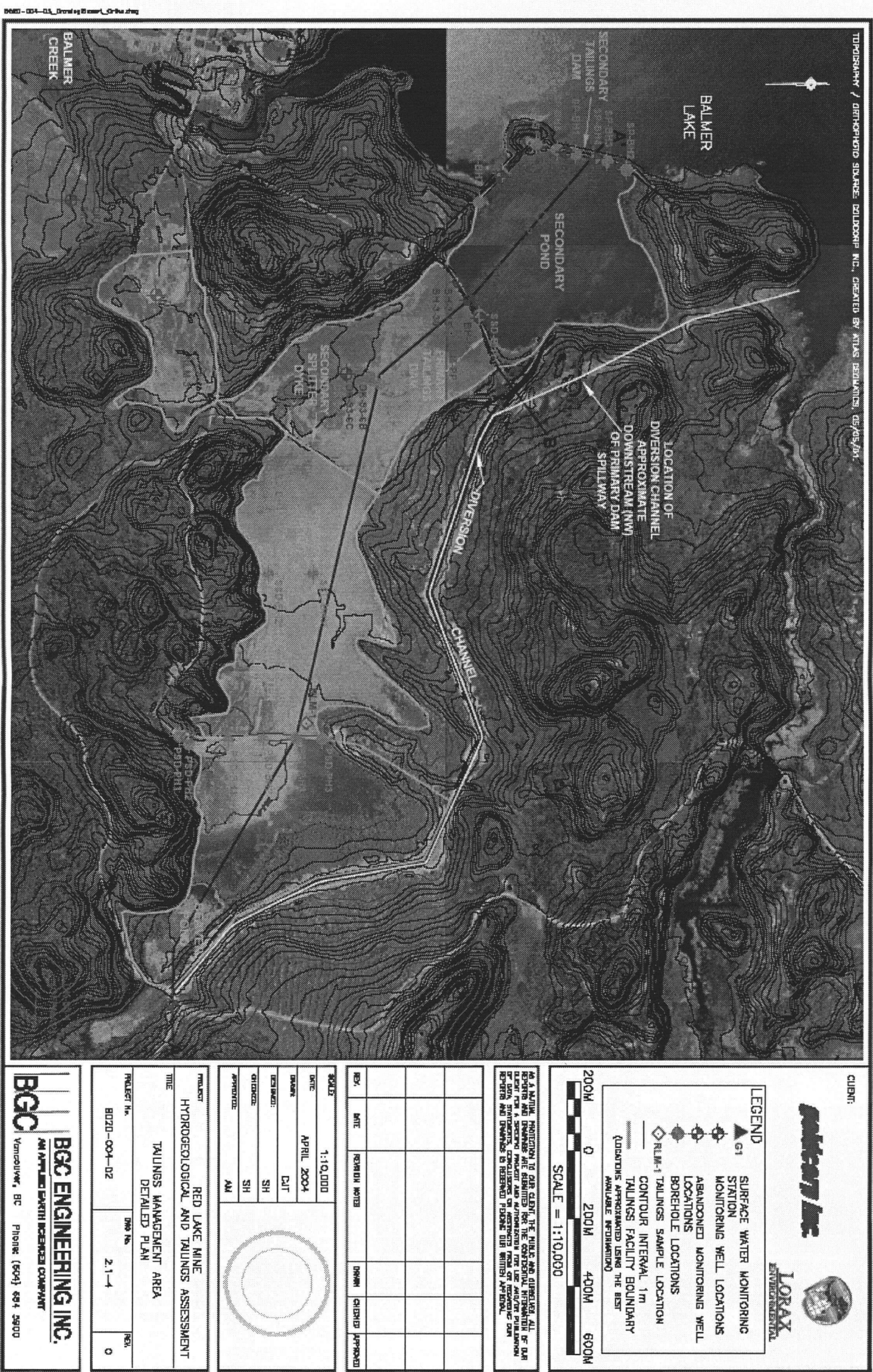


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Figure 5: Groundwater Well and Tailings Sampling Locations in Inactive Tailings Management Area

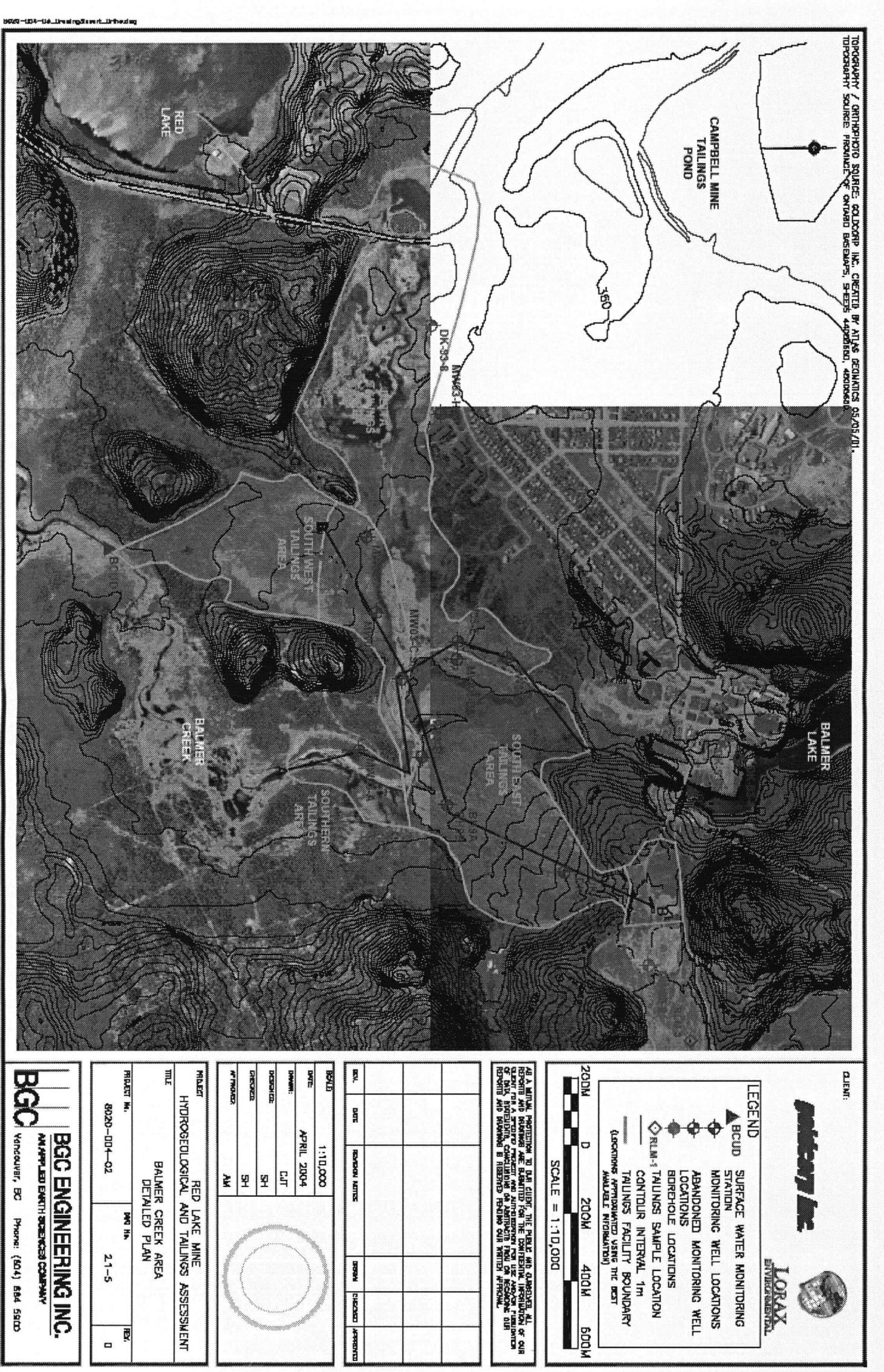


Figure 4: Groundwater Well and Tailings Sampling Locations in Active Tailings Management Area



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2 of 2

Figure 5: Groundwater Well and Tailings Sampling Locations in Inactive Tailings Management Area



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Figure 5
2 of 2

Figure 5: Groundwater Well and Tailings Sampling Locations in Inactive Tailings Management Area



Meilleux, D
M.A.Sc
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Figure 5
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the historical tailings deposit south of the mine site, on the east side of Balmer Creek.

In the active TMA it was found that groundwater flows horizontally from southeast to northwest, and flows vertically upward. Groundwater concentrations of dissolved arsenic in the historical tailings in the active TMA (in Primary Pond, and under the Primary and Secondary dams) are significantly elevated. These arsenic levels are significantly lower than what is observed in the tailings deposit located near Balmer Creek, however the concentrations are still significantly higher than background levels. Vertical movement of groundwater from the tailings layer upward to the overlying pond waters, and horizontal seepage through the dams provide the most significant groundwater contributions of arsenic to the surface water bodies.

It was found that groundwater moves horizontally from northeast to southwest and vertically downward in the inactive TMA located southeast of the mine. Arsenic concentrations in the tailings layer are extremely elevated, and increase closer to the creek. These are the oldest tailings located on the site, and they were produced at a time when roasting was a part of the milling process. This area was revegetated in the late 1980's. Starting in 1997 nitrogen and iron concentrations in groundwater were seen to increase. At the same time, a more than 10 fold increase in arsenic concentrations was observed. It is speculated that the large increase in the concentration of ammonia nitrogen was from fertilizer used during the revegetation of the area. The applied nitrogen from the fertilizer appears to have migrated downward into the groundwater likely resulting in the increased arsenic concentrations that have been observed.

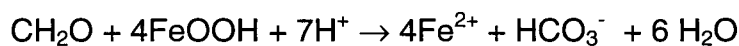
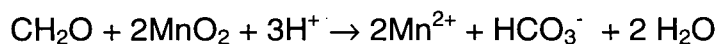
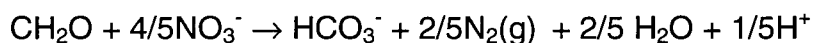
3.0 Literature Review

Arsenic has a complex chemistry and is readily mobile under many conditions. As a result of gold mining activities in Canada, thousands of tonnes of arsenic bearing rock are brought to the surface, crushed and ground to a small particle size, chemically and mechanically treated, and disposed of into tailings impoundments. The largest source of arsenic in gold mining ore is arsenopyrite (FeAsS). Arsenopyrite is stable deep beneath the earth surface, however as a result of milling processes high concentrations of arsenic may be released into solution, and less stable secondary minerals containing arsenic may be created.

There are various methods available to remove arsenic from solution, however it is the stability of the solid phase by-product of the treatment process that is of the greatest concern. The preferred arsenic treatment method of both the US EPA and the Canadian metallurgical industry is co-precipitation with ferric iron (Riveros et al., 2001). High iron arsenical ferrihydrite has been shown to be stable for many years under the correct storage conditions (Krause and Ettel, 1985, 1987, 1988, 1989). Unfortunately the correct storage conditions involve maintaining an oxidizing environment, which can be difficult to do in natural tailing impoundment systems.

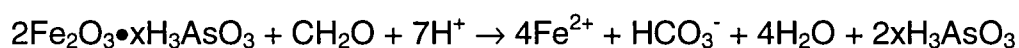
McCreadie et al. (2000) report that oxidized arsenic phases occurring in tailings deposits, as a result of oxidation of arsenopyrite during processing, are potentially susceptible to dissolution under saturated conditions. The combination of organic matter and a water cover can lead to the onset of microbially mediated reducing conditions in tailings impoundments. Water covers are used to limit oxygen flux to tailings surfaces as a method to prevent the onset of acid rock drainage. By limiting the flux of oxygen, reducing conditions can be maintained. When arsenic bearing oxyhydroxide phases are present in a tailings pond the onset of reducing conditions can lead to the release of arsenic from the sediments.

Bacteria play a major role in the development of reducing conditions. Bacteria use dissolved organic carbon as an electron donor in order to reduce various chemical species for energy. There is a well known sequence of reactions that occur when water becomes anaerobic (Stumm and Morgan, 1995). The following equations describe the sequence of steps involved in the development of biologically mediated reducing conditions.



Initially all O_2 is reduced (CH_2O gives off electrons that oxygen takes, organic carbon is oxidized and oxygen is reduced). Once all of the oxygen is consumed, nitrate (NO_3^-) is reduced to NO_2^- and the gases N_2O and N_2 . Solid phase manganese and iron oxides are reduced to Mn^{2+} and Fe^{2+} . This is followed by the reduction of sulphate (SO_4^{2-}) to sulphide (S^{2-}). Fermentation and methanogenesis occur next, resulting in the production of CH_4 . Finally, nitrogen gas (N_2) is reduced to NH_4^+ . It is thought that the reduction of As^{5+} to As^{3+} occurs after the reduction of iron but before sulphate reduction (Smedley and Kinniburgh, 2002).

The exact mechanism of release of arsenic from iron oxide phases is not completely understood. A combination of reductive dissolution of the iron oxide (Fe^{3+} being reduced to Fe^{2+} resulting in the solubilization of the iron oxide phase and the release of sorbed arsenic) and the direct reduction of arsenate to arsenite is thought to occur (Smedley and Kinniburgh, 2002). Arsenite has a much lower affinity to iron oxide phases at near neutral pH than arsenate (Jain et al., 1999). McCreadie et al. (2000) propose the following equation to describe the release of arsenic via reductive dissolution from roaster-derived ferric oxides.



Where CH_2O represents a model dissolved organic carbon molecule and x is the amount of non-structural arsenic associated with hematite grains in the roaster tailings.

There are numerous studies that document the increase in aqueous arsenic concentrations following the development of anaerobic conditions in sediments containing arsenic bearing iron oxyhydroxides. These studies include: Deuel and Swoboda (1972), McGeehan and Naylor (1994), Azcue and Nriagu (1995), McCreadie et al. (2000), and Martin and Pedersen (2002).

Little evidence of arsenic removal as an arsenic sulphide species has been documented (Smedley and Kinniburgh, 2002), and it is unclear as to why high dissolved arsenic concentrations are observed under reducing conditions in the presence of sulphide. McCreadie et al. (2000) saw increased arsenic concentrations in a sulphate reducing zone of the Campbell Mine tailings impoundment. Meng et al. (2003) indicate that biotic reductions can convert arsenic and sulphide into arsenian pyrite, although there is limited evidence of this occurring in natural systems. Martin and Pedersen (2002) report that in the deeper sediments of Balmer Lake arsenic is consumed as an authigenic sulphide phase. In the shallow sediment, arsenic is released to the surface water due to

seasonal anoxia that develops in the near surface pond sediments (Martin and Pedersen, 2002). It is speculated that conditions may not be reducing enough in some situations to cause the formation of an arsenic sulphide phase, and or not enough sulphide is available (not enough sulphate available to be reduced to sulphide) to precipitate all of the arsenic (plus other dissolved metal species).

Pyrite formation in low temperature sedimentary environments has been studied intensively, however there is only limited information available on arsenopyrite formation in low temperature sedimentary environments.

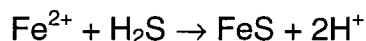
Iron sulphide formation has been documented in oceans, lakes, moors, swamps and aquifers, and it has been suggested that pyrite may have played a crucial role in the origin of life on earth (Rickard et al., 1995). There are three major reactants involved in pyrite formation that can become limiting: metabolizable organic matter, dissolved sulphide, and reactive iron minerals (Morse, 1999).

There are three essential processes in the formation of pyrite: production of hydrogen sulphide, formation of iron monosulphides, and formation of iron disulphides (i.e. pyrite). In the sequential order of redox processes, iron reduction has an overall higher energy yield than sulphate reduction, therefore, it is generally thought that significant sulphate reduction will not occur in the presence of ferric iron. Postma and Jakobsen (1996) suggest that the reduction sequence is better explained as a partial equilibrium process rather than from the overall energy yield of the different reactions. From a thermodynamic point of view Fe(III) and sulphate reduction may proceed simultaneously over a wide range of environmental conditions (Postma and Jakobsen, 1996). The stability of the iron oxyhydroxide species and the pH are the dominant factors in determining which reduction is energetically favoured (Postma and Jakobsen, 1996). Field data confirms that simultaneous reduction of Fe(III) and sulphate occurs and that the reduction order, as predicted by the overall energy yield, can even be reversed. The boundaries between Fe(III) and sulphate reduction are strongly

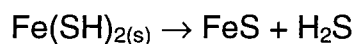
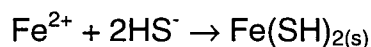
affected by the variability in the stability of iron oxyhydroxides present. The more variability that exists, the more blurred the boundaries will be (Postma and Jakobsen, 1996).

Iron monosulphide formation is kinetically limited, and the amount of iron in sulphide bearing waters is higher than predicted by equilibrium suggesting that significant amounts of iron may be maintained in solution as sulphide complexes (Rickard et al., 1995). Rickard et al. (1995) listed two competing pathways for iron (II) monosulfide formation in solution:

- a) hydrogen sulphide pathway (direct precipitation of Fe(II) monosulfide)



- b) bisulphide pathway (involves the formation of complexes)



The bisulphide pathway is faster at neutral to alkaline pH and $\text{S}^{2-} > 10^{-3}\text{M}$, while the hydrogen sulphide pathway dominates under acidic conditions and $\text{S}^{2-} < 10^{-3}\text{M}$, however the hydrogen sulphide pathway becomes more important at temperatures below 25°C (Rickard et al., 1995).

In most sedimentary environments pyrite is the stable iron sulphide, and ultimately all iron and sulphide species will become pyrite, implying that there are multiple competing pathways for its formation (Rickard et al., 1995). Iron monosulphides are scarce in modern low temperature sedimentary systems. Pyrite is stable and forms rapidly under oxidized/reduced boundary conditions, however the reaction mechanisms of pyrite formation at low temperatures is incomplete (Furukawa and Barnes, 1995).

Rickard et al. (1995) describe three pathways for pyrite formation:

a) Polysulphide Pathway

Involves the reaction of Fe(II) monosulphide and polysulphide. Numerous experiments have shown that in order for iron monosulphides to be converted to pyrite, a sulphur source of an intermediate oxidation state (elemental sulphur, thiosulphate, or polysulphides) must be present. The early studies (such as Berner (1970)) suggest that pyrite forms due to the addition of a sulphur atom to the precursor monosulphide rather than through the loss of iron. Furukawa and Barnes (1995) show theoretically that in order for the change in volume of the solids to be negative (a requirement of thermodynamics), pyrite formation must proceed through the loss of iron and not the addition of sulphur. Furukawa and Barnes (1995) suggest that intermediate sulphur species, required in the experiments, act as oxidizing agents rather than as a source of sulphur. Intermediate sulphur species are efficient oxidizing agents, however other species may be able to act as oxidizing agents which may explain why many natural pyrite forming systems are not found to contain a high concentration of intermediate sulphur species (Furukawa and Barnes, 1995). Wilkin and Barnes (1996) used sulphur isotope ratios to show experimentally that pyrite formation proceeds via the loss of iron from the precursor monosulphide rather than via the addition of zero-valent sulphur.

b) FeS Oxidation Pathway

Involves a progressive oxidation mechanism starting with the aging of amorphous FeS to Mackinawite ($\text{FeS}_{0.94}$). Mackinawite is transformed to greigite (Fe_3S_4) under slightly oxidizing conditions and greigite is transformed to pyrite. The individual steps are not completely understood, but it is stated that the transformation to mackinawite is slow. This pathway is really the same as in a), as it has been shown that polysulphides act as oxidants.

c) H₂S Pathway

It has been shown that iron monosulphides could react with H₂S to form pyrite at 100°C in a few days ($\text{FeS} + \text{H}_2\text{S} \rightarrow \text{FeS}_2 + \text{H}_{2(g)}$). The rate of the reaction is suggested to depend on pH, FeS, surface area, temperature, and hydrogen sulphide concentration. This reaction however, has not been observed in a number of carefully controlled experiments (Wilkins and Barnes (1996), Berner (1970), Schoonen and Barnes (1991), etc.). In these experiments it was shown that pyrite formation only proceeded at significant rates when an oxidant other than H₂S was present. Benning et al. (1999) showed that if iron monosulphides are kept in a reducing environment with no other reactant than H₂S, the formation of pyrite is inhibited (over a wide range of temperature and pH) and mackinawite is the stable phase. It was shown that only oxidation of the aqueous sulphur species or of the precursor iron monosulphide species resulted in pyrite formation (Benning et al., 1999).

Crystal growth of sedimentary iron disulfides becomes important once FeS₂ nuclei are formed. The nuclei can grow from solution once they are formed. The FeS₂ nuclei are formed as a result of porewaters in reduced sediments being close to saturation with respect to iron monosulphide phases (iron monosulphides are about nine orders of magnitude more soluble than iron disulphides) (Rickard et al., 1995). The rate of dissolution of iron monosulphides may exceed the growth of pyrite, leading to increased aqueous iron concentrations. The low concentrations of polysulphides in natural waters suggest that the polysulphide pathway may not be a viable mechanism under all conditions (Rickard et al., 1995).

Benning et al. (1999) showed that pyrite will only form at low temperatures if some degree of oxidation is present (the importance of oxygen vs polysulphides

is unknown), and that pyrite forms at negligible rates in H_2S solutions. Sulphur compounds with an oxidation state greater than S^{2-} have the potential to act as terminal electron acceptors in biologically mediated oxidation of organic material (Neal et al., 2001). Morse and Wang (1997), and Morse (1999) suggest that at low pH's pyrite formation proceeds via the faster H_2S pathway, however at near neutral (and higher) pH's the formation of pyrite proceeds via the much slower polysulphide pathway. Morse and Wang (1997) showed that high DOC concentrations could significantly reduce the rate of pyrite formation possibly due to the complexation of dissolved iron with organic matter making it unavailable for iron sulphide mineral formation. At higher pH the Fe(II) is not readily available due to the competing reaction of Fe(III) oxyhydroxide formation (Wei and Osseo-Asare, 1996).

Although pyrite is by far the most abundant sulphide mineral, other metals can react with sulphide to form sulphide minerals, and/or metals can coprecipitate and adsorb onto iron sulphides (Morse and Luther, 1999). There exists the potential for trace metals to be immobilized by incorporation into sulphide minerals (Di Toro et al. (1992), and Morse (1994)). Huerta-Diaz and Morse (1992), and Huerta-Diaz et al. (1998) state that reactions occurring at the surfaces of iron sulphides play a major role in metal retention, mobility, and bioavailability. Arsenic species must first be reduced to arsenite before they can be incorporated into sulphide minerals. Next to mercury, arsenic is the most likely metal to be incorporated with pyrite (Morse and Luther, 1999). Moore et al. (1988) found that diagenetic sulphides were important sinks for metals and arsenic in the reduced sulphidic sediments of the Milltown Reservoir. It can be assumed that arsenic will be incorporated into pyrite or will form arsenopyrite under similar conditions that favour pyrite formation.

Pyrite represents a relatively stable sink for toxic trace metals, however pyrite is susceptible to dissolution by iron oxidizers (such as *Thiobacillus ferrooxidans*) if conditions are allowed to become oxidizing (Neal et al., 2001). If sulphides are

moved into oxidizing environments, trace elements may be released into solution (Moore et al., 1988). It is essential to know the forms of arsenic present in a tailings impoundment to apply appropriate management strategies.

4.0 Solids Identification

To effectively manage the mine site, it is essential to understand and characterize the form of the arsenic in the Red Lake Mine tailings. The long history of the Red Lake Mine Site, and the multitude of milling methods used over the years have resulted in the production of various different types of tailings that have been deposited in several areas around the mine site. In addition, tailings have been subject to a number of different post depositional conditions. Each tailings type is expected to contain different types of arsenic bearing solids, in varying quantities. Accordingly, a major effort was undertaken to characterize the tailings material in various depositional environments.

The objective of this work was to identify the type of arsenic in each of the various tailings samples. Type of arsenic refers to the minerals that arsenic is associated with, whether it is part of the mineral structure or adsorbed to the surface of the mineral, and the speciation of the arsenic (XANES). It was also desired to determine the amount of each type of arsenic in the samples (via the Rietveld method, XANES, and sequential extractions). Based on this information, recommendations for optimal long term storage conditions for each type of tailings are made.

4.1 Sample Collection and Preparation

Tailings samples were collected in the fall of 2002 from 9 locations around the Red Lake Mine site. The samples included fresh tailings, historical tailings, historical tailing produced at a time when roasting was used in the milling process, and pond sediments. Figure 4 shows the sampling locations.

4.1.1 Sample Collection

A soil corer was used to collect the samples. In some cases a sample was taken at the surface using the corer and a pit was dug so that deeper samples could be

obtained. Tailings samples were labelled RLM-1 – RLM-7, with samples from different depths at the same location being identified by a second number (e.g. RLM-2-1, RLM-2-2, and RLM-2-3). The samples and sample locations are described below.

RLM – 1: Downstream of SD#1, north of the culvert

The tailings at this location are either new tailings (after the shutdown), or historical non-roaster tailings produced before SD#1 was constructed. The tailings were soft (it would not have been possible to sample the tailings if the ground was not frozen), dark grey and fully saturated. Core from the surface down to approximately 1 ft was recovered.

RLM – 2: Downstream of SD#2, on tailings beach

Roaster tailings were co-disposed with cyanidation and flotation tailings in this area from 1960 until roaster operation ceased some time around late 1979 to early 1980. After roaster operation ceased, tailings that had been subjected to cyanidation and flotation were deposited in this area until 1987 when the tailings pipeline was extended to its current location. The exact flow path that the tailings took between 1960 and 1987 is unknown, therefore it is not clear whether the tailings sampled at this location were derived from the roaster.

The tailings were solid and unsaturated for approximately 3 feet. The corer had to be pounded into the ground with a sledgehammer in order to obtain samples. Samples were taken from three depths at this location.

RLM-2-1

Core was obtained from the ground surface down to approximately 6 inches. The tailings were visibly oxidized, with several different-coloured layers present. The top of the tailings was orange, followed by a thin grey layer, followed by a red layer. The tailings in this sample were unsaturated.

RLM-2-2

Core was taken from approximately 1.5 feet to 2 feet below the ground surface. The tailings were grey and unsaturated.

RLM-2-3

Core was obtained from approximately 2.5 feet to 3 feet below the ground surface. The tailings were grey and saturated.

RLM – 3: Old tailings on south side of access road

Roaster tailings were co-disposed with cyanidation and flotation tailings in this area from 1960 until roaster operation ceased some time around late 1979 to early 1980. After roaster operation ceased, tailings that had been subjected to cyanidation and flotation were deposited in this area until 1987 when the tailings pipeline was extended to its current location. It is likely that the cyanidation/flotation tailings overlie the roaster tailings in this area therefore the tailings sampled (at least in the shallow depth samples) are not likely to be roaster derived tailings.

The tailings were solid and unsaturated for approximately 3 feet. The corer had to be pounded into the ground with a sledgehammer in order to obtain samples. Samples were taken from three depths at this location.

RLM-3-1

Core was taken from the ground surface down to approximately one foot. The tailings were unsaturated and were noticeably oxidized (orange in colour).

RLM-3-2

The sample was taken at the top of the grey layer (underlying a red layer), from approximately 1.5 feet to 2.5 feet below the ground surface. The tailings were grey but still unsaturated.

RLM-3-3

The sample was taken at the top of the saturated zone, from approximately 3 feet to 3.5 feet below the ground surface.

RLM – 4: Upstream of SD #1 in flow path of new tailings

The tailings at this location are newly deposited, fresh tailings. The tailings were soft but were covered by a layer of ice making it possible to walk on them. A shovel was used to take the sample as the tailings were too wet to use the corer.

RLM – 5: End of Pipe

Several buckets of tailings were collected from the tailings pipeline discharge while the Paste Backfill Plant was not operating. The tailings were allowed to settle in the field and the water was decanted off. The tailings were then filtered in a pressurized filter apparatus.

RLM – 6: Revegetated Tailings east of Balmer Creek, in between groundwater wells DK-93-3 and BH-9

Tailings were deposited in this area from 1948 – 1960. From 1951 – 1960 the tailings that were deposited were derived from the roasting process (i.e. a large portion of the sulphides likely underwent oxidation during the milling process). Prior to sampling, thick vegetation and a thin sand/soil layer were removed to

expose the top of the tailings layer. The tailings were solid and unsaturated for approximately 4 feet. Dead wood was encountered throughout the tailings, making sampling quite difficult. Samples were taken from two depths.

RLM-6-1

Core was taken from the surface down to approximately two feet. Tailings were a brownish orange colour and were unsaturated.

RLM-6-2

Core was taken at the top of the saturated zone, approximately 4 feet below the ground surface. The tailings were a brownish orange colour.

RLM – 7: CIP tailings from carbon safety screen

To obtain a sample of tailings that had not gone through the Detox and Ferric circuits, a bucket of CIP tailings was collected from the carbon safety screen. The tailings were filtered in a pressurized filter apparatus.

Secondary Pond Sediment

A hole was augured through the ice on the Secondary Pond (in the vicinity of the Limnocorrals) and a dredge sampler was used to collect a sample of the tailings/sediments on the bottom of the Secondary Pond.

Primary Pond Sediment

A hole was augured through the ice on the Primary Pond (in the vicinity of the columns) and a dredge sampler was used to collect a sample of the tailings/sediments on the bottom of the Primary Pond.

Primary Pond Backhoe

During installation of a column experiment in the Primary Pond, a sample of the tailings in the pond was taken from the Backhoe bucket. The tailings were sticky and grey.

4.1.2 Sample Preparation

Air temperatures were below zero at the time of sampling, ensuring that tailings samples would freeze upon exposure to the air. Samples were stored frozen, and were shipped frozen via refrigerated truck to Vancouver, where they were stored in a freezer. These precautions were taken in order to minimize potential oxidation of the solids.

Several of the tests to be conducted required that the samples be dry. After some deliberation, it was decided that in order to minimize oxidation during drying the samples should be freeze dried (as opposed to being dried at room temperature). A portion of each sample was dried for approximately 8 days in a freeze dryer, the remaining portion of each sample was returned to the freezer. The dried portion of each sample was subsampled for the various analyses to be conducted on it, and was shipped to the appropriate facilities.

4.2 Analytical Methods Performed on Samples

A variety of analytical methods were used to characterize the nature of the tailings and in particular the form and nature of the arsenic in the tailings. The methods used in this study include whole rock analysis, scanning electron microscopy, Rietveld refined X-ray powder diffraction, sequential extractions, and X-ray Absorption Near Edge Structure using a Synchrotron light source.

4.2.1 Whole Rock Analysis

Whole rock analysis is the simplest method of determining the total amount of each element in a sample. Total element concentrations, on their own, only provide general information on the types of minerals that may be present in a sample. A portion of each tailings type was dried for approximately 8 days in a freeze dryer and a representative subsample from each dried material was submitted to ALS CHEMEX in Vancouver for whole rock analysis using a four acid near total digestion. A 25-element scan was done on the samples that been HF- HNO₃-HClO₄ acid digested and HCl leached. In addition, total organic carbon analysis was also conducted.

4.2.2 Scanning Electron Microscopy

Using Scanning Electron Microscopy (SEM), mineral phases can be identified and the amount of each phase present can be determined qualitatively. The sample is bombarded by a beam of electrons, some of the electrons are adsorbed by the sample while some are scattered off the sample surface (backscattered electrons). The backscattered electrons create a greyscale image that can be used to identify individual mineral crystals. The heavier the unit weight of the mineral phase the brighter the mineral appears on the backscattered image. It is also possible to examine the texture of the individual grains. Most SEM's contain an energy dispersive spectrometer (EDS) that is used to collect the X-ray spectra emitted by the sample when it is hit by the beam

of electrons. The X-ray spectra can be analysed to determine the grain's elemental composition. The position of each peak in the spectrum identifies the elements that are present, while the relative height of each peak gives an indication of the concentration of each element in the grain. The detection limit for each element in the X-ray spectrum is about 1 wt%. Electron Microprobes have the ability to determine the quantitative chemical formula of minerals in a sample, however the amount of each mineral present can still only be determined qualitatively.

A portion of each tailings type was dried for approximately 8 days in a freeze dryer and a representative subsample from each dried material was submitted to Vancouver Petrographics Ltd. for polished thin section preparation. Vancouver Petrographics Ltd. was instructed to prepare 26 x 46 mm sections using the submitted material without screening or pulverization. They were also instructed not to use water during the preparation of the sections in order to minimize potential oxidation and the dissolution of water-soluble minerals that may have been present in the samples.

The polished thin sections were examined by a Phillips XL-30 scanning electron microscope (SEM) located in the Department of Earth and Ocean Sciences at the University of British Columbia. For most of the analysis the beam was set at a current of 20 kV in order to distinguish arsenic peaks, and a count of 60 seconds was used.

4.2.3 Rietveld Refined X-Ray Powder Diffraction

X-Ray powder diffraction is also used to determine which mineral phases are present in a sample, however used alone it is not possible to quantitatively determine the amount of each phase present. Quantitative phase analysis using Rietveld refined X-Ray powder diffraction data is the most versatile method of quantitative phase analysis. Crystalline matter is composed of periodic arrays of

atoms in three dimensions. The crystal structure is determined using X-ray powder diffraction by passing a beam of monochromatographic X-rays through a crystal and recording the intensities and angles of the diffracted beams (Raudsepp and Pani, 2003). An X-ray diffraction pattern is produced with peaks that are a function of the size and symmetry of the crystalline unit cell of the substance, and with peak intensities that are a function of the atomic arrangement within the unit cell (Raudsepp and Pani, 2003). By comparing the positions and intensities of the peaks to a reference database the identities of the minerals contributing to the powder-diffraction pattern can be determined.

The Rietveld method fits a simulated model to the diffraction pattern and uses a least-squares refinement to minimize the error between the modelled pattern and the actual pattern. The model that is fitted to the diffraction pattern is the sum of three models: a model for the shapes and widths of the diffraction peaks, a model for any aberrations in the shapes and positions of the peaks and a model for the background (Raudsepp and Pani, 2003). The models are obtained from a database, mineral phases are added into the model and the relative weight fraction of each phase is adjusted during the least squares reduction until the best fit is obtained. One weakness of the Rietveld method (and x-ray diffraction methods in general) is that it is not possible to identify amorphous phases; it is however possible to determine the quantity of amorphous phases present. The Rietveld method is most accurate when mineral phases are present in high weight percentages. The error increases as the weight percentage decreases and is possibly as high as 100% for percentages less than 1 wt% (Raudsepp and Pani, 2003). Freeze dried representative subsamples were submitted to M. Raudsepp of the UBC Department of Earth and Ocean Sciences for Rietveld-refined X-ray diffractometry.

4.2.4 Sequential Extractions

A five-step sequential extraction procedure, designed specifically for arsenic, was conducted on 4 samples in duplicate (RLM-2-1, RLM-5, RLM-6-1, and Secondary

Pond Sediments). Several arsenic extraction procedures were reviewed including Keon et al. (2001), Wenzel et al. (2001), Lombi et al. (1999), Gleyzes et al. (2001), and Loeppert et al. (2003). The extraction procedure selected was based on the method of Keon et al. (2001), slightly modified after the fourth step to reflect the methods of Wenzel et al. (2001), Lombi et al. (1999), and Gleyzes et al. (2001). The fractions in order were;

Step 1: Ionically Bound + Pore Water

1 M MgCl_2 , pH 8, room temperature, 2 hours (2 repetitions, 1 water wash)

Step 2: Strongly Adsorbed

1 M NaH_2PO_4 , pH 5, room temperature, 16 and 24 hours (1 repetition at each time, 1 water wash)

Step 3: Coprecipitated with acid volatile sulphides (AVS), Manganese oxides, and very amorphous iron oxyhydroxides

1 N HCl, room temperature, 1 hour (1 repetition, 1 water wash)

Step 4: Coprecipitated with amorphous iron oxyhydroxides

0.2 M ammonium oxalate/ 0.2 M oxalic acid, pH 3, room temperature in the dark (1 repetition, 1 water wash)

Step 5: Coprecipitated with crystalline iron oxyhydroxides

0.2 M ammonium oxalate/ 0.2 M oxalic acid/ 0.1 M ascorbic acid, pH 3, 30 minutes in water bath at 96 °C (1 repetition, 1 water wash)

Reagents were prepared using distilled-deionised water, and were de-aired in a nitrogen filled glove bag by bubbling nitrogen into the reagents. The pH of the reagents was adjusted inside an anaerobic chamber using environmental grade hydrochloric acid and sodium hydroxide. The extractions were carried out in

disposable 50 ml centrifuge tubes. Approximately 0.4 g (dry equivalent) of frozen sample was placed inside each tube and the first reagent was added to it inside the anaerobic chamber. Wet sediment was used as Keon et al. (2001), Buykx et al. (2000) and Zhang et al. (2001) indicated that all means of drying sediment can potentially result in changes in arsenic speciation. The tubes were sealed and shaken by hand, and then transferred to a shaker table for the duration of the extraction step. Tubes were centrifuged for 10 minutes at 3000 rpm at the end of each extraction step and then transferred back to the anaerobic chamber. The reagent was decanted from each tube and filtered, using 0.45 μm filters, into a sample bottle. The next reagent/water was added to each tube, the tubes were sealed and shaken and then transferred to the shaker table for the duration of the extraction step.

Forty ml of reagent were used in each step, and 10 ml of de-aired, distilled-deionised water were used for the water rinses. For the water washes, the tubes were shaken by hand for several minutes after the water was added to them, the tubes were then centrifuged, transferred back to the anaerobic chamber, the water decanted and filter into a sample container, and the next reagent added.

In step four, the tubes were covered with tinfoil and placed into a sealed box to exclude all light. In step five, the tubes were set in a test tube rack and placed in a water bath that had been preheated to approximately 96 °C.

4.2.5 X-ray Absorption Near Edge Structure

X-ray absorption fine structure (XAFS) spectra were collected for all of the samples. X-ray absorption spectra were collected on April 28-29, 2003 and June 13-16, 2003 at the National Synchrotron Light Source located at Brookhaven National Laboratories, Upton, New York. The bending magnet beam line X11A (Navel Research Laboratory-Synchrotron Radiation Consortium) was used. The

study was conducted through the Canadian Light source (CLS), and spectra were analyzed by CLS.

A fixed exit double crystal monochromator with Si (111) crystals, detuned by approximately 15% to eliminate higher energy harmonics, was used to scan the energy region around the arsenic K-edge absorption energy ($E_o = 11867$ eV). The inflection point of the Au L_{III} -edge of a thin gold foil at 11919.7 eV was used as an internal energy scale reference. Both fluorescence yield (samples oriented at 45° with respect to the incident beam) using a Lytle detector and transmission modes (samples oriented perpendicular to the incident beam) were used for the collection of X-ray absorption spectra. Previously freeze dried samples were packed into a slit in a manufactured sample holder and covered on both sides with Kapton tape. XAFS spectra were collected over the photon energies from 11667 eV – 12825 eV, using 10 eV steps from 11667 – 11817 eV, and 0.75 eV steps from 11817 – 11917 eV (XANES region). At least 4 scans were collected for each sample and were averaged for the analysis. The fluorescence yield mode was used for all the tailings samples. All spectra were collected at ambient temperature and pressure.

XAFS spectroscopy can be used to investigate the local coordination environment around the arsenic atom in a mineral phase, including the oxidation state (Moldovan et al., 2003). In addition to Moldovan et al. (2003), McGeehan (1996), Rochette et al. (1998) and Reynolds et al. (1999) also used XAFS spectroscopy to speciate arsenic in soil solids. The technique has been shown to be effective in determining the molecular level speciation of arsenic over the concentration range of 50 mg/kg to several weight percent in mine tailings solids (Jiang, 2002).

Synchrotron light sources are electron accelerators that confine high energy charged electrons traveling in a circular orbit at a speed close to that of light (relativistic speed) (Sham, 2002). When an electron is accelerated it produces

electromagnetic radiation. In a synchrotron, the electrons are accelerated centrifugally into a circular orbit using bending magnets. Synchrotron radiation is emitted tangential to the orbit as a result of the bending. A linear accelerator and a booster synchrotron are usually used to first accelerate the electrons to the desired energy of the storage ring. The pre-accelerated electrons are then injected into the storage ring that consists of straight and bending sections of stainless steel tubes kept under ultra-high vacuum (Sham, 2002).

An atomic absorption edge occurs when an X-ray photon is absorbed in a single scattering event, resulting in the transfer of the photons energy to the production of a photoelectron escaping the atomic potential well (Jiang, 2002). Each element has specific binding energies of the atomic core level electrons (absorption edges, i.e. K-edge absorption energy). The binding energy for each element shifts slightly due to different oxidation states, in general the higher the oxidation state the higher the absorption edge energy. The absorption edges of different elements are well separated allowing the X-ray absorption spectra of different elements to be analyzed separately (Jiang, 2002). XAFS refers to the entire spectrum of absorption coefficient vs. photon energy. The region within approximately 50 eV of the absorption edge is referred to as the X-ray near edge structure (XANES) while the region above the near edge region is referred to as the extended X-ray absorption fine structure (EXAFS). A bound core level photoelectron is excited from the absorbing atom into a free electron state when an X-ray photon is absorbed. The excitation of the 1s (K edge) core state is one of the most commonly used absorption edges

XANES is an element specific, non-destructive method that is very sensitive to the oxidation state, electronic structure and local symmetry of a mineral phase (Bancroft and Hallin, 2002). Model compounds are required to characterize the unknown oxidation states of the element of interest in a sample. By doing this the valence speciation and an estimate of composition can be made (Jiang, 2002). Data from multiple scans are overlain and averaged. The first step in the

data analysis is to remove the pre-edge background. Usually the pre-edge background is fit with a linear function of energy that is extrapolated into the post-edge region (Jiang, 2002). The linear function is then subtracted from the data. A kinetic energy zero point (E_0) must then be determined. In most cases the first peak of the derivative (first inflection point) is used for E_0 (Jiang, 2002). The data is then normalized using the determined E_0 value. The post-edge data background must be fit and subtracted from the data. A cubic spline is commonly used to fit the post-edge background.

Three model compounds were used in the study: arsenopyrite (FeAsS ; As^{1-}), arsenic trioxide (As_2O_3 ; As^{3+}), and iron arsenate (scorodite – $\text{FeAsO}_4 \cdot 2(\text{H}_2\text{O})$; As^{5+}). Principal Component Analysis (PCA), a linear algebraic technique, was used to semi-quantitatively determine the composition of the tailings samples (i.e. the number of unique components present within the spectra).

The model compounds listed above were used along with a deconvoluted XANES spectra to semi-quantitatively determine the amount of arsenic present in each oxidation state in the various samples. The XANES spectra were deconvoluted using a linear least-squares fitting procedure (Kotzer, 2003). According to Kotzer (2003), linear least-squares fitting of XANES spectra has been shown to be a good technique to compositionally determine the relative amounts of various oxidation states within complex materials.

4.3 Results and Discussion

4.3.1 Whole Rock Analysis

Table 1 shows a summary of the results from the ICP scan, complete results can be found in Appendix II. Arsenic concentrations range from 1180 mg/kg to 5690 mg/kg (0.12% – 0.57%). Historical tailings samples (RLM-2, RLM-3, and RLM-6) exhibit significantly higher arsenic concentrations than the samples containing newer tailings (RLM-1, RLM-4, and RLM-5). The results from RLM-7 are somewhat irrelevant as the sample was taken prior to the removal of high arsenic content sulphides via flotation. The concentration of arsenic in the Primary and Secondary Pond sediments is 3000 mg/kg and 2950 mg/kg respectively, higher than in the new tailings samples. The high sulphur content in the RLM-2 samples, ranging from 1.86 – 2.63 %, indicates that these tailings were produced during a period of time when roasting and concentration of the sulphide portion of the ore had ceased. The remaining samples have relatively low sulphur contents, none greater than 1%. The newer tailings have low sulphur contents as the majority of the sulphides are concentrated and removed from the tailings during the milling process for further gold recovery. The older historical tailings likely have low sulphur contents as a result of the roasting process (sulphides were burnt off during roasting).

Several interesting results are present in the Secondary Pond sediment data. The concentrations of copper, nickel and zinc are much higher in the Secondary Pond sediments than in the tailings samples. The copper concentration is 2330 mg/kg (0.2%) in the Secondary Pond sediment, the next highest Cu concentration in a tailings sample is 182 mg/kg at end of pipe (RLM-5). The nickel and zinc concentrations are 826 mg/kg, and 1860 mg/kg, respectively (the next highest Ni and Zn concentrations in a tailings sample are 192 mg/kg and 395 mg/kg). These results indicate that metals are concentrating in the pond sediments. The organic carbon concentration in the Secondary Pond sediments

is also relatively high, at 1.66%. The high organic carbon concentration is due to the vast amount of biological activity in the pond over the last few years.

Table 1: Summary of Whole Rock Analysis Results

Sample	As	Cu	Fe	Ni	Pb	Zn	S	OC
	mg/kg	mg/kg	%	mg/kg	mg/kg	mg/kg	%	%
RLM-1-1	1990	98	7.22	139	13	127	0.68	0.26
RLM-2-1	3230	104	9.77	174	68	179	1.86	0.18
RLM-2-2	4130	128	10.35	192	82	225	2.63	0.07
RLM-2-3	4100	125	9.93	176	114	258	2.34	0.09
RLM-3-1	3300	111	9.14	152	263	294	0.80	0.18
RLM-3-2	3210	119	9.16	142	347	300	0.80	0.18
RLM-3-3	2660	112	8.70	144	351	202	1.00	0.30
RLM-4	1180	111	7.71	138	146	148	0.72	0.11
RLM-5	1995	182	8.00	134	232	183	0.66	0.22
RLM-6-1	2630	121	9.01	171	66	395	0.99	0.25
RLM-6-2	2050	130	9.12	154	174	345	0.57	0.30
RLM-7	5690	133	8.03	168	142	335	1.34	0.02
RLM-SP	2950	2330	7.35	826	322	1860	0.58	1.66
RLM-PP	3000	491	7.32	320	393	1325	0.54	0.64
RLM-PP-BH	2150	303	6.34	104	140	184	0.74	0.18

4.3.2 Rietveld Refinement

The results from the Rietveld refinement of the X-Ray powder diffraction data taken for the majority of the samples are presented in Table 2. The complete reports from the analysis including the Rietveld refinement plots can be found in Appendix III. The whole rock analyses indicate that none of the samples contain even as much as 1 wt% As, and it is therefore unlikely that the samples would contain 5% or more of an arsenic containing mineral phase that is necessary for accurate determination by Rietveld analysis. Some general conclusions can, however, be drawn from the analysis.

The major mineral in all of the samples is quartz. Other major constituents include plagioclase, biotite, chlorite, dolomite and amphibole, with the new tailings containing considerably more dolomite and amphibole than the old

tailings. The unsaturated old tailings (RLM-2-1, RLM-3-1, and RLM-6-1) contain gypsum which is an indication that sulphide oxidation has occurred. When sulphides are oxidized to sulphate, the sulphate will often precipitate with calcium present in the tailings to form gypsum.

Table 2: Rietveld Refinement Results (wt %)

Mineral	RLM 1	RLM 2-1	RLM 2-3	RLM 3-1	RLM 3-3	RLM 4	RLM 5	RLM 6-1	RLM 6-2	RLM 7	2° Pond Sed.	1° Pond Sed.
Quartz	36.5	43.5	48.7	49.2	50.5	33.6	32.1	46.9	42.9	32.3	37.3	36.0
Plagioclase	15.9	14.1	15.6	12.5	12.7	18.3	16.4	9.7	8.3	15.3	16.6	15.0
Biotite	4.0	5.8	4.8	6.5	7.3	3.5	5.7	5.0	6.6	5.3	9.3	10.7
Muscovite		3.6						4.7	5.9			
Chlorite	3.5	8.0	5.1	14.8	8.8	4.5	7.9	10.4	12.8	8.0	18.0	15.1
Talc												
Gypsum		3.9		0.8				3.8				
Calcite	0.8					1.1	3.0		0.9	2.4		2.0
Dolomite	24.1	9.1	10.6	9.1	11.9	22.0	21.2	10.2	14.9	19.0	11.3	13.2
Siderite		0.7			1.1			3.2	2.9			
Amphibole	12.9	4.7	4.7	5.2	4.0	13.7	12.5	1.2	1.2	13.2	6.6	6.8
Pyrite			1.5									
Arsenopyrite		1.9	0.8				0.2	1.6	1.7	1.2	0.2	0.3
Pyrrhotite	1.5	0.6	3.2	0.4	2.3	2.1		0.7	0.6	2.2		
Titanite												
Hematite												
Magnetite	0.8	2.9	2.5	1.6	1.4	0.9	0.8	1.9	1.3	0.7	0.7	0.5
Goethite		1.4					0.2	0.7		0.5		0.4
Rutile			2.4			0.2						

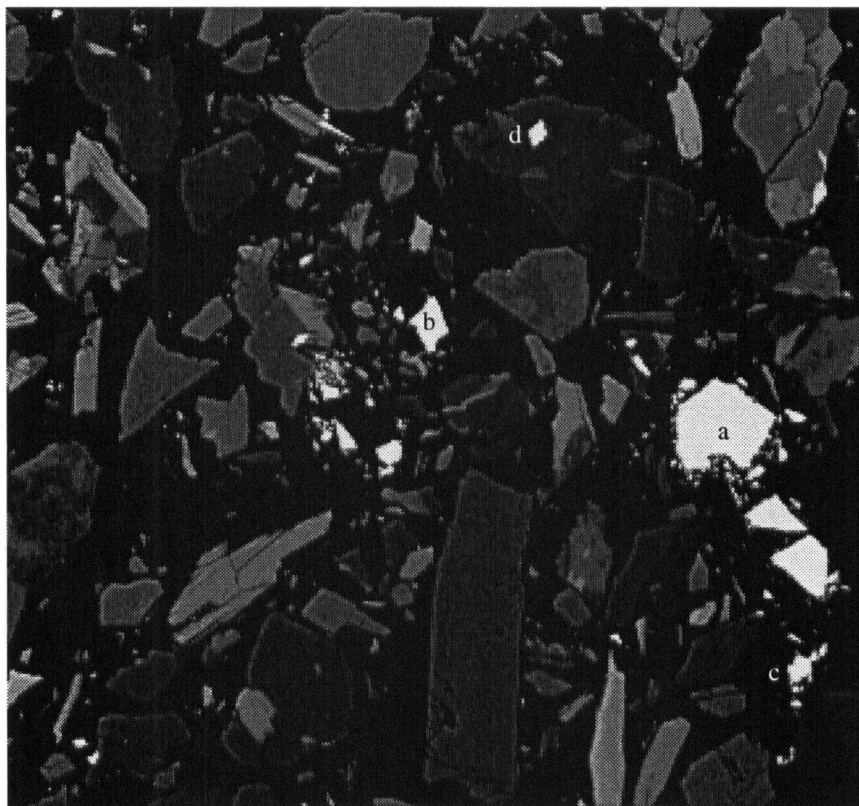
4.3.3 Scanning Electron Microscopy

A scanning electron microscope (SEM) was used to identify the arsenic containing minerals in each tailings sample. After spending some time becoming familiar with the samples it was determined that all grains containing arsenic appeared bright under the SEM. After this was determined little time was spent looking at the less bright, grey particles. In general, there are three types of arsenic bearing minerals that appear bright: arsenopyrite being the brightest followed by pyrite/pyrrhotite, and iron oxides (some containing arsenic).

RLM-1 – Downstream of SD#1

The only arsenic containing species detected in this sample was fine-grained Arsenopyrite, found both as liberated grains and included with other minerals. Figure 6 shows a typical spot of the thin section. Particle (a) is pyrrhotite, particles (b) and (c) are iron oxide, and particle (d) is encapsulated arsenopyrite. The grains are clean, with no visible signs of weathering. The grains are sparsely distributed throughout the sample, however, since arsenopyrite is 46% As by mass (in the ideal formula), the total amount of arsenic found in the sample could be explained by the small percentage of arsenopyrite grains found (Jambor, 2003). Some iron oxide grains were located, however no arsenic was found to be associated with the iron oxide grains. These results were expected as the tailings are believed to have been non-roaster tailings that have remained saturated.

Figure 6: Backscattered Electron Image for RLM-1. Particle (a) is pyrrhotite, particles (b) and (c) are iron oxide, and particle (d) is arsenopyrite.



Figures 7, 8 and 9 show the X-Ray spectrum patterns from RLM-1 for pyrrhotite, iron oxide, and arsenopyrite, respectively. Although these patterns were obtained from RLM-1 they are indicative of what was seen for these minerals in all of the samples.

Figure 7: X-Ray Spectrum for RLM-1, showing pyrrhotite pattern.

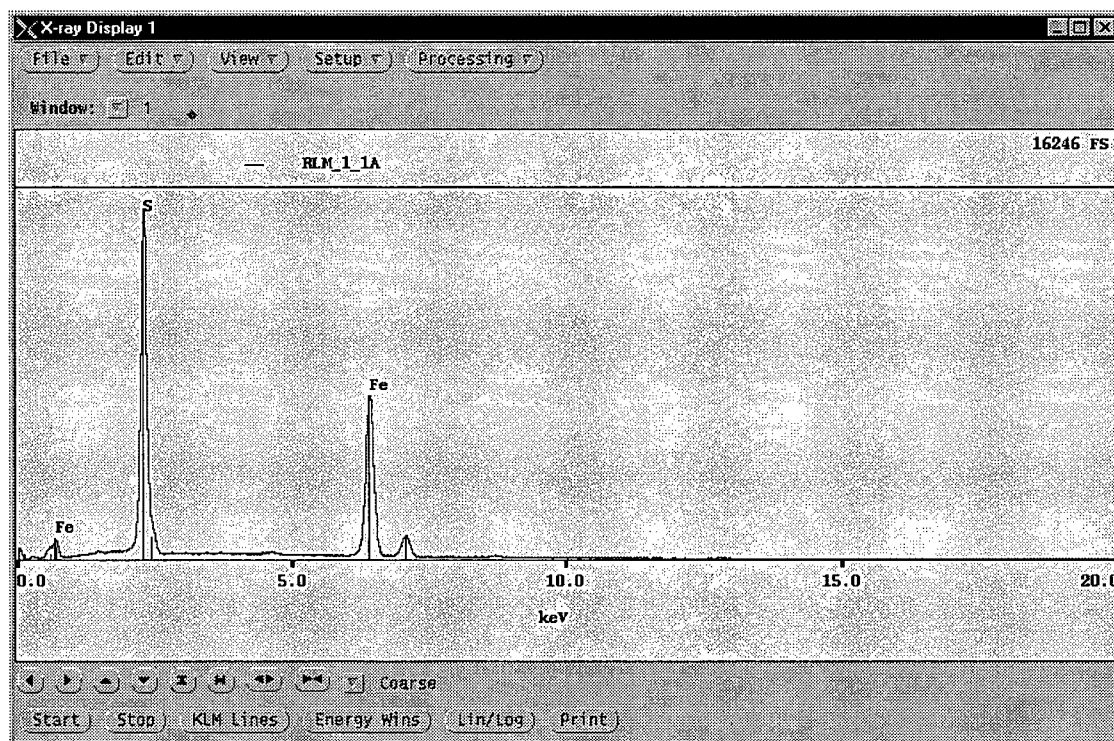


Figure 8: X-Ray Spectrum for RLM-1, showing iron oxide pattern

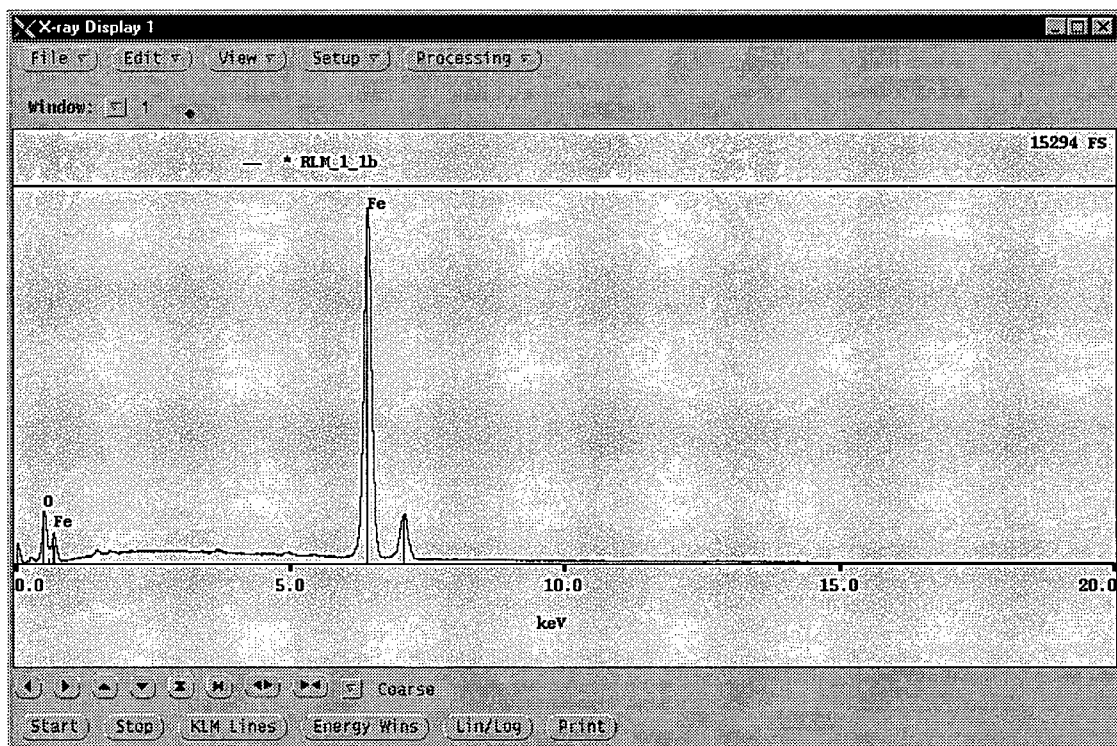
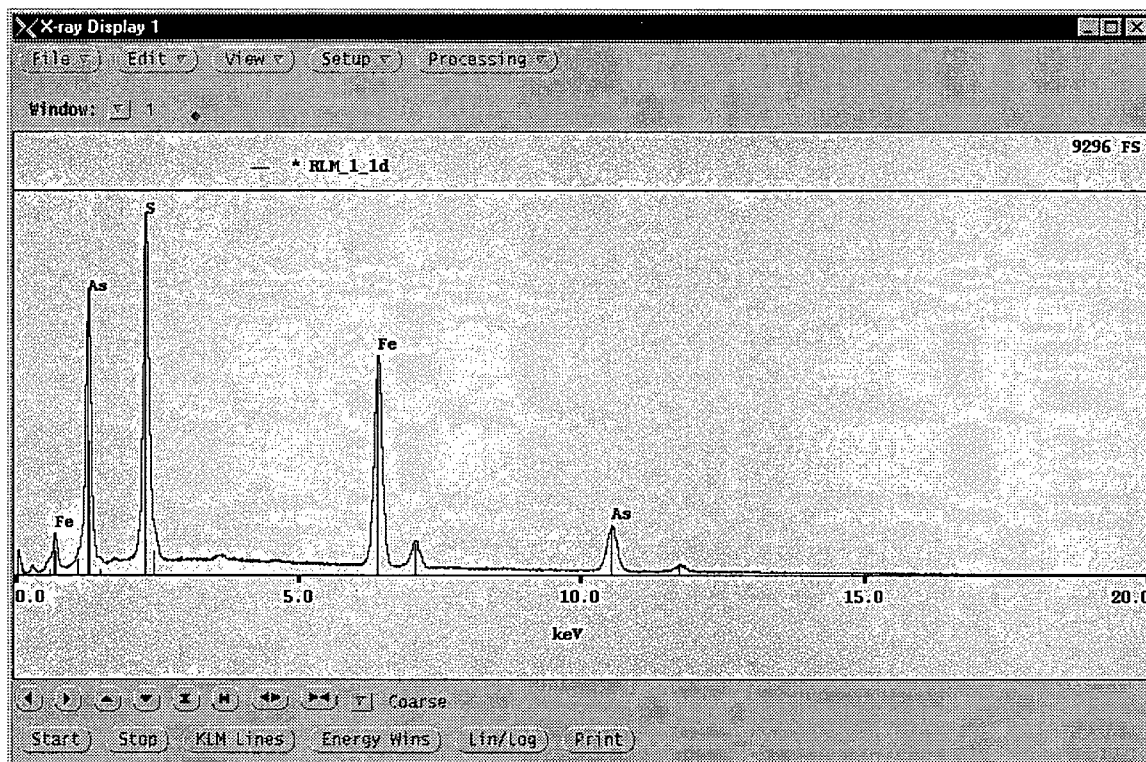


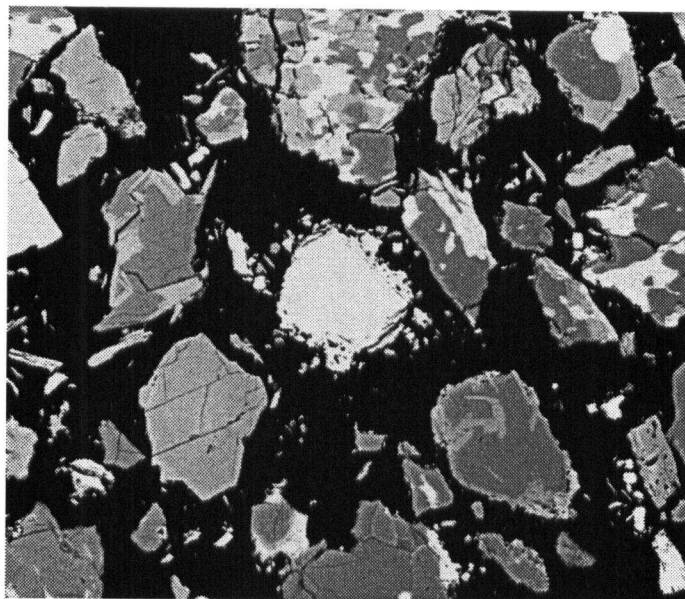
Figure 9: X-Ray Spectrum for RLM-1, showing arsenopyrite pattern



RLM 2-1 – Downstream of SD#1, from 0 – 0.5 ft

Weathering was observed on some grains, namely pyrrhotite and pyrite. Arsenic was found both as arsenopyrite and on the edges of weathered pyrrhotite/pyrite grains. Arsenic was also found in encapsulated particles that appeared to have been altered by cyanidation. These tailings were believed to have been derived from the roasting process, however upon examination it is more likely that the iron oxides in the sample were a result of oxidation of sulphides. Indeed, the quantity of iron oxide observed could easily have been produced by the oxidation of sulphides in the unsaturated tailings. Figure 10 shows a bright pyrite grain (at the center of the image) that has undergone oxidation and is surrounded by a rim of iron oxide.

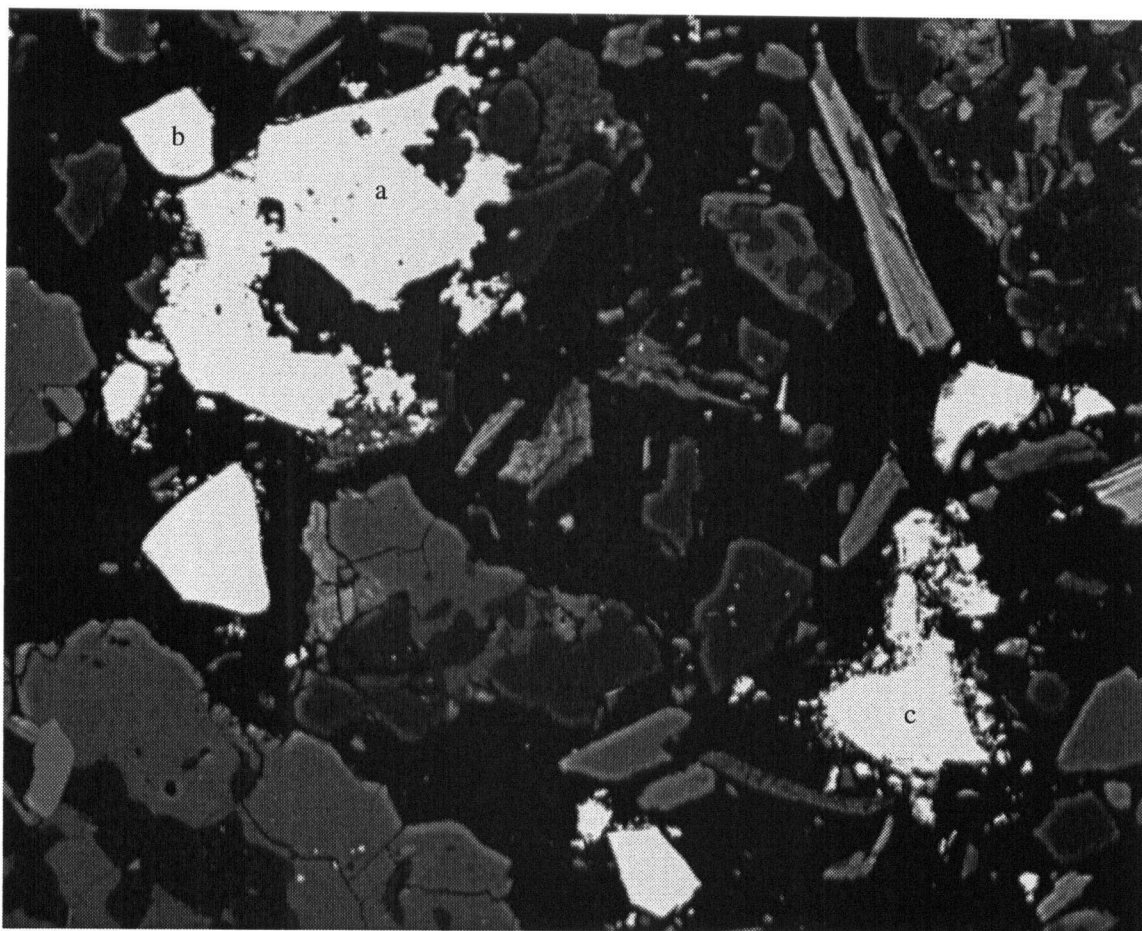
Figure 10: Backscattered electron image for RLM-2-1. Shows pyrite grain with a weathered rim of iron oxide (center of image)



RLM-2-2 – Downstream of SD#1, from 1.5 – 2.0 ft

Many large grains of arsenopyrite and pyrrhotite/pyrite were seen in this sample. The arsenopyrite and pyrrhotite/pyrite were found both as liberated and encapsulated grains. Arsenic was found predominately in the form of arsenopyrite. Some weathering of pyrrhotite/pyrite grains was visible, and a small amount of arsenic was found on the weathered edge of one grain. Figure 11 shows the large size of the sulphide grains. Particle (a) is arsenopyrite and is about 50 μm wide. Particle b is iron oxide, and particle c is pyrrhotite. Weathered edges can be seen all around particle (c).

Figure 11: Backscattered Electron Image for RLM-2-2. Particle (a) is arsenopyrite, particle (b) is iron oxide, and particle (c) is pyrrhotite.

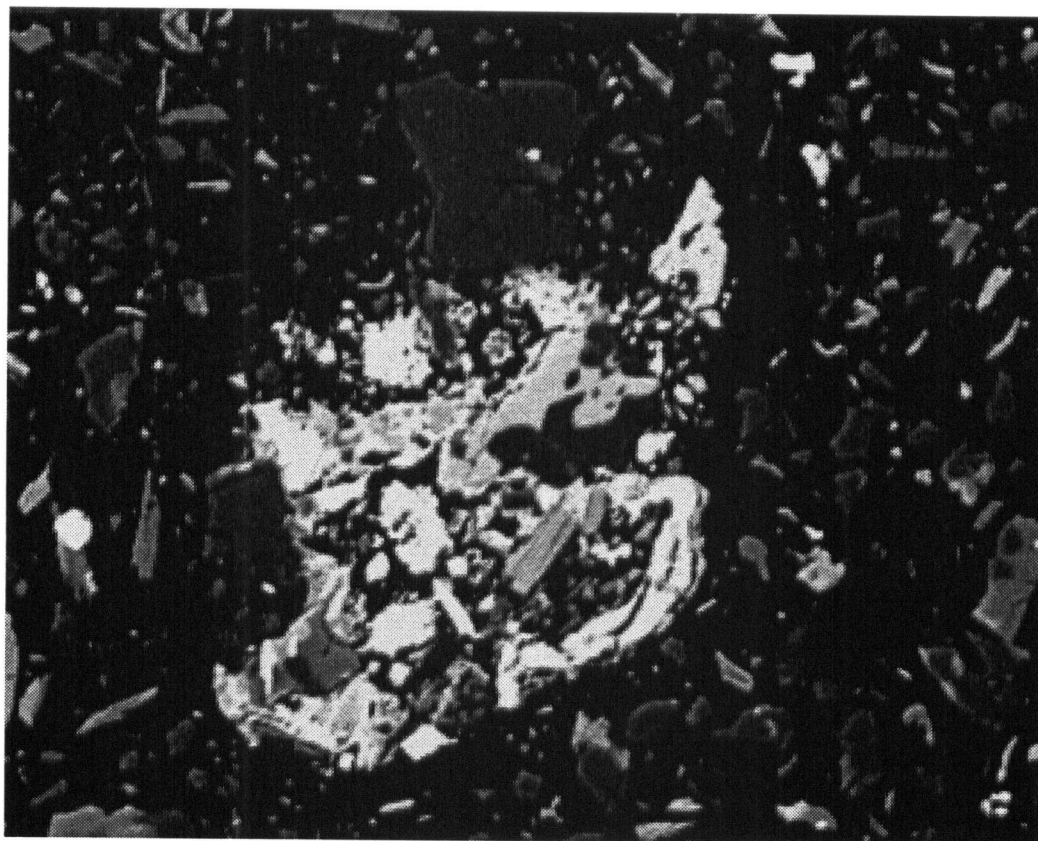


The tailings in the RLM-2 samples were likely not roaster-derived. These tailings contain a higher than average amount of sulphide grains suggesting that they were produced at a time when roaster operation had ceased and sulphide concentration was not being carried out. The upper few feet of these tailings have remained unsaturated and have undergone visible oxidation. Arsenic is predominately present as arsenopyrite, however, due to oxidation of the sulphides some arsenic has been released from the arsenopyrite and has become associated with iron oxide grains (iron oxides are produced during the sulphide oxidation process).

RLM -3-1 – Old tailings on north side of access road from 0-1 ft

Arsenic was found predominately in small grained arsenopyrite. Spongy textured iron oxide particles with distinct rings were found, some of which contained arsenic. In addition, the outer ring of weathered pyrrhotite/pyrite was also found to contain a small amount of arsenic. Figure 12 shows a large mass of spongy material made up of arsenopyrite, iron oxides (both arsenic and non-arsenic bearing), pyrite and pyrrhotite. The spongy nature of this mass suggested that it was produced during roasting.

Figure 12: Backscattered Electron Image for RLM-3-1. Large spongy mass containing arsenopyrite, iron oxides, pyrite and pyrrhotite.



RLM -3-2 – Old tailings on north side of access road from 1.5-2.5 ft

Many spongy textured iron oxide grains containing arsenic were found. Several arsenopyrite grains were also located. Figure 13 (a, b, and c) shows examples of the arsenic containing iron oxide material. The lighter coloured material in each of the particles is the arsenic bearing iron oxide, while the bright spots are arsenopyrite and pyrite. Figure 14 shows a typical X-Ray spectrum pattern for the arsenic bearing iron oxide material in this sample. The height of the arsenic peaks varied from grain to grain.

Figure 13: Backscattered Electron Image for RLM-3-2. Particles (a), (b), and (c) show iron oxide grains that contain arsenic.

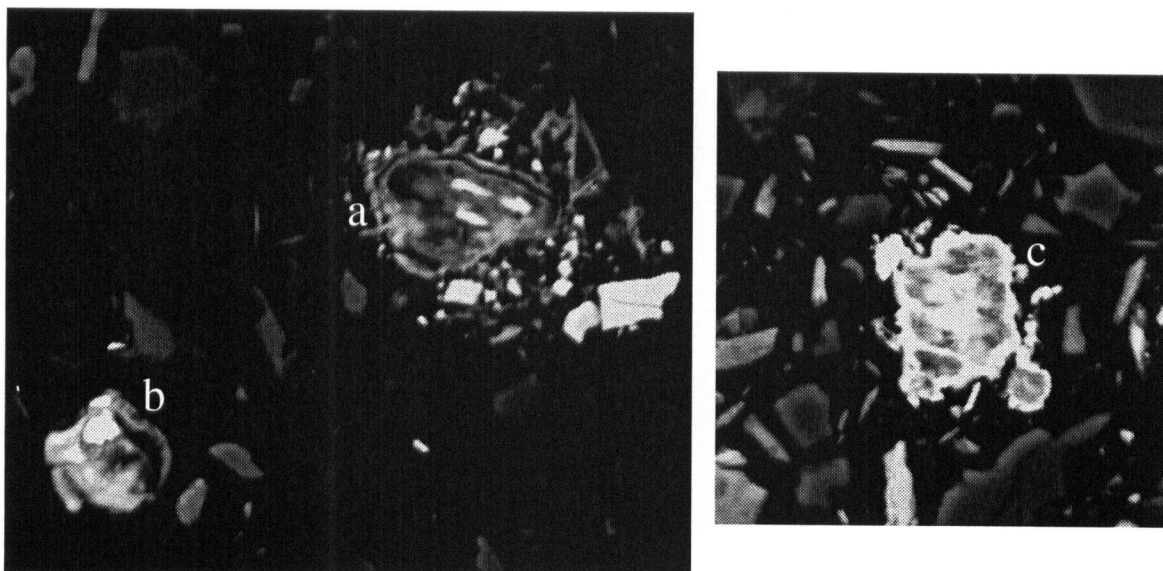
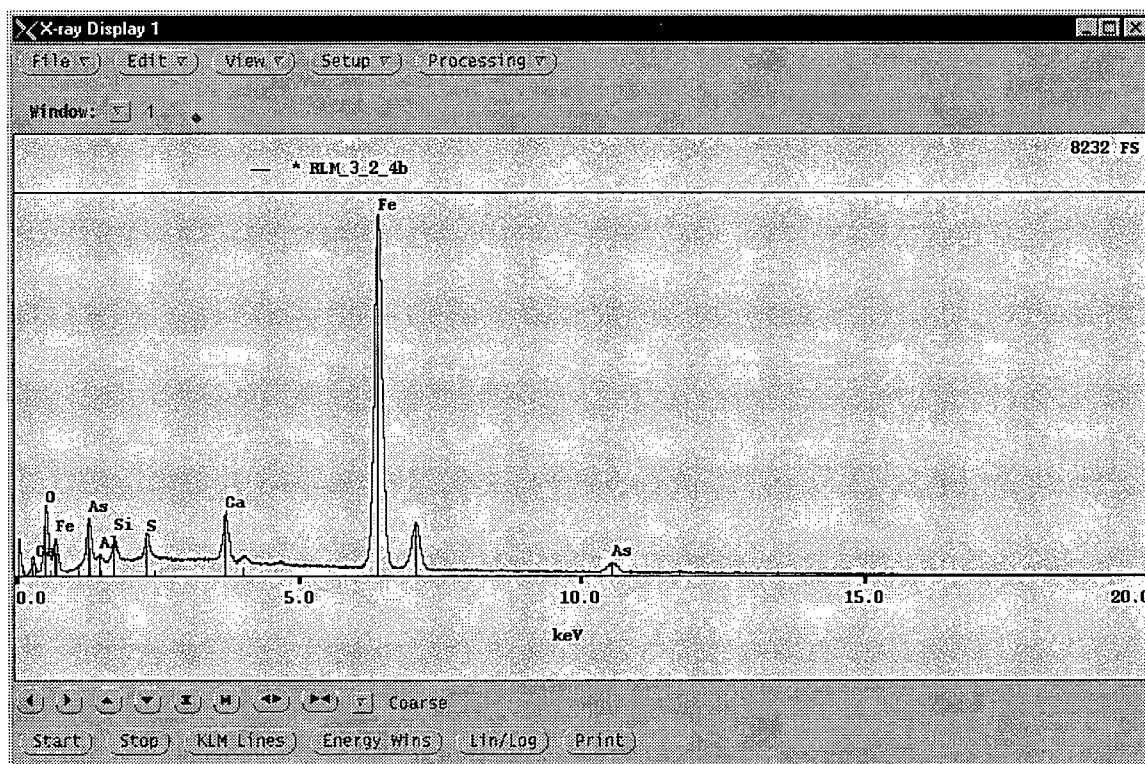


Figure 14: X-Ray Spectrum for RLM-3-2, showing arsenic bearing iron oxide pattern.



RLM -3-3 – Old tailings on north side of access road from 3.0-3.5 ft

A significant amount of arsenopyrite was detected along with some iron oxide grains. None of the iron oxide grains were found to contain arsenic, however upon further examination it is possible that arsenic containing iron oxide grains would have been found. This sample was saturated, where as RLM-3-1 and RLM-3-2 where not. This could explain why particles appeared unweathered and no arsenic containing iron oxides were observed. It is also possible that iron oxide grains may have undergone reduction as a result of the oxygen depleted conditions that exist in the saturated zone. Reduced iron oxide grains are soluble and would have dissolved into the surrounding groundwater.

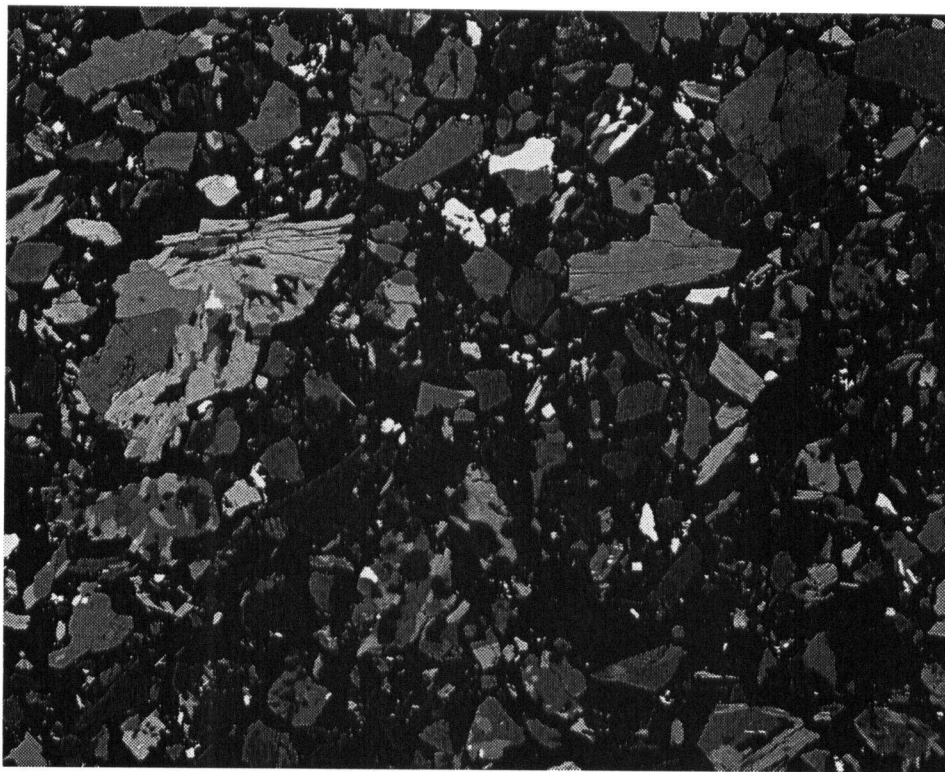
It appears as if the tailings located near the RLM-3 sample site contain material that has been roasted. Arsenic is present both as arsenopyrite and in arsenic

bearing iron oxides, however under reducing conditions that develop in the saturated subsurface it is the arsenic associated with the iron oxides that is likely to be the most mobile and will cause the greatest problem in the near future.

RLM-4 – Upstream of SD #1 in flow path of new tailings

This sample contained relatively large grains with few small grains present. Most of the particles ranged between 50 – 200 μm . The large particle size can be explained by the proximity of the sample location to the end of pipe. Indeed, larger particles settle out closer to the tailings discharge location while smaller particles travel further before being deposited. Arsenopyrite was found as liberated and encapsulated grains and was the predominant form of arsenic. Some small grains of highly heterogeneous and amorphous material containing As, Fe, Ca, Cl, S, O and other components were found. The arsenic was just barely detectable in these grains. It is speculated that these “junky” grains are secondary minerals formed during the milling process, either on their own or with the help of the addition of ferric in an attempt to form ferric arsenate. Figure 15 shows a typical section of the RLM-4 sample, where the bright spots are arsenopyrite, pyrite and pyrrhotite.

Figure 15: Backscattered Electron Image for RLM-4



RLM-5 – End of Pipe Discharge

Small arsenopyrite particles were numerous in this sample. Small grains of iron oxide were also observed, but did not contain detectable arsenic. Some small particles of very heterogeneous and amorphous material containing As, Fe, Ca, Cl, S, O and other components were found, similar to the material seen in RLM-4, but contained more arsenic. This material was also found as a coating around pyrrhotite/pyrite grains. No iron arsenate grains were detected. Figure 16 (a) shows a mass of the “junky” arsenic material, while Figure 16 (b) shows a rim of the “junky” arsenic material surrounding a pyrrhotite grain. A typical X-Ray spectrum for this arsenic material can be seen in Figure 17. The higher arsenic content of the “junky” arsenic material in the RLM-5 sample compared to the RLM-4 sample may indicate that arsenic has mobilized from the material located near RLM-4.

Figure 16: Backscattered Electron Image for RLM-5, (a) showing arsenic precipitate, and (b) showing rim of arsenic containing substance on pyrrhotite.

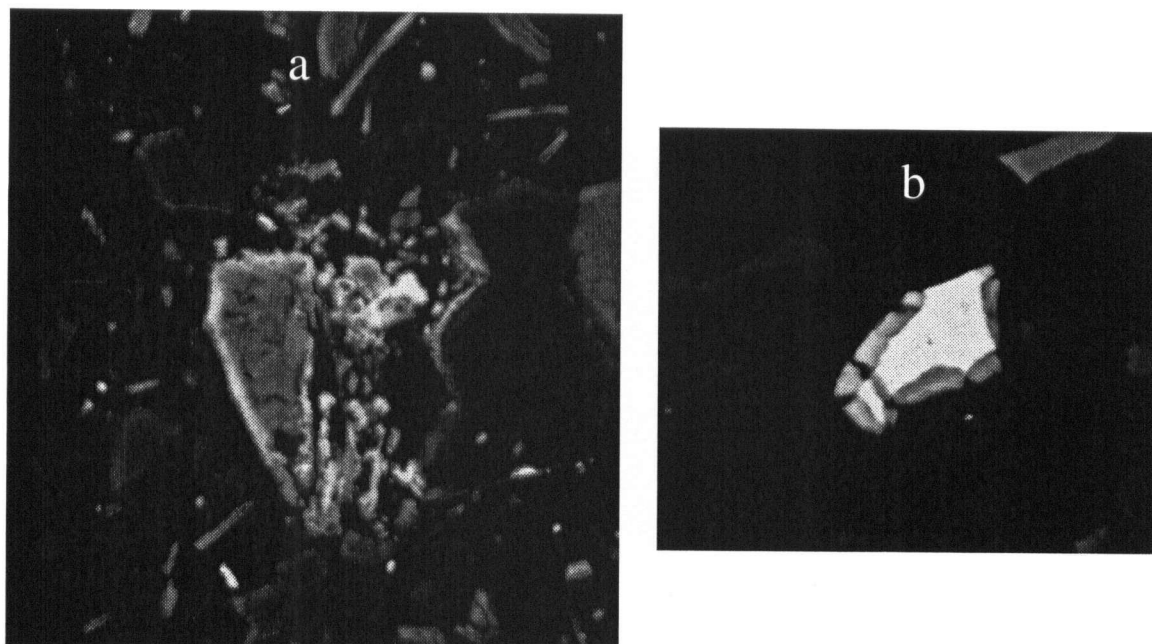
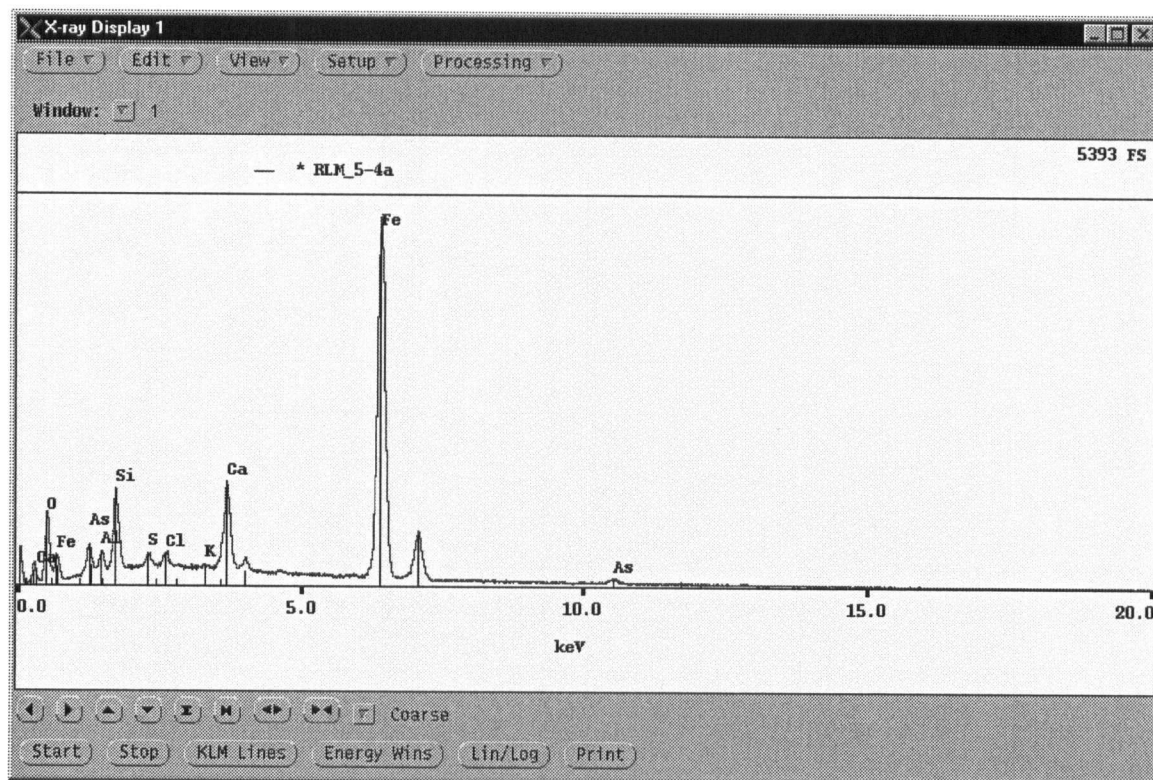


Figure 17: X-Ray Spectrum for RLM-5, showing arsenic precipitate.



RLM-6-1 – Revegetated Tailings east of Balmer Creek from 0-2 ft

This sample consisted of relatively large grained material, however most of the arsenopyrite was found as small grains. Many particles with neatly defined rims were found in this sample. The rims contained arsenic, at relatively high concentrations in some cases, along with numerous other components including Fe, Ca, S, and O. Figures 18 and 19 show two nice examples of benign material (quartz, chlorite, dolomite, etc.) surrounded by a rim of arsenic containing material. The particles in Figures 18 and 19 are approximately 100 μm wide. Moderate amounts of iron oxide material were found both within a loose “spongy” state and in a more solid state. Much more arsenic was contained in the rims and in the iron oxide material in this sample than in any of the previous samples.

Figure 18: Backscattered Electron Image for RLM-6-1, arsenic bearing iron oxide coating around quartz particle.

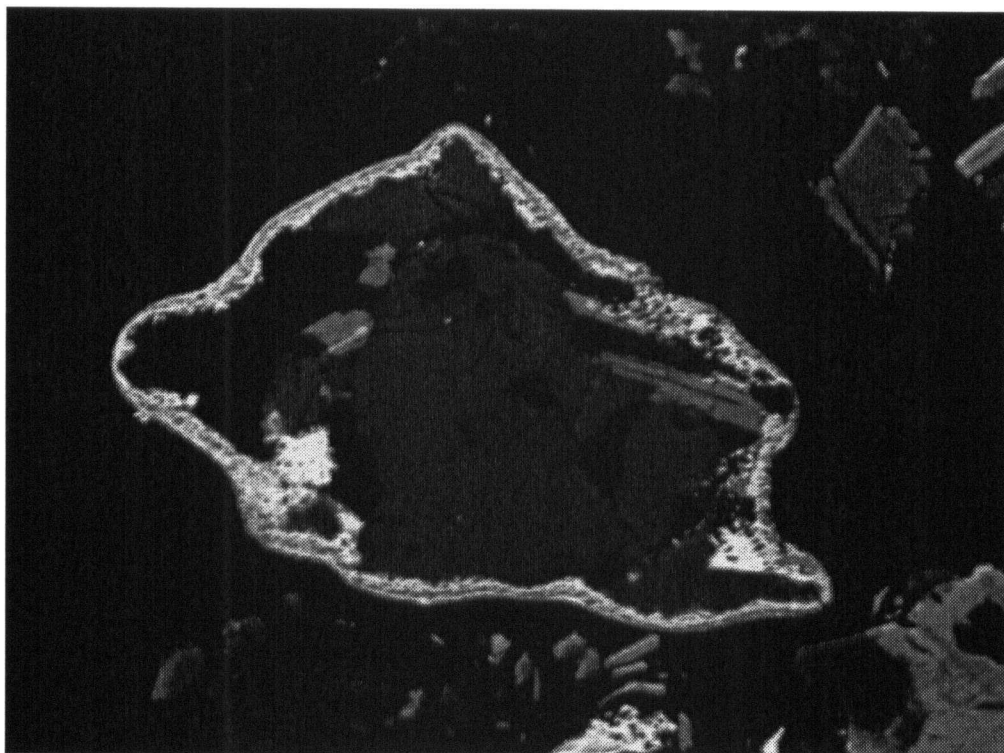


Figure 19: Backscattered Electron Image for RLM-6-1, showing arsenic bearing iron oxide coating around quartz particle.



RLM-6-2 – Revegetated Tailings east of Balmer Creek from 4-5 ft

This sample was similar to RLM-6-1 in that a moderate amount of iron oxide particles were found, however the concentration of arsenic in these particles was much lower than in RLM-6-1. Arsenopyrite was found mostly as small grains. An iron oxide particle with a relatively high arsenic concentration was found, the digital image and X-Ray pattern can be seen in Figures 20 and 21, respectively. In Figure 20, the bright particle near the center of the image is pyrrhotite, the particle to the left of it is a typical arsenic bearing iron oxide particle, while the large particle towards the bottom of the image is the iron oxide particle containing a high concentration of arsenic. Some iron oxide was found included in quartz, biotite, and other minerals, indicating that these particles have been roasted.

Figure 20: Backscattered Electron Image for RLM-6-2, showing pyrrhotite, and two arsenic bearing iron oxide particles.

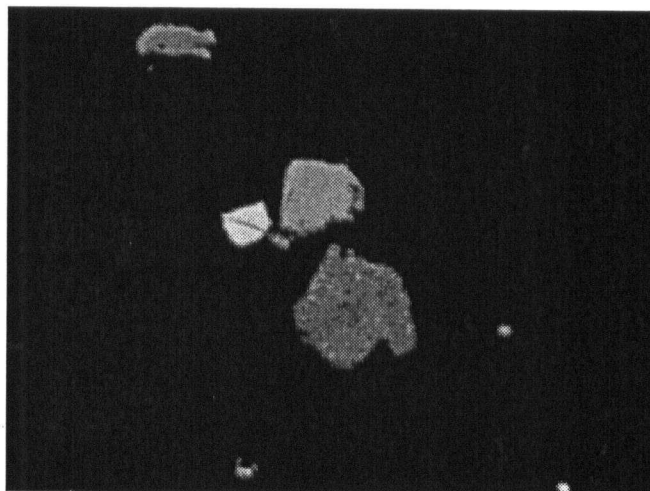
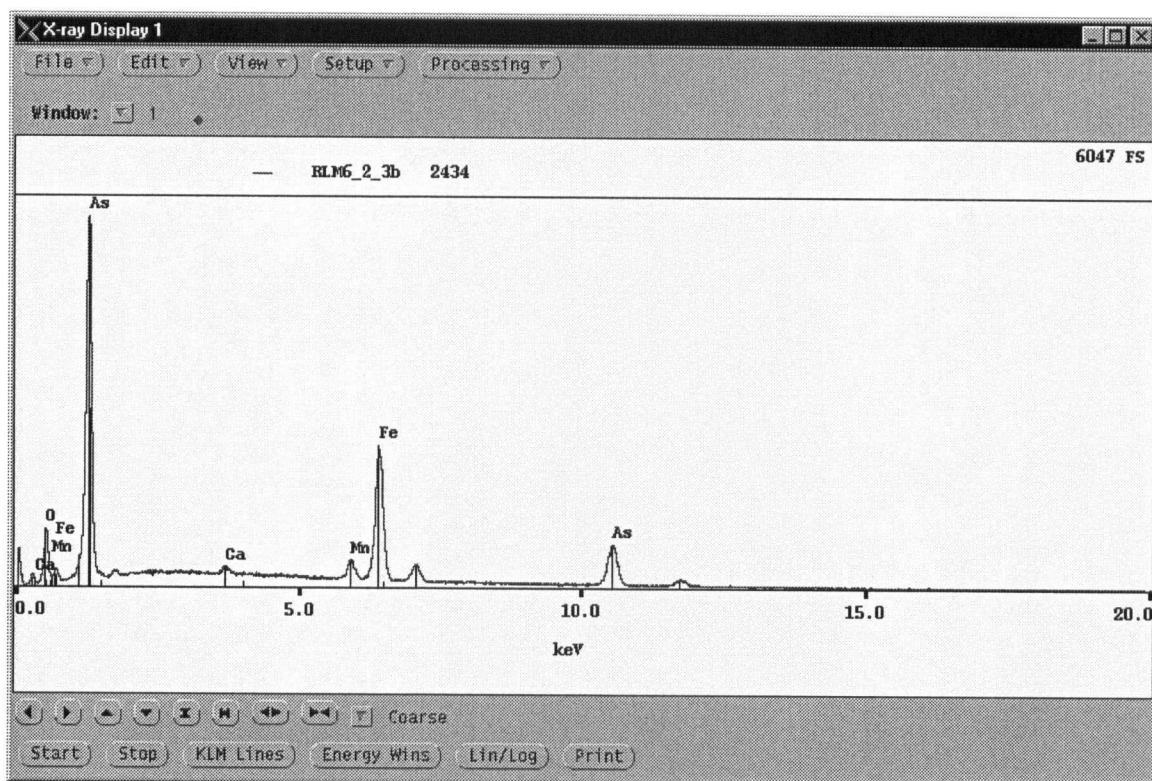


Figure 21: X-Ray Spectrum for RLM-6-2, showing high arsenic content iron oxide pattern.



The material found in RLM-6 was produced from the roasting process. Substantial arsenic is associated with iron oxide material and will provide a large source of readily mobile arsenic in an oxygen depleted environment (i.e. under reducing conditions).

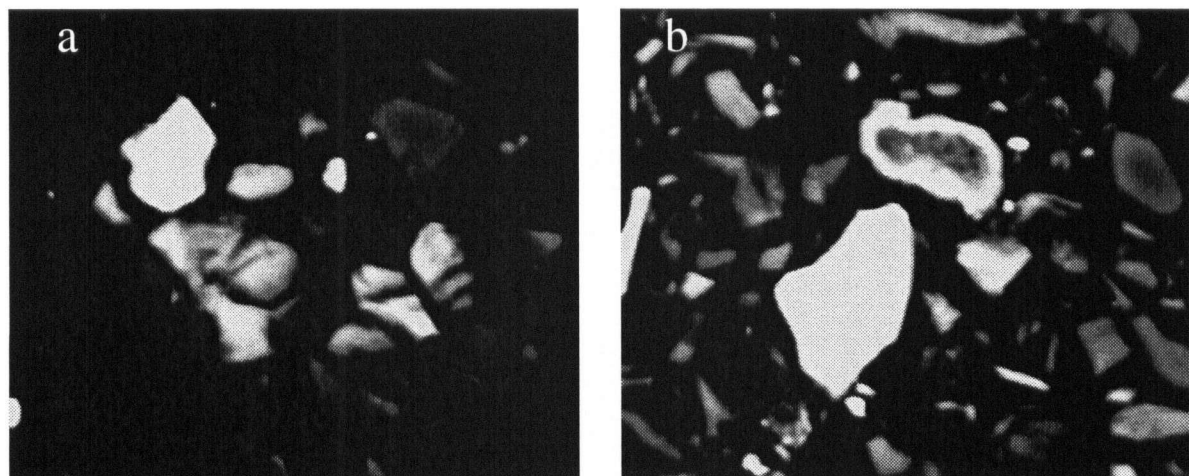
RLM-7-1 – CIP Tailings

Arsenic was found only as arsenopyrite. Large and small particles of arsenopyrite were found as well as liberated and encapsulated grains. The large amount of arsenopyrite found in this sample was expected as at this point in the milling process the sulphides had not been removed from the tailings stream via flotation. A moderate amount of pyrrhotite/pyrite was also found, and as expected only a small amount of iron oxide material was observed.

Primary Pond Sediment

This sample was made up of fine grained material. A small amount of arsenopyrite was found, along with a greater amount of pyrrhotite/pyrite. Some iron oxide grains were seen, however few contained arsenic. A few grains of iron oxide had a brighter ring surrounding them that contained arsenic. Figure 22 (a) shows arsenic bearing iron oxide material (lighter area's within the bright material), and in (b) a rim of arsenic oxide material surrounds an iron oxide particle.

Figure 22: Backscattered Electron Image for Primary Pond Sediment, showing arsenic bearing iron oxide particles in (a) and arsenic bearing iron oxide coating in (b).



Primary Pond Backhoe

This sample was similar to the Primary Pond Sediment sample, however one noticeable difference was that the grains were a bit larger. No iron oxide grains containing arsenic were found, arsenic was found only as arsenopyrite.

Secondary Pond Sediment

As in the Primary Pond Sediment, the grains were small (most less than 10 μm). Most of the sample appeared as the same shade of grey and consisted predominately of quartz, and chlorite. Both pyrite and pyrrhotite were found. A small amount of iron oxide was seen, however no arsenic was detected in it. The only arsenic bearing mineral detected was arsenopyrite.

Work done by Jambor (2003) on tailings samples from the near by Cochenour mine indicated that the importance of iron oxides as a source of arsenic is greatly underestimated by X-Ray analysis using the SEM. He found that most of the iron oxide grains contained greater than 0.3 wt% when analyzed with the more sensitive microprobe. Some of these same grains did not show the presence of

arsenic using the SEM. He concluded that the proportion of As-bearing iron oxide particles is much higher than was estimated from his X-Ray analyses. He stated that the arsenic contained within roaster oxides is highly susceptible to mobilization due to the porous texture of the roaster oxides and the sorbed association of the arsenic. He also stated that although weathering of arsenopyrite will continue to contribute arsenic to the surrounding pore waters over the long term, the roaster oxides will likely be responsible for contributing the bulk of the arsenic over the short term. The roaster tailings at the Red Lake mine are similar in nature to the roaster tailings at the Cochenour mine, therefore it can be inferred that the same sort of mechanism is occurring and will continue to occur at the Red Lake mine.

In summary, material located around RLM-3, and RLM-6 is derived from the roasting process. A relatively large fraction of the arsenic in these locations (more so at RLM-6) is associated with iron oxide material and is and will continue to be mobile, especially under oxygen deficient conditions (i.e. saturated conditions). According to the findings of Jambor (2003) the amount of arsenic bearing iron oxides determined through X-Ray analysis using the SEM is likely significantly less than what is actually present. This means that there is a high probability that the source of readily mobile arsenic is much larger than it appears through the results of the SEM work.

The material sampled at RLM-2 does not appear to contain roasted material, however deeper down there is likely roaster material present. The material sampled at RLM-2 contains significant sulphides and the top few feet, which are unsaturated, have undergone substantial oxidation over the years. During the post depositional oxidation processes, some of the arsenic has been released from arsenopyrite and has become associated with iron oxide material, also formed during oxidation. The arsenic associated with the iron oxide material is likely to be much more mobile under reducing conditions than the arsenic contained within arsenopyrite.

RLM-1, RLM-4, and RLM-5 contain essentially fresh tailings that have remained saturated. The vast majority of arsenic in these samples is contained within arsenopyrite that will continue to be stable as long as conditions remain reducing. A small amount of arsenic was found to be associated with a “junky” precipitate containing many species in the RLM-4 and RLM-5 samples. This material was likely formed during the milling process as a result of the addition of ferric iron. The stability of this material is unknown, however this material is likely to be a larger contributor of dissolved arsenic than arsenopyrite if the post depositional storage conditions for the fresh tailings remain saturated

The material in the Primary and Secondary pond sediment was so fine that it was difficult to adequately characterize it. Past work performed on the pond sediment (Lorax, 2001) and analytical trends in the Secondary Pond water indicate that much of the arsenic in the Secondary Pond is associated with readily mobile iron oxide material. It is likely that this is the case in the Primary Pond as well. Under oxic conditions arsenic that is present in the pond water will naturally co-precipitate with iron that is also present in the water. In addition, arsenic and iron will reprecipitate from groundwater that is advecting and diffusing up into the ponds. Porewater profiles collected by Lorax (2001) indicate that arsenic and iron are reprecipitated in the Secondary Pond when the porewater from the pond sediments encounters the oxic interfacial layer. When conditions change (i.e. depleted oxygen), these precipitates readily dissolve releasing arsenic into the water column. The sequential extractions and XANES work performed on these samples give better insight into the composition of the precipitates.

4.3.4 Sequential Extractions

A five-step sequential extraction procedure, slightly modified from Keon (2001), designed specifically for arsenic, was conducted on 4 samples in duplicate (RLM-2-1, RLM-5, RLM-6-1, and Secondary Pond Sediments). The fractions in order were: Ionically Bound + Pore Water; Strongly Adsorbed; Coprecipitated with acid

volatile sulphides (AVS), Manganese oxides, and very amorphous iron oxyhydroxides; Coprecipitated with amorphous iron oxyhydroxides; Coprecipitated with crystalline iron oxyhydroxides; Residual.

Samples were sent to SGS Chemex Environmental in Vancouver for low level arsenic and iron analysis using ICP – MS. The detection limits for aqueous arsenic and iron were 0.1 µg/L and 10 µg/L, respectively. Based on these limits, and a sediment to extractant ratio of 0.4 g to 40 ml, the detection limits for extractable arsenic and iron in each step were less than 1 mg As/kg sediment and 2 mg Fe/kg sediment.

Total arsenic and iron concentrations in each of the four sediment types tested were determined via near total four acid digestion at SGS Chemex in Vancouver, the results are shown in Table 3. The percent solids of each of the frozen samples was determined and used to calculate the dry equivalent mass of sample used in each of the extractions. Using the dry equivalent mass and the total arsenic and iron concentrations for each sample, the total mass of arsenic and iron, potentially available for extraction, was calculated. The data is tabulated in Table 3. Complete results can be found in Appendix IV.

Table 3: Sequential Extraction Data

ID	Location	Average % Solids	mass (wet) g	mass (dry) g	Total [As] mg/kg	Total As mg	Total [Fe] mg/kg	Total Fe mg
1	2° Pond Sed	51.4	1.04	0.53	2670	1.426	71300	38.090
2	2° Pond Sed		1.02	0.52		1.399		37.358
3	RLM-5	82.4	0.54	0.44	2015	0.896	74500	33.138
4	RLM-5		0.55	0.45		0.913		33.751
5	RLM-2-1	79.1	0.58	0.46	3440	1.578	89700	41.137
6	RLM-2-1		0.6	0.47		1.632		42.556
7	RLM-6-1	80.7	0.45	0.36	2550	0.926	85800	31.168
8	RLM-6-1		0.46	0.37		0.947		31.861

Reagent blanks were assayed and for the most part were found to contain negligible amounts of arsenic and iron. The Step 2 reagent (NaH_2PO_4) contained $91.8 \mu\text{g/L}$ of arsenic. Solution assays that would have been affected by this contamination (Step 2b solutions of RLM-5) were adjusted by subtracting this value from the concentration reported for each of the solutions. The overall affect of this small amount of contamination was minor.

The mass of arsenic in each of the solution samples obtained during the extraction process was calculated using the appropriate solution assay value and the measured volume of solution in each sample. The calculated mass of arsenic in each sample was divided by the dry equivalent mass of sample used in the extraction, to obtain a value in mg As/kg of sediment (Table 3). The calculated mass of arsenic in each sample was also divided by the total amount of arsenic in each sample (from Table 3) to obtain percent of total arsenic removed values. Repetitions and water washes within each extraction step were added together to obtain the total amount of arsenic extracted in each step. The average was taken for the duplicates of each sediment type to obtain the values in Tables 4 and 5. Appendix IV contains all of the calculated data.

Table 4: Percent of Total Arsenic Removed in Each Extraction Step

Location	Average % Total Arsenic					
	Step 1	Step 2	Step 3	Step 4	Step 5	Residual
Secondary Pond Sediment	6	50	7	1	2	35
RLM-5	4	12	0	0	0	83
RLM-2-1	1	22	18	10	0	49
RLM-6-1	1	38	27	13	0	20

Table 5: Amount of Arsenic Removed in Each Extraction Step

Location	Average mg As/Kg dry sediment					
	Step 1	Step 2	Step 3	Step 4	Step 5	Residual
Secondary Pond Sediment	161	1334	176	20	53	926
RLM-5	86	233	9	1	1	1681
RLM-2-1	19	754	605	360	3	1700
RLM-6-1	36	978	686	338	12	499

The values shown in Tables 4 and 5 are depicted graphically in Figures 23 and 24.

Secondary Pond Sediment

A small fraction (6%) of the arsenic was ionically bound/exchangeable (including the aqueous fraction contained in the pore water of the sample) in the Secondary Pond Sediment. The majority of arsenic in this sample was strongly adsorbed (Step 2), 50% or 1334 mg/kg was removed during the second extraction step. Only seven percent of the arsenic was coprecipitated with acid volatile sulphides (AVS), carbonates, Mn oxides, and very amorphous Fe oxyhydroxides (Step 3). Minimal amounts of arsenic were coprecipitated with amorphous Fe oxyhydroxides (Step 4) and crystalline Fe oxyhydroxides (Step 5). The residual fraction of the arsenic was calculated to be 35% and was likely associated with sulphides. In summary, approximate 65% (1744 mg As/kg Sediment) of the arsenic contained in the Secondary Pond Sediment is likely to be fairly mobile under the changing redox conditions that exist in the Secondary Pond.

RLM-5

The vast majority of the arsenic in the RLM-5 samples (End of Pipe discharge) was not mobilized by the extraction procedure. A small fraction (4%) of the arsenic was ionically bound/exchangeable (including the aqueous fraction contained in the pore water of the sample) and 12% was strongly adsorbed (Step 2). Negligible amounts of arsenic were removed during Steps 3, 4, and 5. The

remainder of the arsenic, 84% (1685 mg As/kg sediment), was calculated to be the residual fraction and was likely associated with sulphides. In summary, only 16%, or 330 mg As/kg sediment of the arsenic contained in End of Pipe tailings (RLM-5) is likely to be fairly easily mobilized, indicating that the vast majority of the arsenic in these tailings should remain stable as long as saturated conditions are maintained.

RLM-2-1

A small fraction (1%) of the arsenic was ionically bound/exchangeable (including the aqueous fraction contained in the pore water of the sample) in the RLM-2-1 sediment. Twenty two percent (754 mg As/kg sediment) of the arsenic was strongly adsorbed and was extracted in Step 2. A relatively significant portion of the arsenic (18%) was coprecipitated with acid volatile sulphides (AVS), carbonates, Mn oxides, and very amorphous Fe oxyhydroxides (Step 3). An additional 10% of the arsenic was coprecipitated with amorphous Fe oxyhydroxides (Step 4) and a negligible amount was coprecipitated with crystalline Fe oxyhydroxides (Step 5). In summary, approximately 23% of the arsenic in this sample is adsorbed, 28% is associated with iron oxyhydroxides, and the remaining 49% (1700 mg As/kg sediment) is likely associated with sulphides. Under the currently unsaturated condition of these tailings the sulphide portion will continue to oxidize, releasing arsenic from sulphides only to be immobilized by sorption on iron oxides phases.

RLM-6-1

A small fraction (1%) of the arsenic was ionically bound/exchangeable (including the aqueous fraction contained in the pore water of the sample) in the RLM-6-1 sediment. The largest fraction of the arsenic (38%) was strongly adsorbed and was extracted in Step 2. A significant portion of the arsenic (27%) was coprecipitated with acid volatile sulphides (AVS), carbonates, Mn oxides, and

very amorphous Fe oxyhydroxides (Step 3). In addition, 13% of the arsenic was coprecipitated with amorphous Fe oxyhydroxides (Step 4). A negligible amount was coprecipitated with crystalline Fe oxyhydroxides (Step 5). In summary, approximately 39% of the arsenic in this sample was adsorbed, 40% was associated with iron oxyhydroxides, and the remaining 20% (2051 mg As/kg sediment) was likely associated with sulphides. Only 20% of the arsenic contained in this sample was calculated to be remaining after the extraction was complete, significantly less than all the remaining samples indicating that the large majority of the arsenic in RLM-6-1 sediment is likely to be fairly easily mobilized.

Figure 23: Percent of Total Arsenic Removed in Each Extraction Step

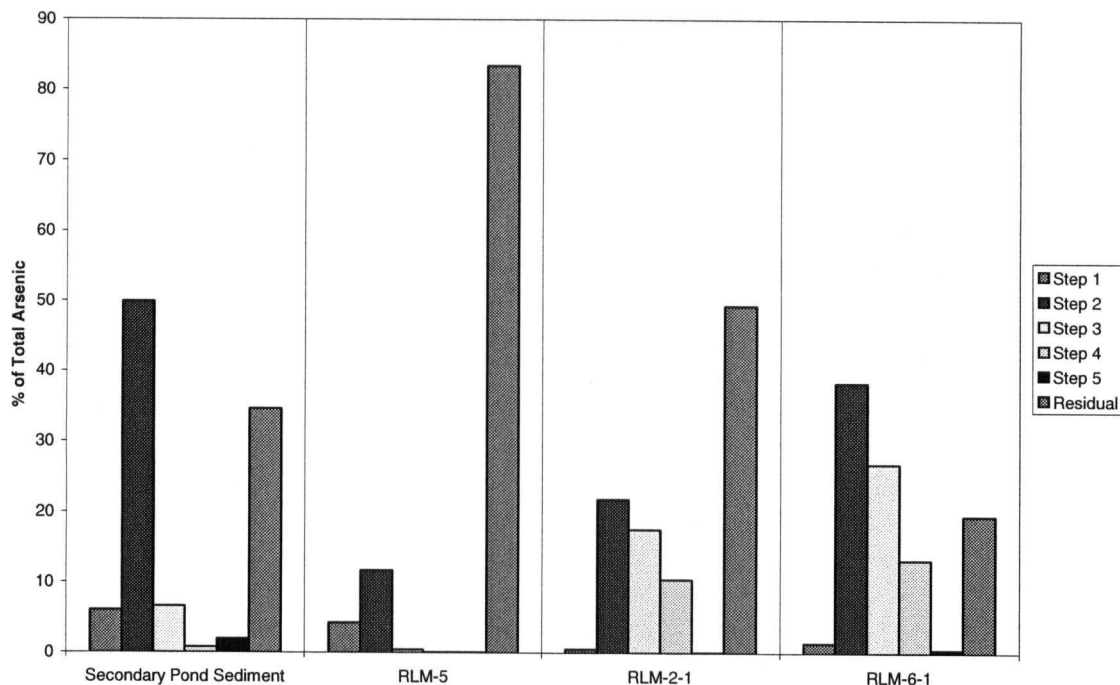
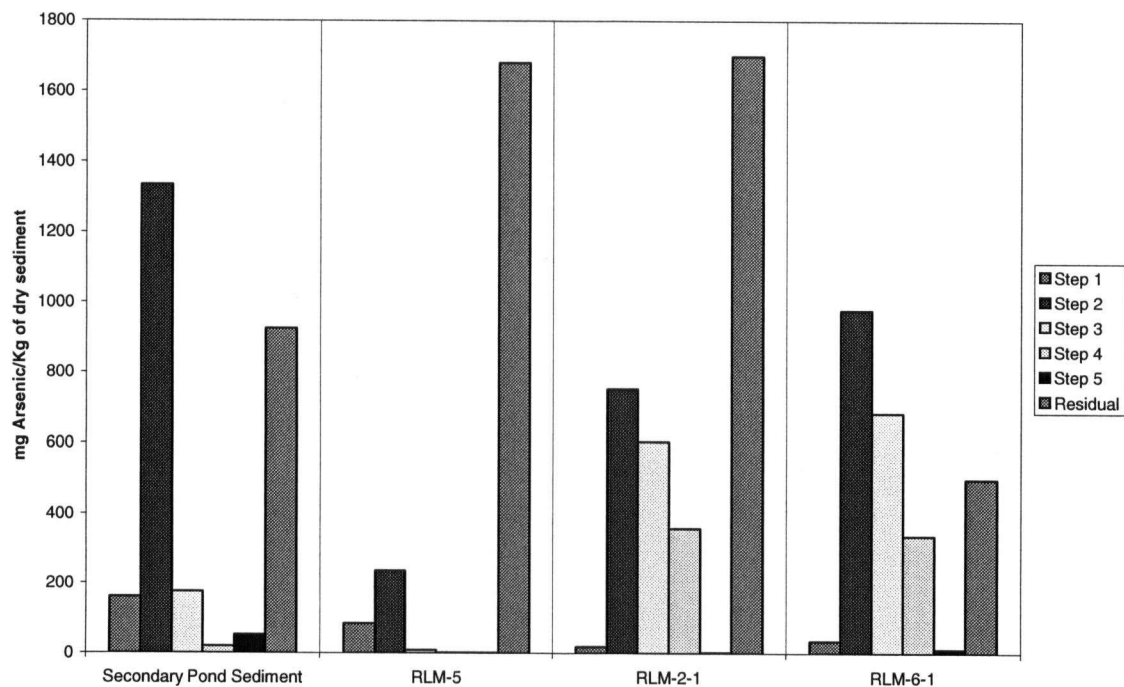


Figure 24: mg As/kg Sediment Removed in Each Extraction Step



Similar calculations were made for iron to determine the percent and amount of iron removed in each extraction step for each sample. This was done for comparison purposes, as arsenic and iron concentrations are usually linked. Tables 6 and 7 show the percent and amount of iron removed in each step, respectively, and Figure 25 depicts the percent of iron removed.

Table 6: Percent of Total Iron Removed in Each Extraction Step

Location	Average % Total Iron					
	Step 1	Step 2	Step 3	Step 4	Step 5	Residual
Secondary Pond Sediment	0	8	26	2	7	57
RLM-5	0	8	23	6	5	58
RLM-2-1	0	4	26	20	4	46
RLM-6-1	0	8	18	23	5	46

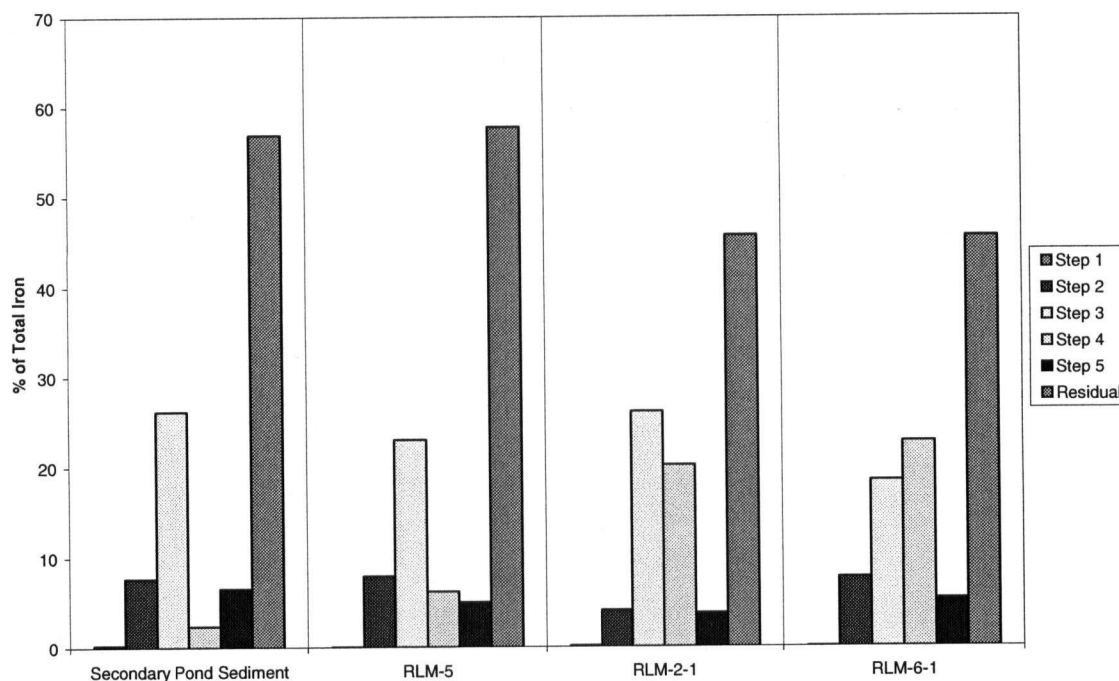
Table 7: Amount of Iron Removed in Each Extraction Step

Location	Average mg Fe/Kg dry sediment					
	Step 1	Step 2	Step 3	Step 4	Step 5	Residual
Secondary Pond Sediment	192	5482	18674	1695	4694	40563
RLM-5	29	5921	17163	4622	3741	43024
RLM-2-1	133	3682	23419	18103	3380	40984
RLM-6-1	32	6648	15854	19529	4636	39101

The reagents used in the extraction procedure were selected specifically for arsenic extraction, therefore not all of the steps are relevant to iron (namely steps 1 and 2). Steps 3, 4, and 5 can be used to give an indication of the fraction of iron associated with AVS/very amorphous iron oxyhydroxides, amorphous oxyhydroxides, and crystalline oxyhydroxides. The amount of iron extracted in Step 3 (AVS/very amorphous iron oxyhydroxides) ranged from 18 – 26%, with RLM-6-1 containing the least amount. RLM-2-1 and RLM-6-1 contained significantly more amorphous iron oxyhydroxides (20% and 23%, respectively) than the other two samples. All the samples contained relatively small amounts of crystalline iron oxyhydroxides (4 – 7%). The Step 4 and 5 iron and arsenic

results correspond well, confirming that Secondary Pond Sediment and RLM-5 contain much less amorphous iron oxyhydroxides than RLM-2-1 and RLM-6-1.

Figure 25: Percent of Total Iron Removed in Each Extraction Step



The sequential extraction results support the SEM results fairly well. Both of the RLM-2-1 and RLM-6-1 samples were found to contain arsenic bearing iron oxyhydroxide material in the SEM work, with much more being found in the RLM-6-1 sample. The sequential extractions indicate that 51% of the arsenic in the RLM-2-1 sample and 80% of the arsenic in the RLM-6-1 sample is sorbed or precipitated with iron oxyhydroxides. An adequate SEM analysis of the Secondary Pond Sediment could not be done due to the fine grained nature of the sample. Historical trends in Secondary Pond water chemistry however, indicate that a large fraction of the arsenic in the sediment must be associated with a readily mobile iron oxyhydroxide phase. The sequential extraction results indicate that over 65% of the arsenic in the Secondary Pond Sediment is sorbed or precipitated with an iron oxyhydroxide phase, with more than 50% of the arsenic being sorbed.

SEM analysis of RLM-5 tailings indicated that the vast majority of the arsenic was associated with arsenopyrite. A small fraction of the arsenic was found to be associated with a "junky" precipitate. The sequential extraction data supports this result as more than 83% of the arsenic reported to the residual phase (likely associated with sulphides) while the remaining 16% was ionically bound or adsorbed.

4.3.5 Synchrotron X-Ray Absorption Spectroscopy

The Canadian Light Source prepared a report summarizing the results of the XANES data collected at the National Synchrotron Light Source located at Brookhaven National Laboratories, Upton, New York. The bending magnet beam line X11A (Navel Research Laboratory-Synchrotron Radiation Consortium) was used. The following is a summary of the results reported in Kotzer (2003).

Three arsenic oxidation states were found in the samples: As^{-1} (as in arsenopyrite), As^{3+} (as in arsenic trioxide), and As^{5+} (as in iron arsenate). An arsenopyrite sample from the high grade zone of the Red Lake Mine was provided for use as a reference material. Figure 26 shows the XANES spectra for each of the three arsenic oxidation states found in the samples.

Figure 26: Arsenic K-edge XANES spectra of three different model compounds with different oxidation states.

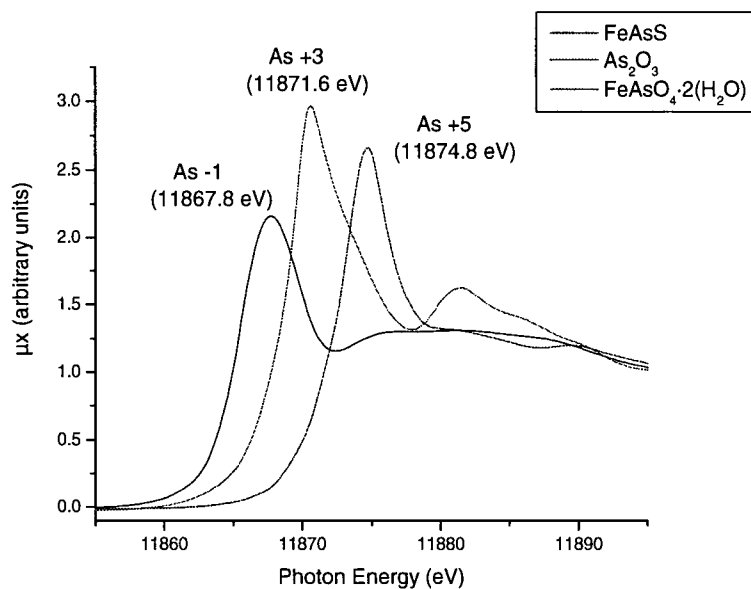


Table 8 summarizes the results of the least squares fitting for all of the samples.

Table 8: Semi-quantitative Arsenic Distribution (+/- 10%). Calculated from linear least-squares fitting of the As K-edge Synchrotron XANES spectra.

Location	% Total Arsenic		
	As(-1)	As(III)	As(V)
RLM-1	89	0	11
RLM-2-1	31	11	58
RLM-2-2	85	8	7
RLM-2-3	88	8	4
RLM-3-1	28	4	68
RLM-3-2	22	5	73
RLM-3-3	93	2	5
RLM-4	78	7	15
RLM-5	77	9	14
RLM-6-1	20	16	65
RLM-6-2	63	10	28
RLM-7	92	0	8
Secondary Pond Sediment	25	40	35
Primary Pond Sediment	50	11	40
Primary Pond Backhoe	84	7	9

RLM-2

Whole rock analysis and SEM results indicated that the tailings located at RLM-2 contained a large amount of sulphide material and were deposited at time when roasting and sulphide concentration practices had ceased. The SEM and Rietveld results indicated that significant post depositional oxidation of the sulphides had occurred in the unsaturated layer of the tailings. The sequential extraction results also indicated that a large portion of the arsenic in RLM-2-1 was sorbed or associated with iron oxyhydroxide phases. The XANES results correspond well with these observations.

RLM-2-1 had only 31% of the arsenic in the As(-1) oxidation state, with 58% present as As(V). RLM-2-2 and RLM-2-3 were similar in composition to each other, with more than 80% of the arsenic present as As(-1), with the remaining portion present as a combination of As(III) and As(V). These results indicate that significant sulphide oxidation has only occurred in the upper most layer of the tailings in the vicinity of RLM-2. Figures 27, 28, 29, and 30 show the XANES spectra for the RLM-2 samples.

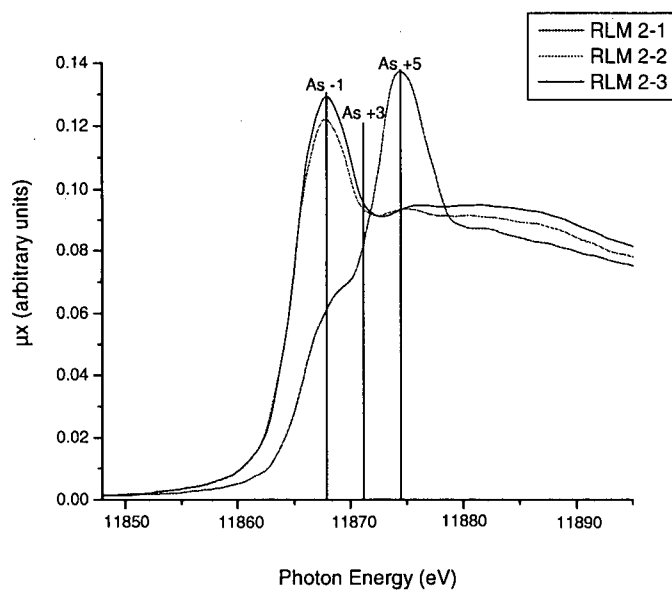
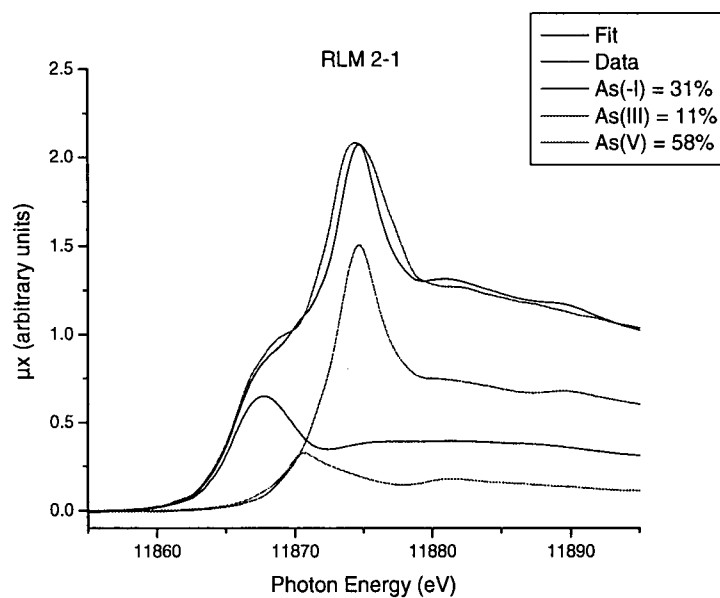
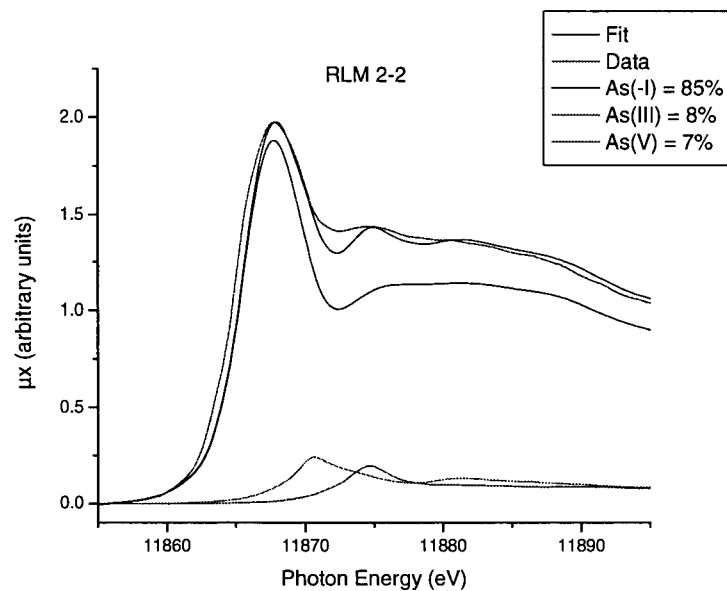
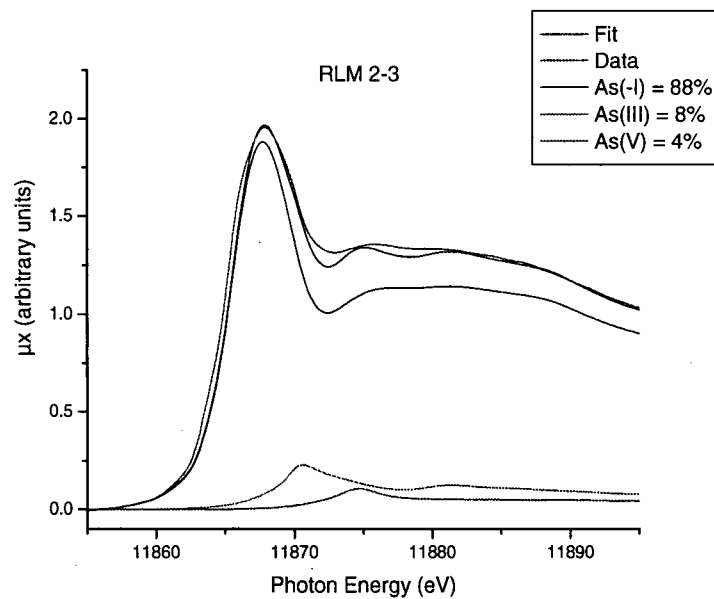
Figure 27: Arsenic K-edge XANES spectra of RLM-2 series samples**Figure 28:** Fitted Arsenic K-edge spectrum of RLM 2-1

Figure 29: Fitted Arsenic K-edge spectrum of RLM 2-2**Figure 30: Fitted Arsenic K-edge spectrum of RLM 2-3**

RLM-3

Historical information and SEM results indicate that the material in the vicinity of RLM-3 consists of roaster tailings, with numerous particles of arsenic bearing iron oxide detected via the SEM in both the RLM-3-1 (0 – 1 ft below ground surface) and RLM-3-2 (1.5 – 2.5 ft below ground surface) samples. The XANES result for RLM-3-1 and RLM-3-2 are similar with only 28% of the arsenic in the form of As(-1) in RLM-3-1 and 22% in RLM-3-2. A small amount ($\leq 5\%$) of the arsenic existed in the form of As(III), with the remainder present as As(V). These results correspond well with a material that has been derived from a roasting process. During the roasting process the material is subjected to extremely oxidizing conditions, therefore it is expected that the majority of the arsenic should be present in the As(V) form in a roasted material. The XANES results, therefore, support the theory that the material sampled in RLM-3-1 and RLM-3-2 is roaster-derived.

RLM-3-3 (3 – 3.5 ft below ground surface) had a much different XANES spectra than the other two RLM-3 samples. Most of the arsenic (93%) was present in the form of As(-1), with 5% present as As(V) and 2% as As(III). This result would seem to indicate that the deeper tailings in the vicinity of RLM-3 were not roaster-derived. However, historical reports indicate that at the point in time when tailings began to be discharged near RLM-3 the roaster was in operation. As well, the low sulphur content of the RLM-3-3 sample also indicates that the material has been roasted.

A possible explanation for the vast difference in arsenic speciation between the deep and shallow tailings at RLM-3 is that the unstable, readily mobile oxidized arsenic species in the tailings could have dissolved into the pore water in the saturated zone (RLM-3). The total arsenic concentration at RLM-3-3 was 2660 mg/kg, while the concentration at RLM-3-2 was 3210 mg/kg. The difference in concentration between the two samples can be reasonably explained by the

above theory (oxidized arsenic species dissolving into pore water). However the difference in concentrations is not great enough to entirely explain the difference in the fraction of arsenic seen as As(-1) in the two samples. It is possible that some of the oxidized arsenic species have been reduced to As(-1) and have formed secondary sulphide mineral species.

RLM-6

Historical information and SEM results indicate that the tailings deposited in the area of RLM-6 were roaster-derived. Only 20% of the arsenic at RLM-6-1 was present in the form of As(-1), with 16% present as As(III) and 65% present as As(V). The XANES spectra for RLM-6-2 was much different than for RLM-6-1 with 63% of the arsenic in the form of As(-1). As in RLM-3, the total arsenic concentration in the saturated zone (RLM-6-2) was less than in the unsaturated zone (RLM-6-1), with total concentrations of 2050 mg/kg and 2630 mg/kg, respectively. The difference in total arsenic concentration and the difference in the distribution of arsenic species indicates that a fraction of the oxidized arsenic has dissolved into the pore water in the saturated zone. Elevated arsenic concentrations have been observed in the pore water in the vicinity of RLM-6, therefore this is plausible. The difference in concentrations however, only accounts for a small fraction (about 5%) in the difference in the fraction of As(-1). A possible explanation for the remaining difference is that oxidized arsenic species have undergone post depositional reduction and may have formed secondary sulphide minerals.

Fresh Tailings

Samples RLM-1, RLM-4, RLM-5, and RLM-7 consisted of fresh or relatively new tailings. The arsenic in RLM-7 tailings was predominately in the As(-1) oxidation state (arsenopyrite), with only 8% of the arsenic in the As(V) state and no arsenic in the As(III) state. The small amount of As(V) was likely produced as a result of

oxidation of arsenopyrite during the milling process. RLM-5 consists of RLM-7 tailings that have gone through a cyanide detox process, have had ferric iron added to them, and passed through a sulphide flotation circuit that removes a large portion of the sulphide material from the tailings. The proportion of oxidized arsenic in the RLM-5 tailings was higher than in RLM-7 tailings, with 9% in the form of As(III) and 14% in the form of As(V).

RLM-4 had a similar composition to RLM-5, as was expected as RLM-4 tailings were located just downstream of the End of Pipe discharge (RLM-5). RLM-1 tailings were more similar in composition to RLM-7 than RLM-4 or RLM-5. RLM-1 contained no As(III), and 89% of the arsenic was in the form of As(-1).

These results all compare well with what was seen via the SEM, and via sequential extractions in the case of RLM-5.

Pond Sediments

The Primary Pond sediment contained 50% As(-1), 11% As(III), and 40% As(V). The vast majority of the oxidized arsenic species were likely formed via the natural precipitation of arsenic oxyhydroxides formed from dissolved arsenic and iron species in the water column. The As(-1) fraction is a result of the tailings that are lining the bottom the Primary Pond.

The Primary Pond Backhoe sample, which is a sample of the deeper tailings/sediment in the primary pond had a similar composition to RLM-2-3. This result makes sense, as the tailings in the Primary Pond were likely to have been the same as RLM-2-3 when they were deposited. Since the tailings are saturated there is limited opportunity for the sulphide (arsenopyrite) fraction to undergo oxidation. However, the total arsenic concentration in the Primary Pond Backhoe sample (2150 mg/kg) was significantly less than in the RLM-2-3 sample (4100 mg/kg), in addition the sulphur content of the Primary Pond Backhoe

sample is much lower than in the RLM-2-3 sample indicating that the tailings in the Primary Pond were deposited at a time when sulphide concentration (i.e. sulphide flotation was a part of the milling process) was occurring.

The Secondary Pond sediment contained 25% As(-1), 40% As(III), and 35% As(V). Past work performed on the pond sediment (Martin, 1996) and analytical trends in the Secondary Pond water indicate that much of the arsenic in the Secondary Pond is associated with readily mobile iron oxide material. Under oxic conditions arsenic that is present in the pond water will naturally co-precipitate with iron that is also present in the water. In addition, arsenic and iron will reprecipitate from groundwater that is advecting and diffusing up into the ponds. Porewater profiles collected by Lorax (2001) indicate that arsenic and iron are reprecipitated in the Secondary Pond when the porewater from the pond sediments encounters the oxic interfacial layer. When conditions change (i.e. depleted oxygen), these precipitates readily dissolve releasing arsenic into the water column. These results correspond well with the sequential extraction data for Secondary Pond Sediments. The aqueous concentration of arsenic in the Secondary Pond is seen to cycle seasonally with higher concentrations appearing in the warmer summer months when biological activity limits the oxygen content of the pond bottom waters resulting in the reductive dissolution of oxidized arsenic species.

4.4 Conclusions

Historical tailings samples (RLM-2, RLM-3, and RLM-6) exhibited significantly higher arsenic concentrations than the samples containing newer tailings (RLM-1, RLM-4, and RLM-5). The high sulphur content in the RLM-2 samples, ranging from 1.86 – 2.63 %, indicates that these tailings were produced during a period of time when roasting and concentration of the sulphide portion of the ore had ceased. The unsaturated old tailings (RLM-2-1, RLM-3-1, and RLM-6-1) contain gypsum, an indicator that sulphide oxidation has occurred.

The tailings sampled at RLM-2 do not appear to contain roasted material, however deeper down there is likely roaster material present. The material sampled at RLM-2 contains significant sulphides and being unsaturated, the top few feet have undergone significant oxidation over the years. RLM-2-1 had only 31% of the arsenic in the As(-1) oxidation state, with 58% present as As(V). From the sequential extractions it was found that approximately 23% of the arsenic in RLM-2-1 is adsorbed, and 28% is associated with iron oxyhydroxides. RLM-2-2 and RLM-2-3 were similar in composition to each other, with more than 80% of the arsenic present as As(-1), with the remaining portion present as a combination of As(III) and As(V). Based on the above information, the surface of this deposit has undergone significant oxidation, resulting in the majority of the arsenic present having undergone post depositional transformation from arsenopyrite to an oxidized form. Deeper in the deposit the majority of arsenic has not undergone oxidation and exists as arsenopyrite. The unoxidized material will be most stable under a water cover. It is likely, however, that roaster tailings are present below the depth of material sampled in this study (based on historical tailings deposition information and observed elevated groundwater arsenic concentrations in the area). Based on the results of the roaster material sampled at RLM-3 and RLM-6, the majority of arsenic present in this material is likely in an oxidized form, and will be most stable under oxidizing conditions. The roasted material, however, is already contained within the saturated zone of this deposit (severely elevated groundwater arsenic concentrations have been observed in the vicinity of the RLM-6 sampling location), therefore flooding the surface of the deposit will not alter redox conditions and will likely not affect the release of arsenic from this material. In summary, flooding of the dry tailings beach in the Primary Pond is not likely to result in a net increase in dissolved arsenic concentrations.

The material located around RLM-3, and RLM-6 was produced from the roasting process. A large fraction of the arsenic at these locations (more so at RLM-6) is

associated with iron oxide material and is and will continue to be mobile under the oxygen deficient conditions (i.e. saturated) that exist in the tailings deposits (extremely elevated arsenic concentrations in the vicinity of RLM-6 have been observed). It would be difficult to maintain aerobic conditions in these subaerial tailings deposits due to the fine grained nature of the tailings, the existence of perched water tables, and the vast amount of biological activity (marsh) growing on top of the tailings.

Less than 30% of the arsenic in RLM-3-1 and RLM-3-2 was in the form of As(-1). A small amount ($\leq 5\%$) of the arsenic existed in the form of As(III), with the remainder present as As(V). Most of the arsenic in the saturated zone in the area of RLM-3 (RLM-3-3) was present in the form of As(-1), with 5% present as As(V) and 2% as As(III), suggesting that the oxidized forms of arsenic present in the unsaturated zone have been mobilized and transformed to As(-1) in the saturated zone.

Only 20% of the arsenic contained in RLM-6-1 the form of As(-1), with 16% present as As(III) and 65% present as As(V). According to the sequential extractions, 39% of the arsenic in RLM-6-1 was adsorbed while 40% was coprecipitated with iron oxyhydroxides. The saturated tailings in the area of RLM-6 (RLM-6-2) contained 63% of the arsenic in the form of As(-1) suggesting that a considerable portion of the oxidized arsenic has been mobilized, and transformed into As(-1).

RLM-1, RLM-4, and RLM-5 contain essentially fresh tailings that have remained saturated. The vast majority of arsenic in these samples is contained within arsenopyrite that should continue to be stable as long as conditions remain saturated. A small amount of arsenic was found to be associated with a "junky" precipitate, containing many species, in the RLM-4 and RLM-5 samples.

Based on the sequential extraction data, only 16% of the arsenic contained in End of Pipe tailings (RLM-5) is likely to be fairly easily mobilized under the existing saturated conditions. The XANES spectra indicate that 23% of the arsenic in RLM-5 tailings is in the oxidized form. All of the solids identification results indicate that the vast majority of the arsenic in the fresh tailings produced at the mine site should remain stable under saturated conditions. RLM-4 tailings were similar in composition to RLM-5 tailings. RLM-1 tailings contained no As(III), and 89% of the arsenic was in the form of As(-1).

The Primary Pond sediment contained 50% As(-1), 11% As(III), and 40% As(V). The material from the Primary Pond (Primary Pond Backhoe sample), contained significantly more arsenic in the As(-1) form.

Approximately 65% of the arsenic contained in the Secondary Pond Sediment is likely to be fairly mobile under the changing redox conditions that exist in the Secondary Pond. The sequential extraction results indicate that over 65% of the arsenic in the Secondary Pond Sediment is sorbed or precipitated with an iron oxyhydroxide phase, with more than 50% of the arsenic being sorbed. The Secondary Pond sediment contained 25% As(-1), 40% As(III), and 35% As(V).

5.0 In situ and Laboratory Experiments

A series of experiments were conducted to investigate the behaviour of arsenic in several tailings types under various conditions. The objective of the experiments was to see if arsenic could be stabilized under reducing conditions, ideally in the form of arsenopyrite or arsenian pyrite.

In general, arsenic can be stabilized in two ways:

- Form a ferric oxide solid phase that will adsorb As^{5+} and keep it under oxidizing conditions
- Form an arsenic sulphide phase (e.g. arsenopyrite or arsenian pyrite) and keep it under reducing conditions

Unfortunately, it is likely not possible to maintain oxidizing conditions throughout a tailings deposit in the natural environment in the long term (even if the tailings are not covered with water). Tailings are fine grained in nature and perched water tables often develop in the deposits. In addition, traditional, non-engineered tailings ponds (i.e. unlined ponds formed in natural valleys and creek beds) are in contact with biological activity. Tailings pond waters are often rich in nutrients (as a result of the reagents used in the mining and milling processes) that promote biological activity, which can bring about reducing conditions.

Maintaining oxidizing conditions throughout the tailings deposits at the Red Lake Mine would likely be impossible, especially considering that some of the tailings deposits are covered with water. Field and laboratory experiments were conducted to investigate whether or not it is possible to stabilize arsenic through the precipitation of an arsenic sulphide phase.

5.1 In situ Column Experiment

The Primary and Secondary Ponds were constructed on top of historical tailings. The surface sediments in the Primary and Secondary Ponds contain a large fraction of arsenic associated with iron oxyhydroxides. Seasonal increases in aqueous arsenic concentration are seen, predominately in the Secondary Pond water, with increases occurring in the summer and winter. The water covering the pond sediments limits oxygen transport into the tailings (remedy for acid rock drainage is to cover tailings with water as dissolved oxygen has a much lower diffusivity in water than in air). Limiting the flux of oxygen into the tailings helps to bring about reducing conditions, which has been shown to lead to the mobilization of arsenic from oxidized tailings.

Bacteria play a major role in the development of reducing conditions. As described previously, bacteria use dissolved organic carbon as an electron donor to reduce various chemical species for energy. The Secondary Pond has become biologically active, due to the low concentrations of cyanide and dissolved metals present, the elevated concentrations of nitrogen and phosphorous present and the addition of Beaver Pond water through the Diversion Ditch. The Diversion Ditch water has introduced a fish population into the Secondary Pond that has resulted in additional biological growth. The biological growth sinks to the bottom of the pond once it dies and provides a source of organic carbon. With an ample source of organic carbon and limited oxygen flux, biologically mediated reducing conditions can develop. As a result of the reducing conditions, arsenic is released from the sediment. The exact mechanism of release of arsenic from iron oxide phases is not completely understood. A combination of reductive dissolution of the iron oxide (Fe^{3+} being reduced to Fe^{2+} resulting in the solubilization of the iron oxide phase and the release of sorbed arsenic) and the direct reduction of arsenate to arsenite (arsenite sorption to iron oxide phases at near neutral pH is far less than arsenate sorption (Pierce and Moore, 1982)) is thought to occur. Another result

of the reducing conditions is the formation of sulphide via the reduction of sulphate.

Any sulphide (S^{2-}) formed (as a result of sulphate reduction) would be expected to combine with reduced dissolved metal species, such as Fe^{2+} , to form low - solubility sulphide species (eventually pyrite). Little evidence of arsenic removal as an arsenic sulphide species has been documented (Smedley and Kinniburgh, 2002), and it is unclear as to why high dissolved arsenic concentrations are observed under reducing conditions in the presence of sulphide.

There are numerous studies that document the increase in aqueous arsenic concentrations following the development of anaerobic conditions in sediments containing arsenic bearing iron oxyhydroxides. These studies include: Deuel and Swoboda (1972), McGeehan and Naylor (1994), Azcue and Nriagu (1995), McCreadie et al. (2000), and Martin and Pedersen (2002).

McCreadie et al. (2000) saw increased arsenic concentrations in a sulphate reducing zone of the Campbell Mine tailings impoundment. Meng et al. (2003) indicate that biotic reductions can convert arsenic and sulphide into arsenian pyrite, although there is limited evidence of this occurring in natural systems. Martin and Pedersen (2002) report that in the deeper sediments of Balmer Lake arsenic is consumed as an authigenic sulphide phase. In the shallow sediment, arsenic is released to the surface water due to seasonal anoxia that develops in the near surface pond sediments (Martin and Pedersen, 2002). It is speculated that conditions may not be reducing enough in some situations to cause the formation of an arsenic sulphide phase, and or not enough sulphide is available (not enough sulphate available to be reduced to sulphide) to precipitate all of the arsenic (plus other dissolved metal species).

Pyrite formation in low temperature sedimentary environments has been studied intensively, however there is only limited information available on arsenopyrite or arsenian pyrite formation in low temperature sedimentary environments.

5.1.1 Methods

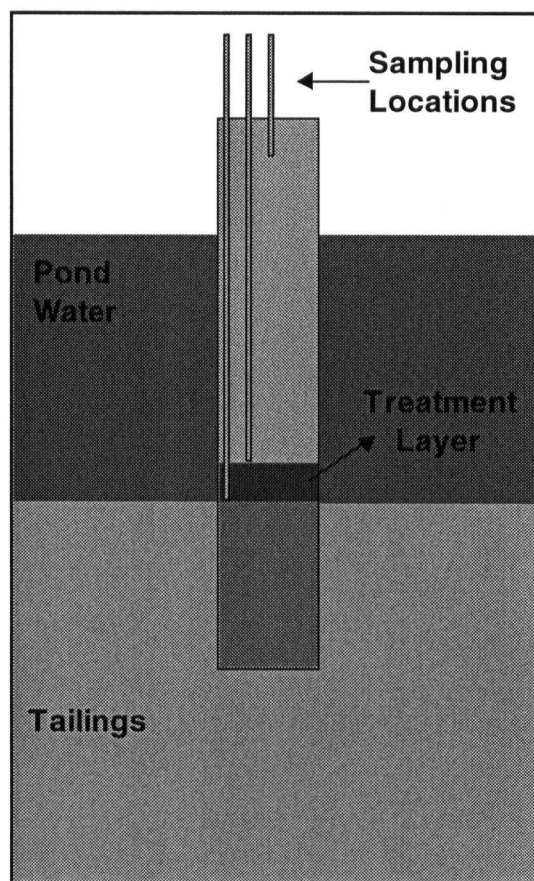
A relatively inexpensive method for conducting an in situ experiment to investigate the geochemistry behind the dissolution of arsenic from the tailings located at the bottom of the tailings ponds was developed. A low-cost limnocoral was developed by sinking pieces of 8 inch (20.3 cm) diameter pipe that extended above the surface of the pond into the tailings sediment, resulting in the isolation of a column of pond water and underlying sediments.

Potential experimental locations were investigated in the Secondary Pond, however no feasible spot was located. An access road needed to be built to the experiment location so that a backhoe could sink the pieces of pipe into place. The logical location for the experiment was off the Primary Dam. Erosion of the Primary Dam, which provides access to the pond, caused the nearby tailings to be covered with sand and gravel, making them inappropriate for the study. Other locations in the pond were too deep, did not contain tailings, or would require too long of an access road to be built. It was decided that the experiment could be much more easily conducted in the Primary Pond as the water was shallower and only a short access road would be needed.

On July 3rd, 2002 four columns of water were isolated in the Primary Pond. The columns consisted of 10-foot lengths of 8-inch diameter fibreglass pipe and were located about 20 feet upstream of the Primary Dam. The pieces of pipe were taken to the correct position in a boat, and held in place while the backhoe operator pushed the pipes into the tailings with the bucket of the hoe. The pipes were sunk approximately 3 feet into the tailings, in about 5 feet of water, leaving 2 feet of pipe to stick up above the water surface.

Figure 31 depicts an installed column. One column was used as an unaltered control, and different treatments were added to the other three columns. Thin tubing outfitted with a filter at one end (landscape cloth was used as a filter) and weighted down with fishing weights was used as sampling ports in the columns. One length of tubing was placed in each column prior to the addition of the treatment layer (bottom sample), and another length of tubing was placed in the columns after the treatment layer had been added (middle sample), enabling sampling at the tailings/treatment layer interface and the treatment layer/water interface. Aqueous samples could also be taken from the surface of the columns using a sampling stick or a pump (surface sample).

Figure 31: Diagram of an installed column



Column #1 (C1) was chosen as the control column. Approximately 150 dry grams of peat were added to Column #2 (C2), and approximately 150 dry grams of peat and 200 g of sulphate (in the form of gypsum from crushed drywall) were added to Column #3 (C3). The treatment added to Column #4 (C4) consisted of approximately 100 dry grams of peat, 200 g of sulphate (in the form of gypsum from crushed drywall), and 5 kg of zero valent iron (in the form of fine iron filings). Peat was used as a source of organic carbon, gypsum was added to ensure that sufficient sulphate was present to be reduced to sulphide, and zero valent iron was chosen as a strong reductant. The treatments were added on July 4th, 2002. Prior to adding the treatments the depth of water was measured and the pH, temperature, specific conductance, dissolved oxygen, and oxidation/reduction potential were measured using a Hydrolab probe. The Hydrolab probe was calibrated using pH 4 and 7 buffers, a 1000 mv specific conductance standard, and a Thermo Orion ORP standard.

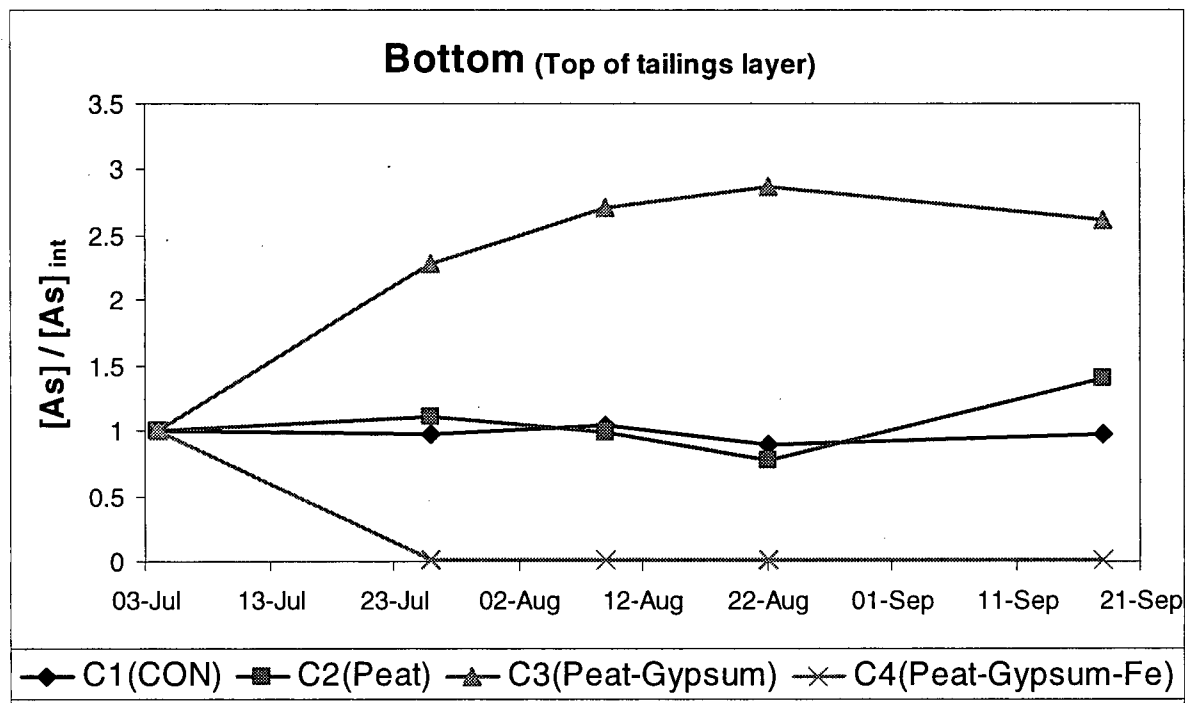
Hydrolab readings were taken again on July 6th, July 8th, and July 10th, and then once per week until August 27th. Aqueous samples were taken from the top and bottom of the columns on July 4th, and the pond surface prior to treatment additions to the columns. Aqueous samples from the top and bottom of the columns were tested for dissolved metals, including arsenic, and surface water samples were also tested for chloride, nitrate and sulphate. Samples were taken again from all locations within the columns and the pond surface for a complete analysis suite (including dissolved metals, ammonia, chloride, dissolved organic carbon, nitrate, phosphate, and sulphate) on July 26th, August 22nd, and September 18th. On August 9th samples were taken for dissolved metals analysis only. Samples were obtained by connecting the thin tubing installed in the columns to a peristaltic pump. All samples were analyzed by Envirotest Laboratories Inc. located in Thunder Bay, Ontario (a CAEAL certified laboratory). Samples for dissolved metals and dissolved organic carbon analysis were field filtered using 0.45 μm syringe filters. Metals analysis was done by ICP-OES, anion analysis was done by ion chromatography, ammonia analysis was

done by colourimetry, and dissolved organic carbon analysis was done by the method APHA 5310 B.

5.1.2 Column Experiment Results

Complete results from the column experiments can be found in Appendix V. The pH in the columns prior to the addition of the treatment layers (July 4th, 2002) was approximately 7.7. After the treatments had been added the pH in C1 – C4 was 7.7, 5.5, 5.7, and 6.0, respectively (measurements taken on July 6th, 2002). The results from each sampling port (bottom, middle, and surface) will be discussed separately.

Figure 32 shows the dissolved arsenic concentration at the bottom sampling port (tailings/treatment layer interface) for C1 – C4. The arsenic concentration is normalized to the initial value in each column (i.e. concentration expressed as the ratio of arsenic concentration divided by the initial arsenic concentration). The average concentration of dissolved arsenic at the bottom location in the control column (C1) was 1.08 mg/L, and was relatively constant throughout the duration of the experiment. The arsenic concentration in C2 remained relatively constant around a value of 1.18 mg/L until September 18th when the concentration increased to 1.72 mg/L. As can be seen from Figure 32, the arsenic concentration at the bottom sampling location in C3 increased to a maximum value of 3.33 mg/L on August 22nd (nearly three times the initial value) and showed a slight decrease to 3.04 mg/L on September 21st. In C4 the arsenic concentration dropped below the detection limit (<0.02) prior to the first sampling time (July 26th) and was not detectable throughout the remainder of the experiment.

Figure 32: Dissolved Arsenic Concentration at the Bottom Sampling Port

The average dissolved organic carbon concentration was elevated above the control concentration of 11 mg/L to 21 mg/L in C2 and 33 mg/L in C3, due to the addition of peat. The DOC concentration in C4 was only slightly elevated and averaged 13 mg/L. The average sulphate concentration in C3 and C4 was 1650 and 1573 mg/L, respectively which, due to the addition of gypsum, was significantly higher than the dissolved sulphate concentration of 440 mg/L in C1. The addition of gypsum to C3 and C4, in the form of crushed up drywall, resulted in an increase in the concentration of dissolved strontium. The concentration of dissolved Sr in C3 and C4 averaged approximately 3.1 mg/L while the Sr concentration in the control column was 0.797.

Nitrate is a redox sensitive species and can give an indication of the redox status of the water. Nitrate is one of the first species to be depleted in the development of reducing conditions, therefore if conditions were reducing at the bottom of the columns no nitrate would be seen. The concentration of nitrate was below detection (<0.03 mg/L) at the bottom sampling port in C3 and C4

indicating that at least some what reducing conditions had developed. The nitrate concentration in C1 and C2 was 6.31 mg/L and 4.27 mg/L, respectively, indicating that conditions were still oxidizing in these columns.

Figure 33 shows the concentration of dissolved iron at the C3-bottom sampling location. As can be seen from the figure the concentration of iron increases in a similar manner as the concentration of arsenic in C3, strongly suggesting that an arsenic containing iron solid phase was being dissolved. The iron concentration at C3 increased from 0.584 mg/L to 11.4 mg/L. The presence of increasing dissolved iron concentration in C3 indicates that conditions are reducing enough for ferric iron to be reduced to ferrous iron. In addition, during sampling on September 18th, a distinct hydrogen sulphide gas smell was noticed, indicating that sulphate was being reduced to sulphide. The iron concentration in C2 averaged 0.458 mg/L while the control iron concentration equaled 0.02 mg/L. The iron concentration in C4 was only slightly elevated above the control concentration (0.07 mg/L). It is believed that the redox status in C4 was strongly reducing as a result of the addition of zero valent iron. Under strongly reducing conditions, arsenic-iron oxides are reductively dissolved and iron and arsenic may be reprecipitated as a reduced solid phase (possible containing sulphide). It is possible that this process was occurring in C4. It is also possible that the arsenic and iron were precipitated on the surface of the zero valent iron in the form of an iron arsenate species. Su and Puls (2001) found zero valent iron to be effective at removing both arsenate and arsenite from solution and also was found to degrade nitrate. According to Oblonsky et al. (2000) zerovalent iron corrodes in solution forming products such as magnetite and maghemite on the Fe⁰ surface. Su and Puls (2001) report that zero valent iron removes arsenic from solution via adsorption of the arsenic onto corrosion products present on the surface of the fillings, they described the adsorption with as a first order reaction.

Concentrations of dissolved manganese were slightly elevated over the control concentration in all of the columns. The concentration of cadmium increased from 0.013 – 0.041 mg/L in C2 and from 0.014 – 0.075 mg/L in C3.

Figure 33: Concentration of Dissolved Iron at the C3 Bottom Sampling Port

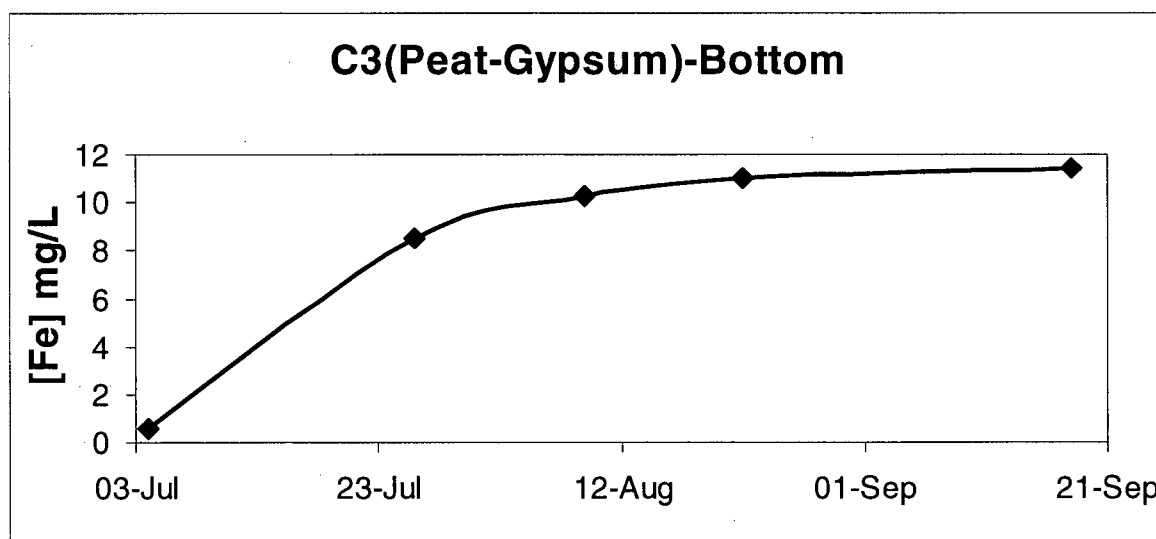
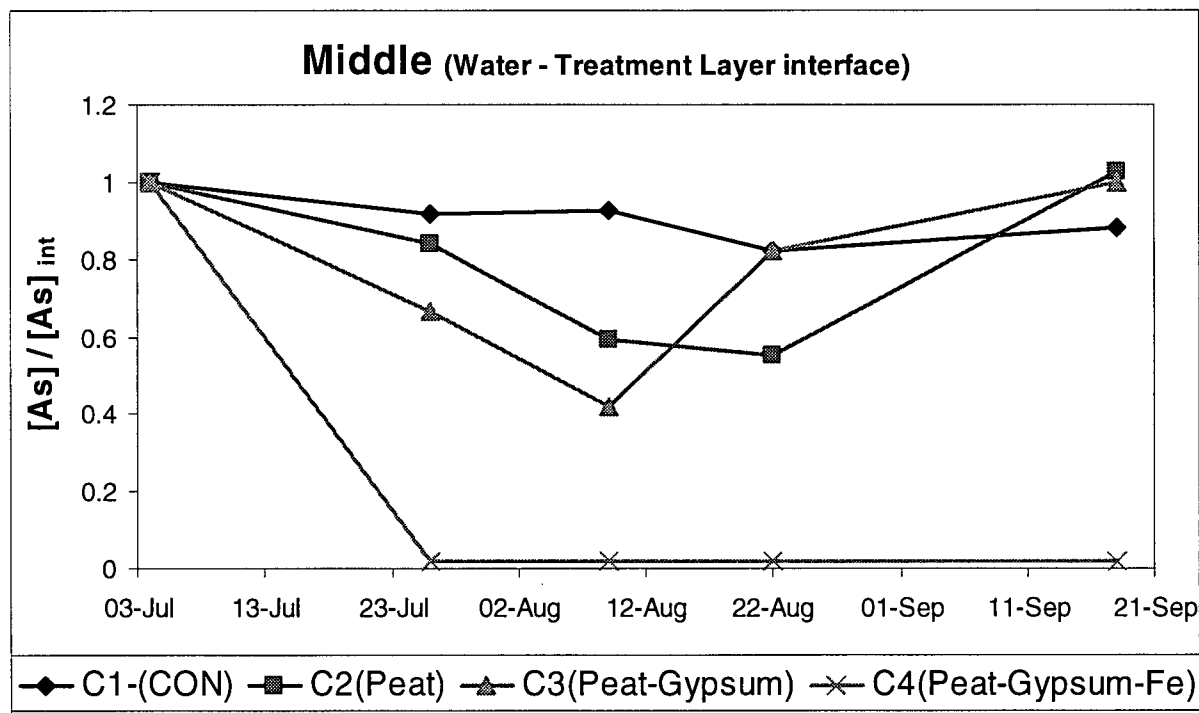


Figure 34 shows the dissolved arsenic concentration at the middle sampling port (treatment layer/water interface) for C1 – C4. The arsenic concentration is normalized to the initial value in each column (i.e. concentration expressed as the ratio of arsenic concentration divided by the initial arsenic concentration). There was no “middle” sample location in the control column, as a treatment layer was not added, therefore the middle sample concentrations in C2-C4 are compared with the surface concentrations in C1.

The average concentration of dissolved arsenic at the surface location in the control column (C1) was 1.08 mg/L, and decreased slightly as the experiment progressed. The arsenic concentration in C2 averaged 0.925, initially decreasing to a minimum value of 0.68 mg/L on August 22nd, then increasing to slightly greater than the starting value. In C3 the concentration of arsenic decreased to a minimum value of 0.49 mg/L on August 9th, then began to increase up to a value of 1.17 mg/L. Up until August 22nd, the treatment layer was able to stop the

released arsenic, from the tailings in C3, from migrating up into the overlaying water column. In C4 the arsenic concentration dropped below the detection limit (<0.02) prior to the first sampling time (July 26th) and was not detectable throughout the remainder of the experiment.

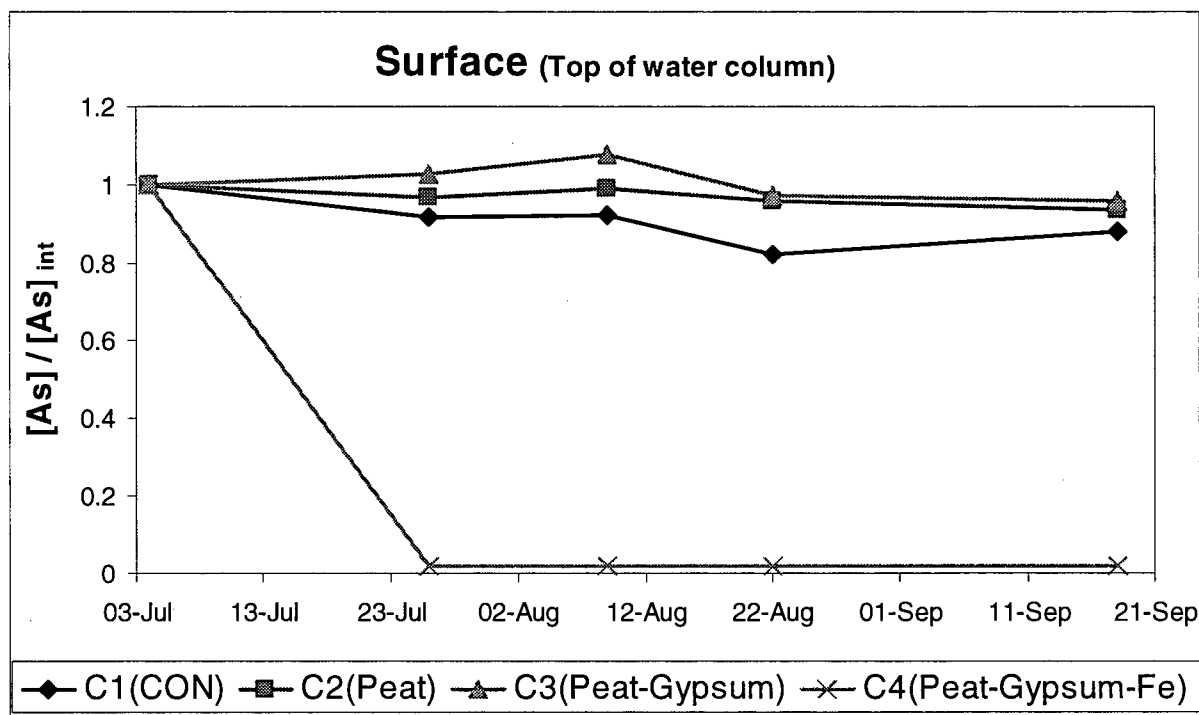
Figure 34: Concentration of Dissolved Arsenic at the Middle Sampling Port



The average DOC concentrations at the middle sampling port were elevated in C2 and C3 to 25 mg/L and 20 mg/L, respectively over the control value of 10 mg/L. The average sulphate concentration in C3 and C4 was 1076 mg/L, which was lower than the bottom sulphate concentration in C3 and C4 but still significantly higher than the control sulphate concentration of 440 mg/L. Strontium concentrations were also elevated at in C3 and C4 at the middle sample location, averaging 2.48 mg/L and 1.81 mg/L, respectively, while the control concentration averaged 0.796 mg/L.

Significant concentrations of nitrate were present in all of the middle sampling locations averaging 6.4, 2.4, 4.0, and 4.3 mg/L in C1 – C4 respectively. The presence of nitrate may indicate that conditions were oxidizing at the treatment layer/water interface in all of the columns, or that kinetic controls prevented the reduction of nitrate. The iron concentration was elevated in C2 averaging 1.11 mg/L while the control iron concentration equaled 0.014 mg/L. The iron concentration was also elevated in C3 and C4, averaging 0.41 and 0.26 mg/L, respectively (the presence of ferrous iron indicates reducing conditions). Concentrations of dissolved manganese were slightly elevated over the control concentration in all of the columns, while the concentration of cadmium was approximately equal to the control concentration in all the columns except C4 in which all the cadmium had been depleted.

Figure 35 shows the dissolved arsenic concentration at the surface of the columns. The arsenic concentration is normalized to the initial value in each column. As can be seen from the figure, the arsenic concentrations in C1 – C3 were nearly constant and similar to each other throughout the duration of the experiment. In C4 the arsenic concentration dropped below the detection limit (<0.02) prior to the first sampling time (July 26th) and was not detectable throughout the remainder of the experiment.

Figure 35: Concentration of Dissolved Arsenic at the Surface of the Columns

The average DOC concentrations at the surface of C2 and C3 averaged 18 mg/L and 17 mg/L, respectively, which was elevated over the control value of 10 mg/L. The DOC concentration at the surface of C4 was slightly elevated over the control value, and averaged 12 mg/L. The average sulphate concentrations in C3 and C4 were 1053 mg/L and 1083 mg/L, respectively, still significantly higher than the control sulphate concentration of 440 mg/L. Strontium concentrations were also elevated in C3 and C4 at the surface sample location, averaging 1.35 mg/L and 1.80 mg/L, respectively, while the control concentration average 0.796 mg/L.

Significant concentrations of nitrate were present in all of the surface water samples from the columns averaging concentrations of 6.4, 5.8, 5.1 and 4.1 mg/L in C1 – C4 respectively. The presence of nitrate indicates that conditions were oxidizing at the surface of all of the columns. This is expected as the surface of the water is exposed to atmospheric oxygen. Concentrations of dissolved manganese were slightly elevated over the control concentration in all of the

columns, while the concentration of cadmium was approximately equal to the control concentration in all the columns except C4 in which all the cadmium had been depleted.

In summary, the addition of a strong reductant (iron fillings) was effective in reducing the dissolved arsenic concentration, and prevented the release of additional arsenic into the water column. The exact mechanism that resulted in the removal of arsenic from the water column in C4 (iron fillings column) is unclear. The arsenic may have been adsorbed onto an oxidized iron corrosion product on the surface of the fillings or may have been incorporated into a reduced iron phase (that may or may not contain sulphide). In column C4, arsenic was likely removed from solution through precipitation/adsorption with an oxidized iron phase at the treatment/layer interface and upwards through the water column. The combination of the addition of organic carbon and sulphate (C3) resulted in the development of reducing conditions at the tailings/treatment layer interface leading to the reductive dissolution of oxidized iron/arsenic phases and the development of high concentrations of dissolved arsenic and iron. Although the redox potential was obviously low enough to bring about the reduction of iron, it is unclear if significant sulphate reduction occurred (hydrogen sulphide gas odour was observed during sampling on some occasions). These results allow one to conclude that released arsenic and iron are not being effectively removed through the precipitation of iron/arsenic/sulphide phases, in the C3 (peat and sulphate treatment).

It is not clear what these results imply for the behaviour of arsenic in the primary pond. The isolated water column was narrow, which limited mixing. In reality the pond waters are usually well mixed which could result in a reduced effectiveness of the iron fillings treatment. In addition, the sides of the columns create an artificial media for precipitates to bind too that would not be present in the pond. A larger scale field experiment would be required to confirm the effectiveness of the iron filling treatment.

To better understand the mechanisms responsible for arsenic release and removal, a laboratory experiment was designed to augment the results of the insitu column testing.

5.2 *Designed Laboratory Experiments*

A series of experiments were conducted to investigate how the manipulation of various factors influenced the stability of solid phase arsenic bearing species. The objective of the experiments was to determine how arsenic concentrations in solution would be affected by adjusting factors that were suspected to have an influence on arsenic stability in tailings samples from the Red Lake Mine. Six factors were identified from research papers and from field observations at the site. The factors selected were: concentration of dissolved organic carbon, concentration of sulphate, concentration of dissolved oxygen, presence of zero-valent iron, tailings source, and presence of elemental sulphur.

The experimental method for the designed laboratory experiments was based on the methods of Reynolds et al. (1999), McGeehan (1996), Dowdle et al. (1996), Rochette et al. (1998), Rochette et al. (2000), Guo et al. (1997) and Rittle et al. (1995). Dowdle et al. (1996) identify lactate as the most effective source of metabolically available organic carbon.

Rochette et al. (1998) synthesized various arsenate minerals, subjected them to reducing conditions (by flooding them in the presence of soil containing organic carbon), and determined the relative solubility of the substances. They found that under reducing conditions scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) was the most soluble mineral. The iron arsenate underwent reductive dissolution releasing As(III) to solution and solid phases (Rochette et al., 1998). Rochette et al. (2000) studied the effect of aqueous sulphide on arsenate minerals. It was found that the presence of sulphide brought about the rapid reduction of arsenate (more so at low pH) and lead to the formation of dissolved arsenic – sulphide complexes that

persisted for days (Rochette et al., 2000). The formation of orpiment only occurred at high S:As ratios.

Rittle et al. (1995) explored whether arsenopyrite could be formed in the Milltown Reservoir sediments by enhancing bacterial sulphate reduction (additional sulphate and organic carbon were added to the sediments in laboratory experiments). It was found that both sulphate and organic carbon amendments were required in order for arsenic to be removed as a sulphide phase (some arsenopyrite with a stoichiometry of approximately 1:1:1 was detected through SEM analysis (Rittle et al., 1995). Reynolds et al. (1999) also detected arsenopyrite formation in their experiments involving the flooding of soils amended with organic carbon.

As described earlier, organic carbon is an energy source for microorganisms. The presence of sufficient organic carbon can result in the development of reducing conditions. Mildly reducing conditions are known to cause certain arsenic bearing mineral phases (namely iron oxyhydroxides) to dissolve, resulting in the release of arsenic into solution. In addition, at $\text{pH} < 6$, arsenate (As(V)) is much more readily adsorbed onto mineral surfaces than arsenite (As(III)). Under reducing conditions, sorbed arsenate will begin to be reduced to arsenite, resulting in the release of previously sorbed arsenic into solution. Under more strongly reducing conditions, it is possible that sulphide minerals such as pyrite, arsenopyrite, and arsenian pyrite will form. Arsenic could potentially be sequestered into these stable sulphide mineral phases if conditions were appropriate. A high concentration of dissolved organic carbon, in the form of lactate (a readily available form of organic carbon) was used in the experiments (there was some additional organic carbon initially present in the tailings samples and pond water used in the experiments).

For sulphide minerals to form there needs to be an ample source of sulphur present that can be easily reduced to sulphide. A high concentration of sulphur,

in the form of sulphate was used in the experiments to ensure that sulphide mineral formation would not be limited by a lack of sulphur.

The atmosphere that the experiments were conducted under was manipulated in order to mimic oxygen sufficient, and oxygen deficient conditions that may develop in the tailings ponds.

Zero valent iron was added with the intention that it would act as a strong reductant, and would bring about strongly reducing conditions in the experiments, potentially resulting in the formation of sulphide minerals. Iron fillings were added in the in situ column experiments and as a result all arsenic was removed from solution and the arsenic release from the sediments ceased. By using iron fillings in the laboratory experiments, the mechanism by which arsenic was removed could be observed.

The tailings source is an important factor in studying the release of arsenic from the tailings. Various types of tailings are located around the mine site, 4 were selected for the experiment. RLM-5 was selected because it represents the tailings that are currently being produced at the mine site. RLM-7 was selected in order to observe the difference between the final tailings currently produced, and the tailings produced prior to the Detox circuit and ferric addition. RLM-2 was selected as it represents tailings that are currently unsaturated in the Primary Pond that may be flooded in the near future. In addition, it was believed at the time that the RLM-2 tailings may have been roaster-derived. Secondary Pond sediments were selected as it has been shown that a large amount of arsenic is released from the sediment every year.

Elemental sulphur was added based on research conducted into sedimentary pyrite formation. All of the literature reviewed stated that in order to get pyrite to form it was necessary to add elemental sulphur or polysulphides. If only sulphide

was added, iron monosulphides would form but would not be converted into pyrite.

5.2.1 Methods

The design of experiment approach was used to evaluate the factors described above, in the most efficient and defensible way. Designed experiments allow for the testing of several variables at one time while being able to determine which factors are significant. By using the design of experiment approach, the individual effects of a factor as well as the combined effects of that factor with other factors, can be determined in the most efficient manner. One of the classes of experimental designs is the two level factorial design.

Two level factorial designs, known as 2^n , develop a linear equation that relates some response to various factors.

$$Y = f(X_1, X_2, \dots, X_n) + e$$

Where Y is the response, X_i is the factor, n is the number of factors and e is the error term. For three factors the equation would be:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_1X_2 + a_5X_1X_3 + a_6X_2X_3 + a_7X_1X_2X_3 + e$$

Where a_i is a constant and the other variables have the same meaning as above. By conducting the appropriate tests, the constants can be calculated to yield a model that gives an estimate of the response. By performing a statistical analysis of the results the significant factors and interactions can be determined. This type of experimentation is referred to as a two-level factorial design because each factor is only tested at two levels, low and high. In a full two-level factorial design all possible combinations of levels are run to determine the above constants. For 3 factors the number of combinations is $2^3 = 8$. If the number of factors is large it is usually desirable to conduct only a fractional two-level

factorial design, such as a half or quarter fraction. In a quarter fraction factorial design 2^{n-2} runs are performed. In fractional designs not all of the interaction effects can be determined as there is not enough information, however, higher level interactions are rarely significant, and the most valuable information can still be determined from the reduced number of experimental runs performed.

Two, 6 factor, $\frac{1}{4}$ fraction, two level factorial experiments were run simultaneously. If the full fraction designed experiment was conducted this would result in 64 runs. By doing a $\frac{1}{4}$ fraction, only 16 runs for each experiment (32 in total) had to be conducted.

Table 9 shows the design matrix for the experiment. The factor levels are coded as either -1 (low level) or $+1$ (high level). For example, run 1 would contain DOC at the high level, Sulphate at the low level (no addition), would have a low level atmosphere (sealed with rubber stopper), low level zero valent iron (no addition), tailings at the low level (in this case RLM-5 tailings), and elemental sulphur at the high level.

Table 9: Design Matrix for Laboratory Experiments

Trial Number	DOC A	SO ₄ B	Atm C	Fe(0) D	Tailings E	S(0) F
1	1	-1	-1	-1	-1	1
2	-1	-1	-1	-1	1	-1
3	-1	1	1	-1	1	-1
4	-1	1	1	1	-1	-1
5	-1	-1	1	-1	-1	1
6	-1	1	-1	1	1	1
7	1	-1	1	1	-1	-1
8	1	-1	1	-1	1	-1
9	1	-1	-1	1	1	1
10	1	1	-1	-1	1	-1
11	1	1	1	1	1	1
12	-1	-1	-1	1	-1	-1
13	1	1	-1	1	-1	-1
14	1	1	1	-1	-1	1
15	-1	-1	1	1	1	1
16	-1	1	-1	-1	-1	1
17	-1	-1	1	-1	-1	1
18	1	-1	-1	1	1	1
19	1	-1	1	-1	1	-1
20	-1	-1	-1	1	-1	-1
21	-1	1	-1	1	1	1
22	-1	1	-1	-1	-1	1
23	1	-1	-1	-1	-1	1
24	-1	1	1	-1	1	-1
25	1	-1	1	1	-1	-1
26	-1	1	1	1	-1	-1
27	1	1	1	1	1	1
28	1	1	-1	-1	1	-1
29	1	1	1	-1	-1	1
30	-1	-1	1	1	1	1
31	1	1	-1	1	-1	-1
32	-1	-1	-1	-1	1	-1

Each run of the experiment was conducted in 250 ml Erlenmeyer flasks. A solution of approximately 2 g of sodium lactate syrup in 100 ml of water was created. High level DOC runs received 1 ml of this solution at the start of the experiment (approximate addition of 20 mg/L DOC). For sulphate, an assumption was made that the Secondary Pond water used in the experiment contained about 250 mg/L sulphate. In order to achieve 1000 mg/L of sulphate in the high sulphate runs, 0.25 g of sodium sulphate was added. Zero Valent iron

was first washed with distilled water to remove the fine iron dust, then 15 g (wet) or iron fillings was added to the high level flasks. Low level atmosphere conditions were created by capping flasks with Teflon lined rubber stoppers. Flasks were only opened in an anaerobic chamber to minimize oxygen influx into the flasks. High level atmosphere conditions were created by leaving the flasks open to the atmosphere throughout the duration of the experiment (flasks were loosely capped with a sponge stopper in an attempt to minimize evaporation).

In the first set of experiments (runs 1 – 16) RLM-5 represented the low level tailings source, while RLM-7 represented the high level. In the second set of experiments (runs 17 – 32) RLM-2 represented the low level tailings source, while Secondary Pond Sediments represented the high level. One gram of elemental sulphur was added too each of the high level flasks.

Fifty grams (dry equivalent) of each tailings type was added to the appropriate flask and secondary pond water was added to make the total amount of solution equal to 225 ml (taking into account the water contained within the wet solids). The appropriate amount of each reagent was added to the flasks. The flasks were stirred and shaken to thoroughly mix the ingredients. The pH in each flask was adjusted to 7.0 using environmental grade HCl. The flasks were capped (rubber stoppers for low level atmosphere, foam stoppers for high level atmosphere) and placed on a shaker table. Buckets of water, and additional flasks full of water were placed inside the shaking table unit in an attempt to minimize evaporation from the foam capped flasks. Figure 36 shows a digital image of the flask set up on the shaker table.

Figure 36: Designed Experiment Laboratory Setup Photograph



Initial samples were taken on Day 1, with additional samples being taken after 7 days, 21 days, and finally after 42 days. During the day 7 sampling, the pH was adjusted to 6.5 and an additional 1 ml of 2 g/100 ml sodium lactate solution was added to the high level DOC flasks. During the day 21 sampling, the pH was also readjusted to 6.5. At the final sampling time (day 42), solid samples were also taken from the flasks. The solid samples were immediately frozen after being removed from the flasks.

5.2.2 Results

Distinct visual changes had occurred in the flasks by day 21. In the first set of samples, flasks #6, #9, #11, and #15 contained black material on the bottom of the flasks with silvery shiny spots present. In addition, an orange coating had appeared on the upper portion of the glass flask. All of these flasks had both iron fillings and elemental sulphur present, and were constructed with RLM-7 tailings. Flasks #4, #7, #12, and #13 had a darker shading present on the bottom of the

flasks. This darker shading was believed to be just the iron fillings, as all four of these flasks had iron filing added to them. Figure 37 shows flask #6, depicting the orange coating on the glass walls of the flask and the bottom black layer with silvery shiny spots.

Figure 37: Flask #6 after Day 21



In the second set of samples, flasks #18, #27, and #30 contained black material, with flasks #18 and #27 also containing spots of a silvery shiny substance. All three flasks contained iron fillings and elemental sulphur and were constructed with Secondary Pond sediments. Flasks #18 and #27 contained DOC while flask #30 did not. Flask #21 also contained iron fillings, and elemental sulphur, however black material did not appear to have formed in this flask. In all flasks containing Secondary Pond Sediment, distinctive layering of the solids was present and bubbles were entrapped throughout the sediment layer. The black material is believed to be iron monosulphides. The shiny spots may have been arsenopyrite.

Arsenic and iron concentrations were measured using a graphite furnace atomic adsorption spectrophotometer. Samples were diluted using 1% environmental grade nitric acid. Blanks and standards were also prepared using 1% environmental grade nitric acid. The detection limits for arsenic and iron were 0.05 mg/L and 0.01 mg/L, respectively. Arsenic concentrations were measured in all the samples, whereas iron concentrations were measured only in the Day 1 samples and in the Day 42 samples (due to time constraints and machine availability). Dissolved organic carbon concentrations were measured using a Carlo Erba NA-1500 Elemental Analyzer in the Day 1 and Day 42 samples. Sulphate and nitrate concentrations were measured in the Day 1 and Day 42 samples as well, using Ion chromatography.

The average sulphate concentration for each tailings type was determined for flasks that had sulphate added to them and for flasks that did not, the values in mg/L are shown in Table 10. Complete sulphate results can be found in Appendix VI. The concentration of sulphate in the Secondary Pond water used in the experiment was 276 mg/L.

Table 10: Average Sulphate Concentration (mg/L) for Each Tailings Type

Tailings Type	Day 1		Day 42	
	No Sulphate	Sulphate	No Sulphate	Sulphate
RLM-5	640	1925	676	2550
RLM-7	682	2189	1149	1778
RLM-2	1679	2550	2536	3591
Secondary Pond	633	2168	1759	3320

The average dissolved organic carbon concentration for each tailings type was determined for flasks that had lactate added to them and for flasks that did not. The values are shown in Table 11 in mg/L, complete results can be found in Appendix VI. The concentration of dissolved organic carbon in the Secondary Pond water used in the experiment was 17 mg/L.

Table 11: Average Dissolved Organic Carbon Concentration (mg/L) for Each Tailings Type

Tailings Type	Day 1		Day 42	
	No DOC	DOC	No DOC	DOC
RLM-5	11.7	18.9	8.4	7.7
RLM-7	11.3	20.1	6.3	5.7
RLM-2	8.8	21.3	8.9	13.2
Secondary Pond	23.5	34.7	4.8	7.9

The concentration of arsenic in the Secondary Pond water used to construct the experimental flasks was 2.7 mg/L.

Arsenic results were graphed for each tailings type and are briefly analyzed below. Complete arsenic and iron results can be found in Appendix VI.

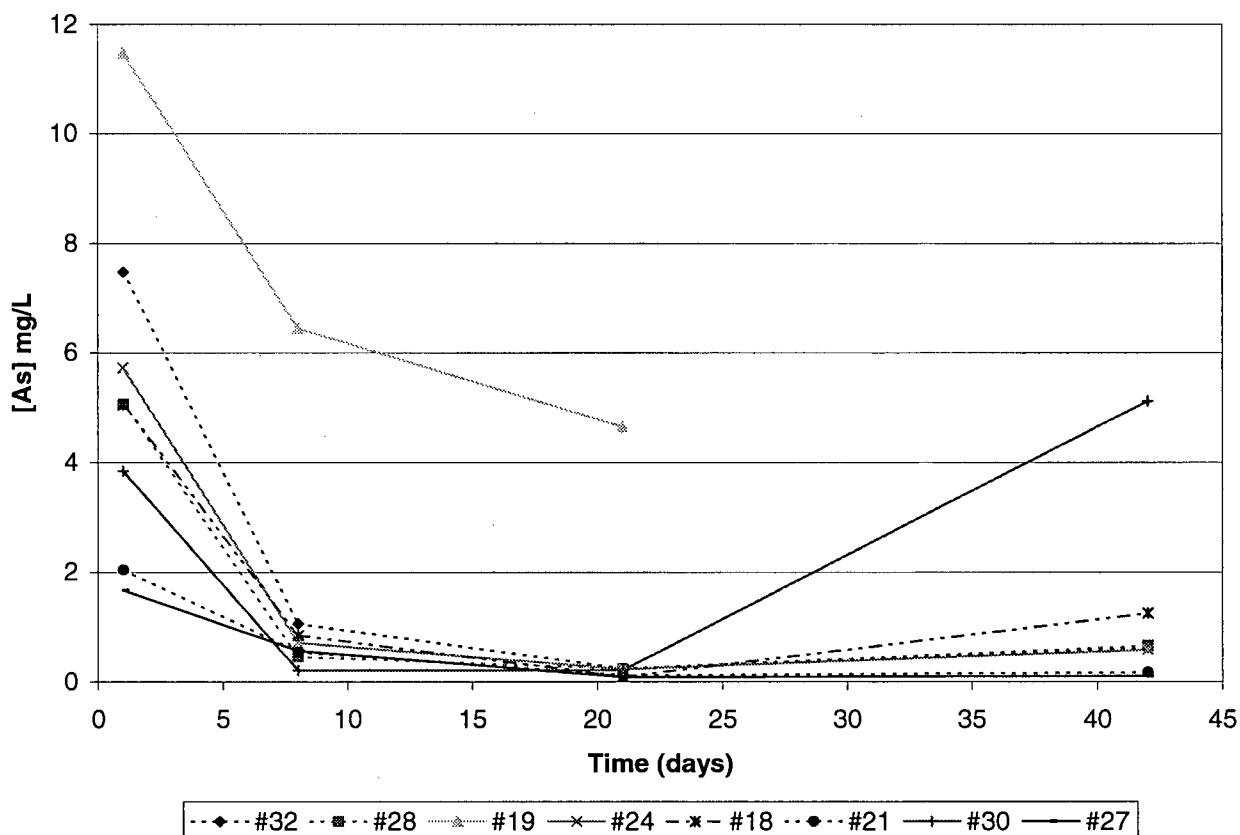
Secondary Pond Sediment

Flask #19 was omitted from the analysis as an unusually high dissolved organic carbon concentration was observed, which resulted in non-representative conditions occurring in the flask. The abnormally high DOC concentration may have been due to error in lactate addition or due to some anomalous growth.

Figure 38 shows the change in arsenic concentration for each of the flasks containing Secondary Pond Sediment. Initial arsenic concentrations (Day 1) were highest in flasks #32 and #24, both did not contain iron fillings or sulphate. Lowest initial arsenic concentrations were seen in flasks #21 and #27, each of which contained both iron fillings and sulphate. After day 21 the arsenic concentration in all the flasks was less than 0.5 mg/L with the lowest values seen in #18, #27, and #21. These flasks all contained both elemental sulphur and iron fillings. After 42 days arsenic concentrations were found to have significantly increased in flasks #18 and #30, and all flasks except for #27 and #21 had arsenic concentrations greater than 0.5 mg/L. Flasks #27 and #21 maintained below 0.5 mg/L arsenic concentrations. Both of these flasks contained sulphate,

elemental sulphur and iron filings. In order to maintain arsenic concentrations below 0.5 mg/L it appears as if (based on this preliminary assessment) elemental sulphur and iron, as well as sulphate are needed.

Figure 38: Arsenic Results for Flasks Containing Secondary Pond Sediment

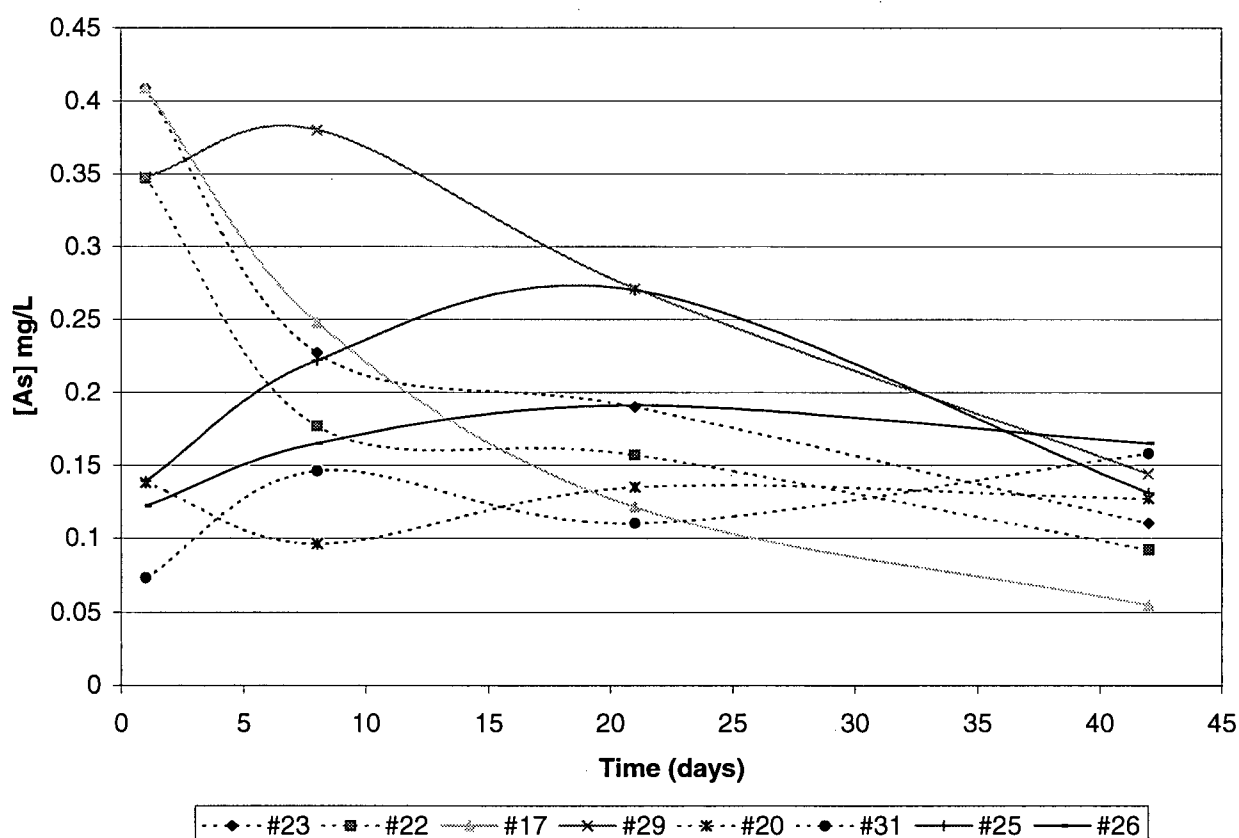


RLM-2

All flasks contained less than 0.5 mg/L arsenic throughout the duration of the experiment. Initially, the highest arsenic concentrations were seen in flasks that did not contain iron or sulphate (#17 and #23), followed by flasks that contained sulphate but no iron (#29 and #22), flasks that contained iron but no sulphate (#25 and #20), and finally the lowest initial concentrations were seen in flasks containing both iron and sulphate (#26 and #31). After Day 21 the arsenic concentration in all of the flasks had dropped below 0.3 mg/L, and at the end of the experiment the concentration in all flasks was less than 0.2 mg/L. Figure 39

shows the change in arsenic concentration over time. With these tailings it does not seem to matter what is done to them, arsenic concentrations still remain low, even the flasks containing organic carbon addition and low oxygen environments did not produce significantly elevated arsenic concentrations. These tailings appear to have a capacity to remove arsenic from solution as even after 1 day the aqueous arsenic concentration was reduced from 2.7 mg/L (concentration in Secondary Pond water added to flask at start of experiment) to below 0.5 mg/L.

Figure 39: Arsenic Results for Flasks Containing RLM-2 Tailings

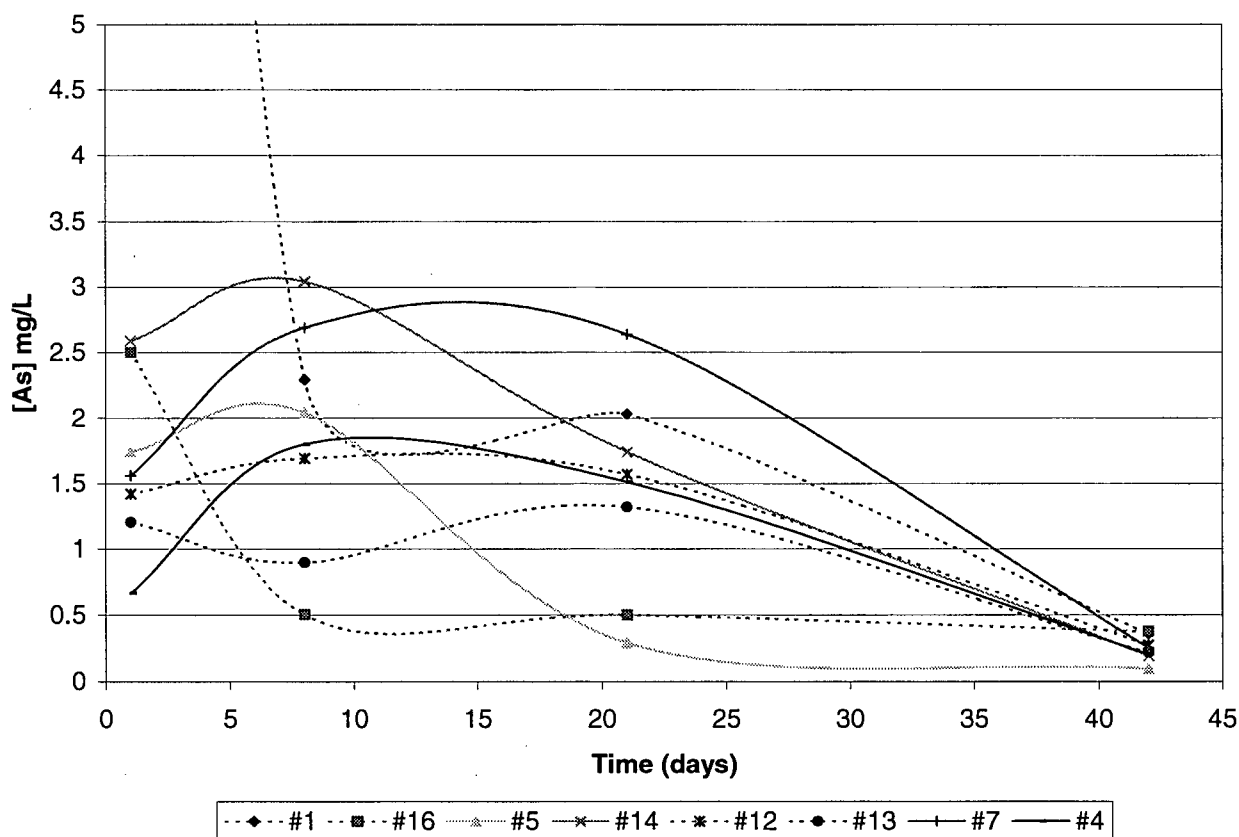


RLM-5

The highest initial concentrations were seen in flasks that did not contain iron fillings (#1, #14, #16, #5). It should be noted that the high concentration seen in flask #1 initially (20 mg/L) is likely due to error as all other concentrations were less than 3 mg/L. Lowest initial concentrations were seen in flasks containing

both iron and sulphate. With the exception of flasks #12 and #16, an increase in arsenic concentration was seen at Day 7 in all flasks, followed by a decrease for the remainder of the experiment. At the end of the experimentation period all flasks contained less than 0.4 mg/L arsenic. In general, the lowest final concentrations were seen in flasks with an oxygen rich atmosphere. Figure 40 shows the change in arsenic concentration over time.

Figure 40: Arsenic Results for Flasks Containing RLM-5 Tailings

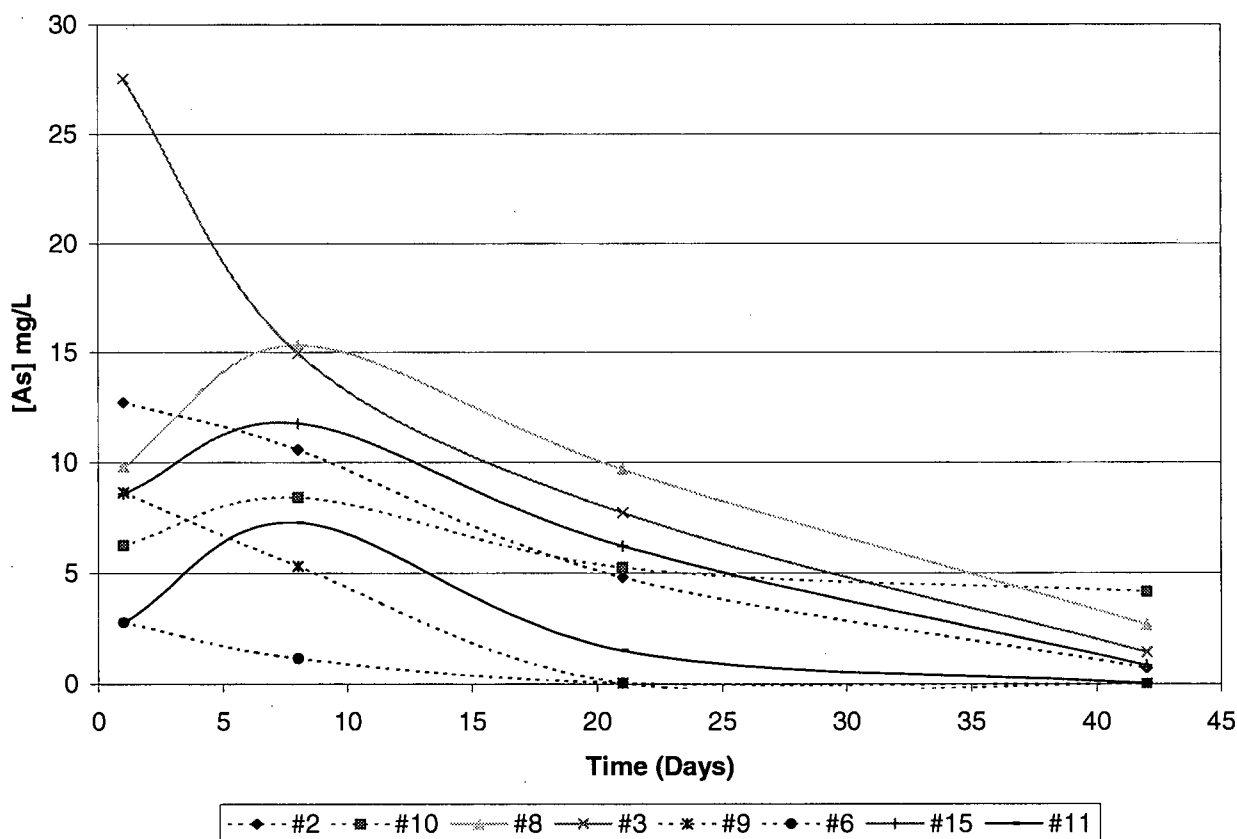


RLM-7

Of the four tailings types, the highest concentrations were seen in the RLM-7 flasks. This result is understandable as the RLM-7 tailings sample contained the highest concentration of total arsenic. The highest initial concentrations occurred in flasks #2 and #3 which both did not contain iron. The lowest initial concentrations were seen in flasks #6 and #11, both of which contained sulphate,

and iron. In some flasks concentrations were seen to rise after Day 7 and then drop, while in other flasks concentrations just dropped from their initial value. By the third week the concentration of arsenic in flasks #6 and #9 had dropped below 0.1 mg/L. At the end of the experiment the arsenic concentrations in flasks #6 and #9 were below detection, and in flask #11 the concentration was 0.02 mg/L. Significantly higher concentrations (greater than 0.5 mg/L) were seen in the remainder of the flasks. Flasks #6, #9, and #11 all contained both elemental iron and sulphur, while flasks #6 and #9 had an oxygen depleted environment. Figure 41 shows the arsenic concentrations over time.

Figure 41: Arsenic Results for Flasks Containing RLM-7 Tailings



The experimental data was analyzed using the Design – Expert software for experimental Design, version 6.0.1.0, created by Stat-Ease Inc. Data and experimental parameters are inputted into the software, a regression is

performed, significant factors determined, and a model is fitted to the data. The first step involves viewing a half normal probability plot. Data points on the plot represent factors and interaction terms. A line is fitted through the points closest to the origin (the points that produced the smallest effect), and any points not falling on the line are initially considered to be important.

Next an analysis of variance table (ANOVA) is created for the selected factors. F values for the model and for each factor/interaction are shown, as well as the sum of squares for each term. F values indicate the importance of the terms, the larger the F value the more likely that the term is significant. Probability greater than F ($\text{Prob} > F$) values are also shown, these values signify the percentage chance that an F value that large could occur due to noise. $\text{Prob} > F$ values less than 0.05 indicate that model terms are significant. Ideally the selected model will account for the majority of the total sum of squares (i.e. the residual values will be close to zero). The closer the residual sum of squares is to zero the better the model was able to fit the experimental data. Another check of the model fit is the predicted R squared value (how good the model predicts the response) compared to the adjusted R squared value (a measure of the amount of variation about the mean explained by the model). These two values should be within 0.2 of each other.

At this point any terms initially selected that are determined to be insignificant can be removed and the model re-regressed. Once the final model has been determined the program gives an equation for the model with calculated constant values. Actual values can be compared to calculated values as an additional check of the adequacy of the model to fit the data. Next the normal probability plot of the studentized residuals is viewed to check for normality of the results. In order to check for constant error the studentized residuals are graphed versus the predicted values. The outlier T graph can be viewed to check for any outlier points. If all of these checks are okay then the model can be concluded to be a

good fit of the data. Model graphs are created so that the impact of each factor and interaction can be easily seen.

Set 1 – RLM-5 and RLM-7

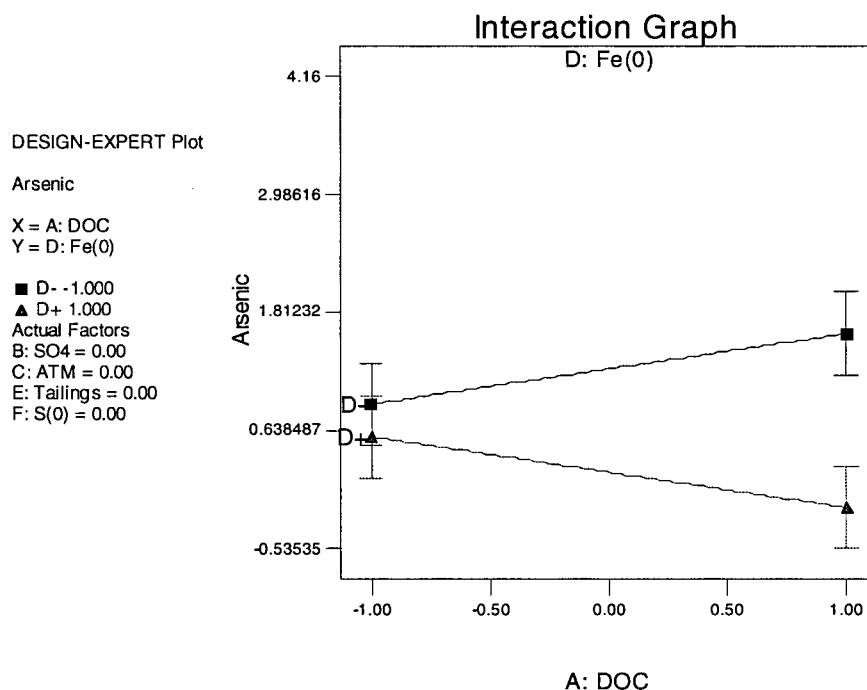
The Day 42 data from Set 1 (RLM-7 represented by factor E at the +1 level, RLM-5 represented by factor E at the -1 level) was analyzed using the Design Ease software. The statistically significant factors and interactions determined by the software were D (iron filings), E (tailings type), F (elemental sulphur), AD (the interaction between DOC and iron filings), and AF (the interaction between DOC and elemental sulphur). The ANOVA table, diagnostic plots, and model graphs can be found in Appendix VII. The predicted model in terms of coded factors (concentrations represented by +1 or -1) is:

$$\text{Arsenic} = 0.74 - 0.51D + 0.49E - 0.5F - 0.35AD - 0.34AF$$

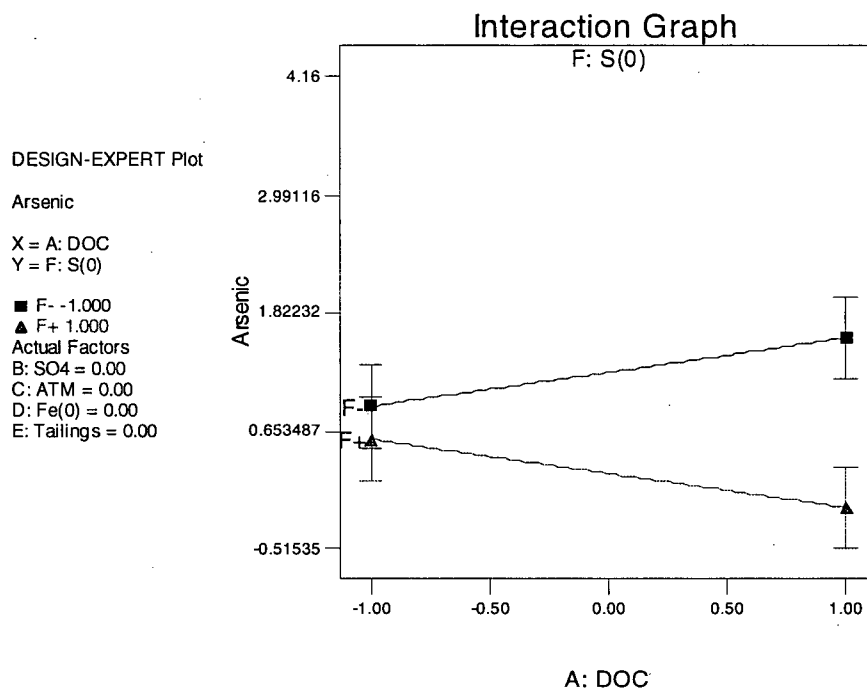
The presence of iron filings (D) and elemental sulphur (F) both resulted in decreased arsenic concentrations for both tailings types. Lower arsenic concentrations were seen with RLM-5 tailings (factor E at a -1 level), the positive constant associated with E in the above equation accounts for this. Both interaction terms involve DOC. Figures 42 and 43 show the effect of the interaction terms AD and AF, respectively. From Figure 42 it can be seen that when no iron is present (D = -1, the black line) lower DOC concentrations are correlated with lower arsenic concentrations. In essence, when iron filling are not present, lower arsenic concentrations were seen in the flasks in the flasks that did not have DOC added. When iron is present (D = +1, the red line), however, the opposite is true. In essence, when iron filings are present, lower arsenic concentrations were seen in the flaks that had DOC added. Therefore when elemental iron is present the addition of DOC results in lower arsenic concentrations, however when elemental iron is not present the addition of DOC results in an increase in arsenic concentrations. This trend makes sense as

when elemental iron is present reducing conditions are induced and the presence of DOC will encourage these reducing conditions (potentially leading to microbially mediated production of arsenopyrite). However when elemental iron is not present, the addition of DOC will lead to the onset of mildly reducing conditions, possibly leading to reductive dissolution of arsenic bearing iron oxyhydroxides. If DOC is present, the addition of iron filings will help to reduce the arsenic concentration.

Figure 42: Set 1 – Day 42 Interaction Graph for AD



The interaction term AF had the same behaviour pattern as AD. When no elemental sulphur was present ($F = -1$, the black line), lower arsenic concentrations were seen with lower DOC concentrations. When elemental sulphur was present ($F = +1$, the red line), lower arsenic concentrations were seen with higher DOC concentrations.

Figure 43: Set 1 – Day 42 Interaction Graph for AF

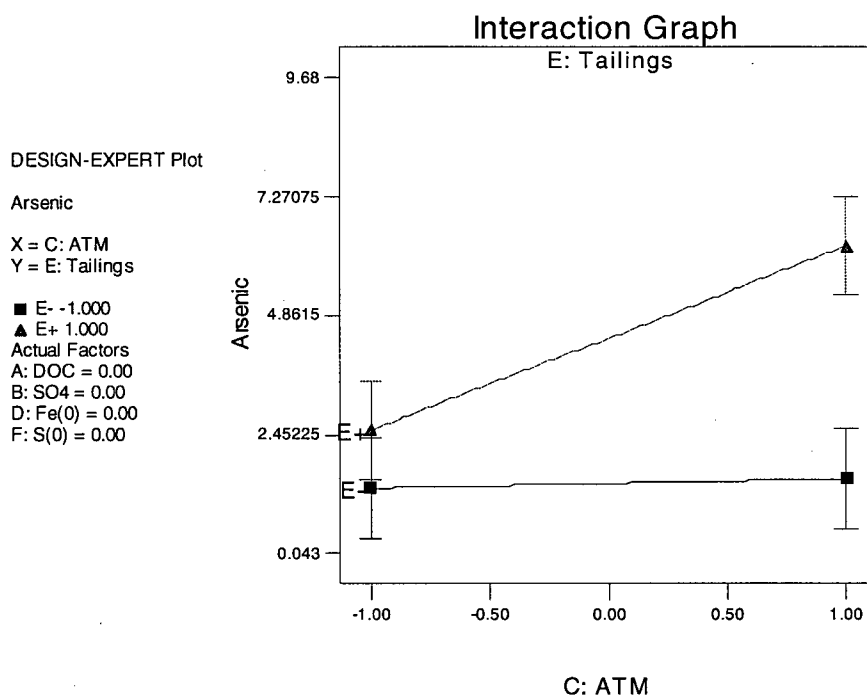
According to the above equation, the lowest arsenic concentrations will be achieved when iron filings, elemental sulphur, and DOC are present (i.e. D = +1, F = +1, A = +1), and when the tailings type is RLM-5 (E = -1). The majority of the arsenic present in both of the tailings types used in Set 1 was in the form of arsenopyrite. Arsenopyrite is most stable under reducing conditions, therefore it is logical that the presence of a strong reductant leads to the lowest arsenic concentrations. Overall, significantly lower concentrations were seen for RLM-5 than for RLM-7. The experiment demonstrated that under all conditions the aqueous arsenic concentrations after 42 days for RLM-5 tailings were less than 0.5 mg/L. RLM-7 tailings will never likely be discharged to the tailings pond as this would result in a large loss of recoverable gold. The experiment showed that in order to obtain aqueous arsenic concentrations less than 0.5 mg/L in water overlying RLM-7 tailings it is necessary to maintain reducing conditions.

Earlier time data (i.e. Day 21 and Day 7) were also analyzed using the software. For Day 21 data the software identified C, D, E, F, and CD as the significant

factors. The presence of C (atmosphere) had a significant impact on RLM-7 tailings ($E = +1$) and only a minimal impact on RLM-5 ($E = -1$) tailings. The CE interaction graph shown in Figure 44 depicts this trend. Arsenic concentrations were significantly higher when $C = +1$ (oxygen present) and $E = +1$ (RLM-7 tailings), then when $C = -1$ (oxygen depleted atmosphere). This result demonstrates the importance of maintaining reducing conditions when tailings with a high arsenopyrite content are present. C was not found to be a significant factor in the Day 42 data, meaning that any additional arsenic that was mobilized due to presence of an oxygen rich atmosphere in early days of the experiment, was later removed from solution via a precipitation or adsorption process (either with a sulphide or an oxide phase). The predicted model for the Day 21 data, in terms of coded factors, is:

$$\text{Arsenic} = 2.93 + 0.98C - 1.07D + 1.48E - 1.38F + 0.89CE$$

Figure 44: Set 1 – Day 21 Interaction Graph for CE



For Day 7 data the software identified the same factors as for the Day 21 data, with the addition of B (sulphate). Higher sulphate concentrations produced lower

arsenic concentrations for both tailings types. The predicted model for the Day 7 data, in terms of coded factors, is:

$$\text{Arsenic} = 5.61 - 0.85B + 1.75C - 1.54D + 3.74E - 1.44F + 1.23CE$$

The presence of sulphate was not found to be statistically significant in the later time data. Either the effect of sulphate was small in comparison to the other effects, or sulphate had no effect in the long term.

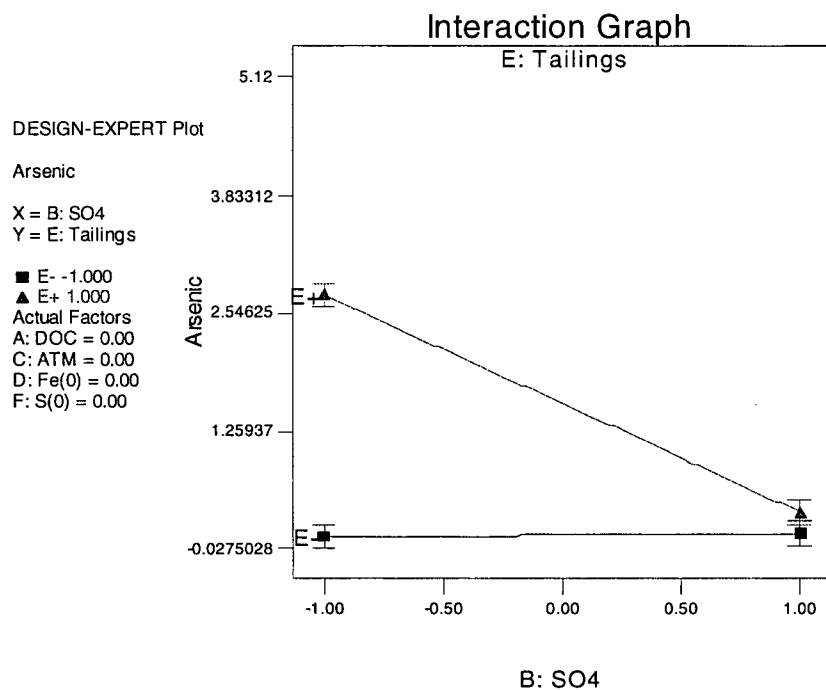
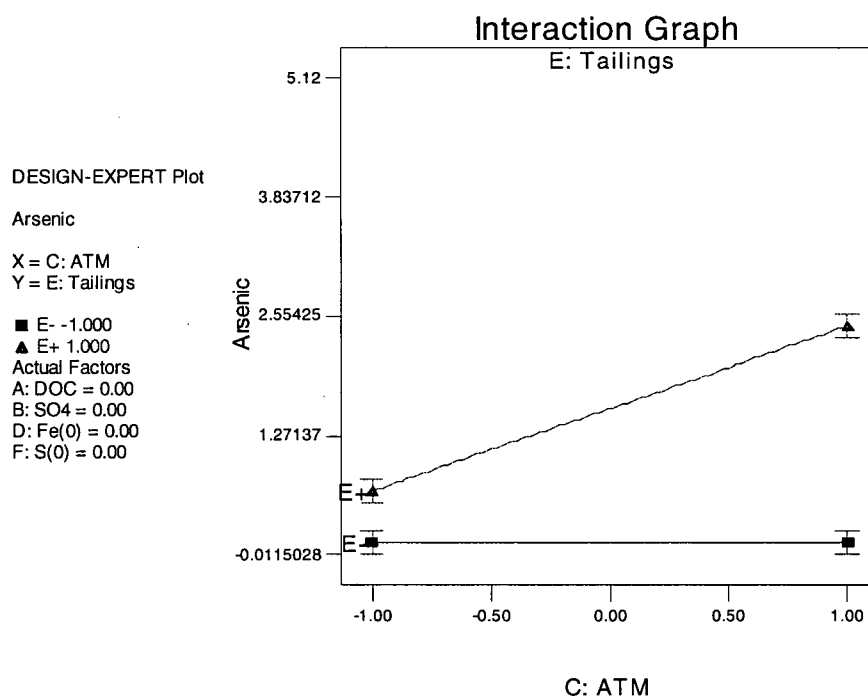
Set 2 – RLM-2 and Secondary Pond Sediment

The Day 42 data from Set 2 (Secondary Pond Sediment represented by factor E at the +1 level, RLM-2 represented by factor E at the -1 level) was analyzed using the Design Ease software. The statistically significant factors and interactions determined by the software were B (sulphate), C (atmosphere), E (tailings type), AC (the interaction between DOC and sulphate), AD (the interaction between DOC and iron filings), AF (the interaction between DOC and elemental sulphur), BD (the interaction between sulphate and iron filings), BE (the interaction between sulphate and tailings type), and CE (the interaction between atmosphere and tailings type). The ANOVA table, diagnostic plots, and model graphs can be found in Appendix VII. The predicted model in terms of coded factors (concentrations represented by +1 or -1) is:

$$\begin{aligned} \text{Arsenic} = & 0.84 - 0.58B + 0.44C + 0.72E - 0.17AC - 0.47AD - 0.45AF - 0.17BD \\ & - 0.6BE + 0.44CE \end{aligned}$$

The presence of sulphate (B) resulted in a decrease in arsenic concentration, while the presence of an oxygen rich atmosphere (C = +1) resulted in an increase in arsenic concentration. Both of these factors, however, were involved in an interaction with tailings type. Tailings type had a major impact on the arsenic concentration, with much lower concentrations being seen with RLM-2 (E

= -1) tailings. The BE and CE interaction terms show that factors B and C are only significant for the Secondary Pond Sediment ($E = +1$). Figures 45 and 46 show the behaviour of the BE and CE interaction terms. For $E = +1$ (Secondary Pond Sediment), the arsenic concentration decreases significantly with increasing sulphate concentration, and the arsenic concentration is significantly higher with a +1 atmosphere (oxygen rich).

Figure 45: Set 2 – Day 42 Interaction Graph for BE**Figure 46: Set 2 – Day 42 Interaction Graph for CE**

The interaction terms AC, AD, AF, and BD have an impact on both tailings types. For AC, when $C = -1$ (oxygen depleted atmosphere), the arsenic concentration increases slightly when DOC is present, however when $C = +1$, the arsenic concentration decreases slightly when DOC is present. For the AD term, the arsenic concentration decreases when iron filings are present as the DOC concentration increases. When iron filings are not present, the arsenic concentration is lowest with lower DOC concentrations. The same situation exists for the AF term as described for the AD term. The effect of the BD term is much more significant for the Secondary Pond Sediments than for RLM-2 tailings. For the Secondary Pond Sediments, the arsenic concentration decreases as the sulphate increases (more so when iron filings are present). For RLM-2 tailings, when iron filings are not present the arsenic concentration increases slightly as the sulphate concentration increases. When iron is present the arsenic concentration decreases slightly as the sulphate concentration increases. The graphs for the interaction discussed above can be found in Appendix VII.

By manipulating the model factors it is possible to predict how the arsenic concentration will be affected under certain conditions.

According to the model, for RLM-2 tailings, the lowest possible arsenic concentrations are seen when all the factors are at the low level, in essence, an oxygen depleted environment with no additional sulphate, DOC, elemental sulphur or iron filing present (the impact of iron filings and elemental sulphur on the concentration is negligible). If the situation arises where DOC will be present under a depleted oxygen environment, and all the other factors remain at the -1 level, the arsenic concentration increases dramatically, from near zero to about 1 mg/L (predicted by the model). If iron and elemental sulphur are added (now at $+1$ level) the arsenic concentration is seen to drop back down to near zero. The addition of sulphate decreases the arsenic concentration slightly, but only when iron filings are present, otherwise the addition of sulphate increases the arsenic

concentration. These results are intuitive, and coincide with the theory of microbially mediated arsenic dissolution. They show that the addition of iron filings can significantly reduce arsenic concentrations.

For the opposite situation for RLM-2 (i.e. under oxygen rich conditions, $C = +1$), the lowest arsenic concentrations are seen when all other factors are at the low level (the impact of sulphate, iron filings and elemental sulphur is minor). If DOC is added ($A = +1$), the arsenic concentration, as predicted by the model, increases from near zero to about 0.7 mg/L. By adding iron filings and elemental sulphur the arsenic concentration is returned to near zero. The addition of sulphate has the same result as under oxygen depleted conditions.

The case of the Secondary Pond Sediments is quite different than for RLM-2. The lowest arsenic concentrations are seen when all factors are at the low level except for sulphate ($B = +1$). The addition of sulphate dramatically decreases the arsenic concentration from approximately 0.6 mg/L, down to near 0 mg/L. Without sulphate the addition of DOC drives the arsenic concentration up to greater than 2.5 mg/L, by adding sulphate the concentration is seen to drop to about 0.75 mg/L. By adding iron and elemental sulphur the concentration can be dropped further to near zero, however without the sulphate the arsenic concentration is greater than 1 mg/L. In this situation it is likely that the sulphate is precipitating with calcium in the water to form gypsum and arsenic is adsorbing and/or coprecipitating with the gypsum. Unfortunately, arsenic - calcium precipitates are known to have limited stability. It was surprising that lower concentrations were seen under an oxygen depleted environment than under an oxygen rich environment, as the release of arsenic from Secondary Pond Sediments due to reductive dissolution of arsenic bearing iron oxyhydroxides is believed to contribute a significant source of arsenic to the Secondary Pond waters.

Under oxygen rich conditions, and with all other factors at the low level, the predicted arsenic concentration in water overlying the Secondary Pond Sediments in the experiment is about 2.7 mg/L (compared with 0.6 mg/L under oxygen depleted conditions, with all other factors the same). A portion of the difference in the concentration can be attributed to evaporation that may have occurred in the flasks open to the atmosphere. When DOC is added, the arsenic concentration climbs to over 4 mg/L. The addition of sulphate drops the concentration down to about 2.2 mg/L, and by adding iron filings and elemental sulphur the concentration can be dropped further to near zero.

In order to confirm the mechanism of arsenic removal in the experiments it is necessary to identify the black/shiny material formed. An attempt was made to mineralogically identify this, however it was not possible to confirm its composition for several reasons. The fine grained nature of the material and the presence of iron filings and pre-existing arsenic mineral phases in the tailings samples, it made it impossible to determine the composition of this material. The black material was also seen to readily oxidize upon exposure to air (changed from black to brownish-orange). The formation of arsenic bearing sulphide phases (e.g. mono sulphides, arsenopyrite, arsenical pyrite) could therefore not be mineralogically confirmed. It is however likely that the black/shiny material was a sulphide phase.

5.3 Conclusions

The addition of iron fillings was effective in reducing the dissolved arsenic concentration, in both the in situ and laboratory experiments. In addition, the release of arsenic from the sediments into the water column was prevented in the in situ experiments. It is unclear as to the exact mechanism that resulted in the removal of arsenic from the water column, however it is speculated that arsenic became associated with an iron sulphide phase. In the laboratory experiments, black sediments were seen to form in some of the flasks containing iron filings.

These black sediments were likely iron monosulphides. The combination of the addition of organic carbon and sulphate in the column experiments resulted in the reductive dissolution of oxidized iron/arsenic phases and the development of high concentrations of dissolved arsenic and iron. In this case, conditions were not appropriate to bring about arsenic removal via the formation of sulphide species. In the laboratory experiments, the black sediment only formed in flasks containing zero valent iron. It appears as if reducing conditions are necessary to bring about the formation of iron sulphide species.

Under all of the conditions tested in the laboratory experiments, RLM-5 tailings did not produce aqueous arsenic concentrations greater than 0.5 mg/L after 42 days. For the RLM-7 tailings the experiment showed that in order to obtain aqueous arsenic concentrations less than 0.5 mg/L it is necessary to maintain reducing conditions.

All flasks contained less than 0.5 mg/L of arsenic throughout the duration of the experiments for RLM-2 tailings. The model does show however that if DOC is present under oxygen deficient conditions, the arsenic concentration will increase significantly. According to the model, if iron filings and elemental sulphur are added the arsenic concentration will drop back down to near zero.

For the Secondary Pond Sediments, sulphate was found to have a major impact on the aqueous arsenic concentration. The addition of sulphate resulted in a dramatic decrease in the arsenic concentration. The model showed that if oxygen deficient conditions exist and DOC is introduced into the system (with all other factors at the low level), the arsenic concentration will increase up to greater than 2.5 mg/L. The addition of sulphate, iron filings and elemental sulphur returns the arsenic concentration to near zero. Lower arsenic concentrations were seen with an oxygen deficient atmosphere than with an oxygen rich atmosphere.

6.0 Conclusions

Arsenic has always been a problem at G1 (discharge from the Secondary Pond), with the concentration exceeding 0.5 mg/L since 1991 except for a brief period during the shutdown and early start up of the new mill. Measures need to be taken to reduce the concentration of arsenic at the discharge of the Secondary Pond if Balmer Lake is to be removed from the Tailings Management facility. Natural degradation has not been successful in reducing the concentration of total arsenic in the effluent from the Secondary Pond to within MISA (and MMER) standards.

Historical tailings samples (RLM-2, RLM-3, and RLM-6) exhibited significantly higher total arsenic concentrations than the samples containing newer tailings (RLM-1, RLM-4, and RLM-5). The high sulphur content in the RLM-2 samples, ranging from 1.86 – 2.63 %, indicates that these tailings were produced during a period of time when roasting and concentration of the sulphide portion of the ore had ceased. The surface of the unsaturated old tailings (RLM-2-1, RLM-3-1, and RLM-6-1) contains gypsum, an indicator that sulphide oxidation has occurred.

The tailings sampled at RLM-2 (downstream of SD#2 on dry tailings beach in Primary Pond) do not appear to contain roasted material, however deeper down there is likely roaster material present (elevated arsenic levels have been observed in the vicinity of RLM-2). The material sampled at RLM-2 contains substantial sulphides and the top few feet have undergone significant oxidation over the years due to the unsaturated conditions present. RLM-2-1 had only 31% of the arsenic in the As(-1) oxidations state, with 58% present as As(V). From the sequential extractions it was found that approximately 23% of the arsenic in RLM-2-1 is adsorbed, and 28% is associated with iron oxyhydroxides. RLM-2-2 and RLM-2-3 were similar in composition to each other, with more than 80% of the arsenic present as As(-1), with the remaining portion present as a combination of As(III) and As(V). Results from the designed laboratory

experiments for RLM-2-1 material indicate that under all conditions tested the aqueous arsenic concentration remained below 0.5 mg/L for the duration of the experiments. The model produced from the experiments for this material shows however, that if dissolved organic carbon is present under oxygen deficient conditions, the arsenic concentration will increase significantly. According to the model, if iron filings and elemental sulphur are added the aqueous arsenic concentration will drop back down to near zero. Based on all of the data for tailings located around RLM-2 (i.e. dry tailing beach in Primary Pond), the flooding of this tailings deposit is not likely to result in a significant increase in aqueous arsenic concentrations.

The material located around RLM-3 (old tailings on south side of access road), and RLM-6 (revegetated tailings east of Balmer Creek) has been subjected to roasting. A large fraction of the arsenic at these locations (more so at RLM-6) is associated with iron oxide material and is and will continue to be mobile, especially under oxygen deficient conditions (i.e. saturated conditions). Severely elevated arsenic levels in the groundwater surrounding RLM-6 support this conclusion.

Less than 30% of the arsenic in RLM-3-1 and RLM-3-2 was in the form of As(-1). A small amount ($\leq 5\%$) of the arsenic existed in the form of As(III), with the remainder present as As(V). Most of the arsenic in the saturated zone in the area of RLM-3 (RLM-3-3) was present in the form of As(-1), with 5% present as As(V) and 2% as As(III), suggesting that the oxidized forms of arsenic present in the unsaturated zone have been mobilized and transformed to As(-1) in the saturated zone. Based on the above results, reducing infiltration into the deposit and maintaining unsaturated conditions will minimize the mobilization of arsenic. The majority of the arsenic present in the saturated zone is in the As(-1) form and should remain stable as long as saturated conditions exist.

Only 20% of the arsenic contained in RLM-6-1 was in the form of As(-1), with 16% present as As(III) and 65% present as As(V). According to the sequential extractions, 39% of the arsenic in RLM-6-1 was adsorbed while 40% was coprecipitated with iron oxyhydroxides. The saturated tailings in the area of RLM-6 (RLM-6-2) contained 63% of the arsenic in the form of As(-1) suggesting that a considerable portion of the oxidized arsenic has been mobilized, and transformed into As(-1). The saturated tailings still contain a significant amount of arsenic in oxidized forms that are likely to continue to be mobilized under the saturated conditions that exist in the deposit. Minimizing infiltration and lowering the water table will help to reduce mobilization of arsenic in the deposit.

RLM-1 (downstream of SD#1), RLM-4 (upstream of SD#1), and RLM-5 (End of Pipe) contain essentially fresh tailings that have remained saturated. The vast majority of arsenic in these samples is contained within arsenopyrite that will continue to be stable as long as conditions remain saturated. A small amount of arsenic was found to be associated with an amorphous and spongy textured precipitate that containing many species, in the RLM-4 and RLM-5 samples.

Sequential extraction data for the End of Pipe tailings indicate that only 16% (or 330 mg As/kg sediment) of the arsenic present is likely to be easily mobilized. The XANES spectra indicate that 23% of the arsenic in RLM-5 tailings is in the oxidized form. All of the solids identification results indicate that the vast majority of the arsenic in the fresh tailings produced at the mine site should remain stable under saturated conditions. Under all of the conditions tested in the laboratory experiments, RLM-5 tailings did not produce aqueous arsenic concentrations greater than 0.5 mg/L after 42 days. RLM-4 tailings were similar in composition to RLM-5 tailings. RLM-1 tailings contained no As(III), and 89% of the arsenic was in the form of As(-1). For the RLM-7 tailings (CIP tailings), containing high concentrations of arsenopyrite, the laboratory experiments showed that in order to obtain aqueous arsenic concentrations less than 0.5 mg/L it is necessary to maintain reducing conditions.

The Primary Pond sediment contained 50% As(-1), 11% As(III), and 40% As(V). The material from the Primary Pond (Primary Pond Backhoe sample), contained significantly more arsenic in the As(-1) form. A large fraction of the arsenic contained in the primary pond sediment will become mobilized if conditions become reducing.

Approximately 65% of the arsenic contained in the Secondary Pond Sediment is likely to be fairly mobile under the changing redox conditions that exist in the Secondary Pond. The sequential extraction results indicate that over 65% of the arsenic in the Secondary Pond Sediment is sorbed or precipitated with an iron oxyhydroxide phase, with more than 50% of the arsenic being sorbed. The Secondary Pond sediment contained 25% As(-1), 40% As(III), and 35% As(V). The laboratory experiments conducted on Secondary Pond Sediments indicate that dissolved sulphate has a major impact on the aqueous arsenic concentration. The addition of sulphate resulted in a dramatic decrease in the aqueous arsenic concentration. The model also showed that if oxygen deficient conditions exist and dissolved organic carbon is introduced into the system (with all other factors at the low level), the arsenic concentration will increase up to greater than 2.5 mg/L. The addition of sulphate, iron filings and elemental sulphur returns the arsenic concentration to near zero.

The addition of iron fillings was effective in reducing the dissolved arsenic concentration, in both the in situ and laboratory experiments. In addition, the release of arsenic from the sediments into the water column was prevented in the in situ experiments. It is unclear as to the exact mechanism that resulted in the removal of arsenic from the water column, however it is speculated that arsenic became associated with an iron sulphide phase. In the laboratory experiments, black sediments were seen to form in some of the flasks containing iron filings. These black sediments were likely iron monosulphides.

In the column experiments, the addition of organic carbon and sulphate resulted in the reductive dissolution of oxidized iron/arsenic phases and the development of high concentrations of dissolved arsenic and iron. In this case, conditions were not appropriate to bring about arsenic removal via the formation of sulphide species. In the laboratory experiments, the black sediment only formed in flasks containing zero valent iron. It appears as if strongly reducing conditions are necessary to bring about the formation of iron sulphide species.

As was found at the neighboring Campbell Mine (McCreadie et al., 2000) the source of high concentrations of dissolved arsenic in groundwater at the Red Lake Mine is likely from the reductive dissolution of arsenic bearing iron oxyhydroxides found in the roaster derived tailings. Field and laboratory experiments confirmed that the creation of semi reducing conditions, via the addition of organic carbon, resulted in increased aqueous arsenic and iron concentrations, supporting the reductive dissolution theory. Field and laboratory experiments also showed that the addition of a strong reductant resulted in significantly lowered aqueous arsenic concentrations, even in the presence of high concentrations of dissolved organic carbon. It is believed that under strongly reducing conditions arsenic contained within a relatively unstable iron oxyhydroxide phase can be stabilized as a sulphide phase.

7.0 Recommendations

In order to effectively manage arsenic bearing solids it is necessary to fully understand the speciation of the arsenic present as well as the mechanisms with which the arsenic is associated with the solids. The solids identification work conducted in this study proved to be useful in understanding the nature of the arsenic associated with the various types of tailings present at the Red Lake Mine. Any new arsenic bearing solids that are produced should be adequately characterized in order to determine the optimal storage conditions and to evaluate the long term stability of the solids.

XANES and or sequential extractions are required to determine the amount of arsenic in each oxidation state. SEM analysis provides a qualitative and visual understanding of the arsenic present in the solids, while whole rock analysis is a simple test to determine the total amount of arsenic present. The combination of these methods will provide the required insight into the material. A further step of laboratory and/or field experimentation can be conducted in order to better evaluate the long term stability of arsenic bearing solids. In the case of solids bearing arsenic stabilized as an oxidized form (e.g. ferric arsenate precipitates, arsenic sorbed to iron oxyhydroxides, etc.) field and/or laboratory experiments should be designed to examine what happens to the solids and to the aqueous arsenic concentrations under an oxygen deficient environment (e.g. solids covered with water in the presence of organic carbon). In the case of solids bearing arsenic stabilized as a reduced form (i.e. arsenic associated with mono sulphides, arsenopyrite, arsenical pyrite, etc.) field and/or laboratory experiments should be designed to examine what happens to the solids and how the pore water arsenic concentrations change under an oxygen rich environment (e.g. solids exposed to the atmosphere).

The key questions to answer in evaluating the production and storage of arsenic bearing solid wastes are:

- What arsenic bearing mineral phases are present?
- How much of each arsenic bearing mineral phase is present?
- How stable are the arsenic bearing mineral phases under changing redox conditions?
- What happens to aqueous arsenic concentrations under changing redox conditions?
- Can optimal redox conditions for the arsenic bearing mineral phases present be maintained?

Once these questions have been answered a decision can be made on whether the arsenic bearing minerals phases should be produced (if this is a choice) and how the solids should be stored.

It is important to store arsenic bearing solids under appropriate conditions so that arsenic mobilization is minimized. Solids containing reduced arsenic species (i.e. arsenopyrite, As(-1)) will be most stable if stored under saturated/reducing conditions where contact with oxygen is minimized. Material containing oxidized arsenic species (As(V) and As(III)) will be most stable if stored under unsaturated/oxidizing conditions, where contact with oxygen is maximized. Often the nature of these solids makes it difficult to maintain unsaturated conditions, and if located in a natural setting (where organic carbon and biological activity are present) the onset of reducing conditions is a realistic concern.

At the Red Lake Mine, fresh tailings (RLM-1, RLM-4, and RLM-5) contain arsenic predominately associated with arsenopyrite, therefore the fresh tailings should be stored under saturated conditions to minimize oxidation. The fresh tailings, however, contain a low concentration of sulphides due to the concentration of sulphides in the milling circuit. Arsenic release from unsaturated fresh tailings, therefore, should be minimal.

Historical tailings located around RLM-3 (south of the access road) and RLM-6 (revegetated tailings on east side of Balmer Creek) contain a significant amount of oxidized arsenic species in the unsaturated zone. Mobilization of arsenic from these solids will be minimized by reducing infiltration and maintaining unsaturated conditions (capping the deposits with an appropriate engineered cover system). In addition, during reclamation efforts the use of fertilizer should be avoided in order to limit the supply of nutrients to the system.

The tailings located around RLM-2 (i.e. dry tailing beach in Primary Pond) can be flooded (i.e. result of raising dams) with little increased arsenic mobilization expected.

The changing redox conditions in the Secondary Pond (and Primary Pond) and the nature of the arsenic species that are present in the pond sediment indicate that arsenic will continue to be released from the sediment over the long term. Amendments to the pond sediments should be further investigated to determine their applicability. For example, Lorax (2001) suggests placing a layer of fresh tailings over the pond sediments to act as a diffusion barrier. In this study it was determined that the fresh tailings contain arsenic predominately in the As(-1) state, as a result the arsenic in these tailings is likely to remain if placed under the water cover of the Secondary Pond. An investigation (i.e. water balance) should be conducted to determine the significance of mobilized arsenic from the pond sediments in the over all arsenic loading to the pond. If arsenic loading from the pond sediments is found to be significant, a feasibility and effectiveness study on the use of fresh tailings as a diffusion barrier should be conducted.

The addition of iron fillings proved to be successful in reducing aqueous arsenic concentrations in both the field and laboratory experiments, however the mechanisms by which the arsenic was being removed are not understood. Additional experiments are required in order to gain an understanding of the mechanism of arsenic removal in the presence of iron fillings. The experiments

must be structured in a manner allowing the produced solids to be mineralogically identified. For example, laboratory experiments could be constructed in which the tailings are separated from the treatment medium by a layer of silica sand. Ideally, newly generated mineral phases would form in the silica sand layer and could be extracted for analysis (in this way the generated solids would not be contaminated with pre existing arsenic phases from the tailings solids or with iron fillings). It is likely that XANES (using a Synchrotron light source) and/or sequential extractions would be required to identify the generated solids. The analysis should be conducted on wet solids under an oxygen deficient atmosphere. In order for the formation of arsenic bearing sulphide phases to be a practical solution for mining operations it is necessary for the solids produced to be stable. The stability of the generated solids would therefore have to be evaluated.

The use of iron fillings in a field setting may not be feasible due to the cost associated with the iron fillings. The addition of organic carbon in the laboratory and field experiments showed that the production of semi reducing conditions results in increased arsenic concentrations, therefore efforts should be made to reduce the influx of organic carbon (i.e. reduce nutrient loading) into tailings deposits containing arsenic in oxidized forms. Strongly reducing conditions are required in order to cause arsenic to be removed from solution.

8.0 References

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Appendix I: Historical Surface Water Data

Date	PP		G1			L2		
	As	CN	As	Fe	CN	As	Fe	CN
Jan-91	1.69	60	1.88		64	0.79		0.34
Feb-91	1.92	59				1.03		0.3
Mar-91	1.61	38				1.14		0.36
Apr-91	1.1	22	1.28		17.25	0.41		1.13
May-91	1.26	15.2	1.62		2.55	0.89		0.71
Jun-91	0.82	3.75	1.02		1.38	0.78		0.31
Jul-91	1.42	7.76	0.81		0.62	0.79		0.11
Aug-91			0.91	1.2	0.5	0.81	0.33	0.06
Sep-91	1.24	10.31	0.86	1.08	2.54	0.95	0.56	0.08
Oct-91	1.16	86.9	1.06	3.65	86.9	0.826	0.7	0.12
Nov-91	2.49	76.1	1.54		11.9	0.746	0.5	0.12
Dec-91	2.57	59.8	2.51	21.2	44.3	0.816	0.61	0.33
Jan-92	1.416	34.8				0.69	0.58	0.25
Feb-92	1.56	44.5				0.71	0.57	0.213
Mar-92	3.61	82				0.489	0.66	0.239
Apr-92	1.24	56.4	1.02	5.79	21.9	0.77	0.76	0.82
May-92	1.6	3.41	1.07	6.57	3.05	0.23	0.9	1.09
Jun-92	0.72	2	0.63	2.23	0.98	0.35	0.52	0.24
Jul-92	1.36	6.76	0.6	1.06	0.45	0.31	0.3	0.15
Aug-92	1.63	2.16	1.26	1.05	1.5	0.293	0.23	0.068
Sep-92	6.69	3.89	2.92	8.18	1.28	0.301	0.6	0.1
Oct-92	3.31	3.75	1.95	6	0.6	0.273	0.74	0.12
Nov-92								
Dec-92			1.94		39			
Jan-93	0.435	34.7				0.28	1.161	0.67
Feb-93	0.15	30.9				0.13	0.7	0.429
Mar-93	1.1	71.7	1.78	8.64	8.8	0.329	0.89	0.464
Apr-93	1.1	17.1	0.76	2.12	9.94	0.37	2.01	0.826
May-93	1.63	6.55	1.31	4.38	4.84	0.234	0.98	0.501
Jun-93	1.22	10.2	1.02	0.424	1.6	0.154	1.01	0.19
Jul-93	1.22	4.9	1.14	1.52	0.29	0.19	0.28	0.06
Aug-93	0.698	7.33	0.517	2.17	0.47	0.19	0.242	0.052
Sep-93	0.824	4.37	0.859	3.31	0.876	0.21	0.38	0.06
Oct-93	1.64	10.3	0.78	3.06	1.74	0.21	0.38	0.06
Nov-93	1.38	16.4	0.935		3.25	0.22	0.589	0.265
Dec-93	1.17	39.6	0.99	1.016	3.17	0.32	0.84	0.74
Jan-94	0.435	34.7				0.24	1.509	0.25
Feb-94						0.937	2.759	0.045
Mar-94						0.354	0.605	0.63
Apr-94	1.14	19.56	0.69	1.54	10.65	0.148	1.09	0.033
May-94	1.34	12.6	0.8	2.11	8.06	0.107	1.864	0.13
Jun-94	0.67	8.17	0.78	1.56	0.67	0.176	0.48	0.093
Jul-94	0.9	7.88	1.42	1.15	0.45	0.16	0.33	0.087
Aug-94	0.9	7.88	1.62	2.96	0.321	0.175	0.14	0.066
Sep-94	1.58	8.42	1.29	1.66	0.445	0.183	0.158	0.08
Oct-94								
Nov-94			0.59	3.74	1.6			
Dec-94	0.98	7.03	0.496	1.97	4.29	0.21	0.611	0.31
Jan-95	1.11	31.3				0.26	0.83	0.66

Date	PP		G1			L2		
	As	CN	As	Fe	CN	As	Fe	CN
Feb-95	2.29	25.5				0.28	0.83	0.83
Mar-95	1.39	73.4	0.86	0.696	0.34	0.041	0.794	0.746
Apr-95	1.25	28.8	1.14	0.955	11.8	0.232	0.918	0.543
May-95	1.08	3.99	0.893	3.13	2.48	0.25	1.01	0.11
Jun-95	1.53	3.5	0.805	2.47	2	0.24	1.02	0.05
Jul-95	1.59	3.4	1.16		0.45	0.22	4.23	0.05
Aug-95	2.68	8.75	1.08	6.98	0.35	0.18	2.75	0.05
Sep-95	2.04	4.88	1.3	0.818	0.22	0.264	0.395	0.06
Oct-95	1.72	6.6	1.26	0.881	0.8	0.302	0.37	0.078
Nov-95	1.58	14	1.05	1.56	2.52	0.321	0.304	0.235
Dec-95	3.23	23.4	1.87	2.09	6.9	0.396	0.31	0.56
Jan-96	1.61	26.9	3.42	17.07	24.1	0.364	0.406	0.239
Feb-96	2.31	11.15				0.42	0.53	0.73
Mar-96	1.12	43.2				0.063	0.648	0.028
Apr-96	1.98	48.7	0.332		3.72	0.107	0.734	0.026
May-96	2	2.89	0.782	7.51	5.38	0.44	0.79	0.14
Jun-96	0.296	10	0.796	2.22	1.6	0.22	0.5	0.09
Jul-96	0.607	0.052	0.821	0.2	0.042	0.22	0.17	0.06
Aug-96	0.257	0.047	0.641	0.349	0.046	0.22	0.14	0.06
Sep-96	0.244	0.063	0.641	0.349	0.046	0.22	0.23	0.06
Oct-96	0.247	0.034	0.658	1.01	0.082	0.27	0.27	0.07
Nov-96	0.201	0.11	0.196	2.1	0.088	0.23	0.36	0.08
Dec-96	0.18	0.151	0.236	2.99	0.046	0.19	0.31	0.1
Jan-97	0.175	0.142	0.316	0.714	0.083	0.19	0.31	0.1
Feb-97	0.264	0.939				0.28	0.68	0.15
Mar-97	0.228	0.266				0.279		0.111
Apr-97	0.215	2.588				0.31	0.71	0.16
May-97	0.278	0.049	0.278		0.024	0.15	0.98	0.05
Jun-97	0.209	0.03	0.228		0.017	0.2	0.389	0.048
Jul-97	0.282	0.024	0.774	0.374	0.034	0.274	0.183	0.039
Aug-97	2.28	0.111	0.864	0.274	0.025	0.42	0.15	0.04
Sep-97	0.434	0.022	1.79	1	0.1	0.45	0.48	0.04
Oct-97	0.318	0.03	0.469	1.45	0.029	0.37	0.25	0.04
Nov-97	0.23	0.067	0.19	0.786	0.017	0.31	0.26	0.06
Dec-97	0.24	0.106	0.355	0.69	0.022	0.27	0.27	0.09
Jan-98	0.327	0.094	2.015	1.63	0.062	0.316	0.419	0.086
Feb-98						0.31	0.66	0.08
Mar-98	0.25	0.158	0.687	0.683	0.108	0.423	0.541	0.07
Apr-98	0.327	0.037	0.183	0.823	0.045	0.174	0.662	0.035
May-98	0.315	0.025	0.194	0.837	0.019	0.261	0.378	0.043
Jun-98	0.145	0.021	0.204	0.318	0.015	0.316	0.196	0.04
Jul-98	0.593	0.026	0.553	0.177	0.024	0.446	0.148	0.053
Aug-98	1.75	0.023	3.24	0.367	0.04	0.732	0.193	0.052
Sep-98	4.05	0.084	1.28	0.171	0.026	0.664	0.18	0.064
Oct-98	0.44	0.029	0.311	0.755	0.068	0.328	0.422	0.041
Nov-98	0.368	0.079	0.841	0.546	0.086	0.454	0.154	0.102
Dec-98	0.454	0.077	1.24	0.338	0.018	0.592	0.199	0.106
Jan-99			1.67	0.370	0.028	0.704	0.229	0.095
Feb-99	12.9	1.950	3.05	0.683	0.037	0.690	0.163	0.106

Date	PP		G1			L2		
	As	CN	As	Fe	CN	As	Fe	CN
Mar-99						0.551	0.341	0.104
Apr-99	0.321	0.068	1.60	0.602	0.047	0.243	0.236	0.038
May-99	0.457	0.052	0.29	0.389	0.019	0.333	0.367	0.073
Jun-99	0.444	0.040	0.44	0.365	0.019	0.442	0.238	0.059
Jul-99	0.566	0.032	0.81	0.271	0.008	0.530	0.247	0.031
Aug-99	0.884	0.040	1.56	0.242	0.034	0.556	0.385	0.046
Sep-99	0.797	0.047	2.25	0.367	0.030	0.534	0.136	0.062
Oct-99	0.453	0.020	0.83	0.490	0.030	0.416	0.244	0.069
Nov-99	0.316	0.043	0.37	0.666	0.012	0.327	0.300	0.081
Dec-99	0.332	0.072	0.36	1.200	0.016	0.328	0.181	0.077
Jan-00						0.333	0.207	0.075
Feb-00	0.559	0.413				0.336	0.230	0.076
Mar-00	0.53	0.225	0.260	0.620	0.015	0.341	0.441	0.071
Apr-00	0.278	0.035	0.210	0.421	0.017	0.175	0.601	0.032
May-00	0.333	0.029	0.341	0.385	0.016	0.254	0.392	0.045
Jun-00	0.328	0.064	0.251	0.341	0.015	0.303	0.308	0.032
Jul-00	0.455	0.047	0.586	0.399	0.022	0.368	0.386	0.036
Aug-00	0.659	0.181	0.851	0.329	0.030	0.381	0.343	0.052
Sep-00	0.798	0.065	0.467	0.387	0.036	0.344	0.304	0.034
Oct-00	1.15	0.111	0.354	0.189	0.040	0.291	0.156	0.052
Nov-00	0.717	0.593	0.322	0.622	0.061	0.240	0.125	0.053
Dec-00	0.931	1.03	0.292	0.653	0.065	0.213	0.252	0.050
Jan-01	1.8	0.736		0.403	0.058	0.223	0.681	0.059
Feb-01			0.348	0.512	0.078	0.225	0.798	0.047
Mar-01	2.25	1.01	0.313	0.409	0.069	0.36	0.787	0.05
Apr-01	1.9	3.58	0.386	0.555	0.262	0.216	0.845	0.043
May-01	3.18	10.5	0.389	0.530	0.104	0.238	0.719	0.035
Jun-01	2.16	0.176	0.376	0.363	0.062	0.255	0.323	0.061
Jul-01	1.24	0.541	0.740	0.213	0.092	0.385	0.266	0.038
Aug-01	2.23	0.646	1.450	0.136	0.099	0.63	0.483	0.033
Sep-01	3.8	7.49	1.285	0.158	0.084	0.569	0.583	0.029
Oct-01	1.97	6.24	1.066	0.137	0.088	0.447	0.239	0.065
Nov-01	1.31	7.57	0.886	0.181	0.099	0.37	0.123	0.545
Dec-01			0.893	0.239	0.097	0.362	0.126	0.044
Jan-02	1.64	2.66	0.81	0.26	0.117	0.576	0.499	0.042
Feb-02	1.12	1.38	0.84	0.358	0.121	0.42	0.579	0.046
Mar-02			0.92	0.316	0.24	0.38	0.683	0.048
Apr-02			0.515	0.371	0.177	0.236	1.17	0.023
May-02	0.98	0.166	0.562	0.442	0.083	0.208	0.598	0.015
Jun-02	1.12	2.68	0.602	0.428	0.022	0.314	0.363	0.019
Jul-02	2.09	0.025	1.24	0.23	0.011	0.56	0.312	0.006
Aug-02	3	0.072	1.3	0.191	0.044	0.648	0.274	0.013
Sep-02	2.3	0.182	1	0.208	0.044	0.512	0.232	0.021
Oct-02	1.82	0.188	0.77			0.393	0.132	0.014

Primary Pond Data

Date	TSS	pH	Total CN	Cu	Ni	Zn	As	Fe	Ammonia
05-Jan-93	16	8	34.7	3.59	2.71	1.98	0.44	4.52	7.53
08-Feb-93	8.4	7.2	30.9	3.42	2.69	0.4	0.15		
01-Mar-93	5.2	9.7	71.7	3.65	3.25	7.19	1.1		
06-Apr-93	4	9.1	17.1	2.62	2.04	1.68	1.1	4.1	4.84
04-May-93	100.4	8.7	6.55	0.81	0.87	0.35	1.63		1.14
17-May-93			10.5	1.01	1.56	0.92	2.15		
26-May-93			10.2	1.2	1.68	0.84	1.28		
03-Jun-93	22.8	8.4	10.2	2.15	1.99	0.62	1.22		
10-Jun-93			7.32	3.08	2.04	0.18	1.42		7.3
15-Jun-93			11.08	3.9	1.63	0.2	1.32		4.6
23-Jun-93			8.03	4.97	2.23	0.12	1.48		7
29-Jun-93			3.95	2.87	1.29	0.13	1.18		7.2
05-Jul-93	120.5	12	4.9	2.45	0.89	0.17	1.22	10.4	3
13-Jul-93			5.46	2.26	1.06	0.19	0.62		3.5
20-Jul-93			11.8	4.04	1.36	0.04	0.61		4.08
29-Jul-93			1.28	0.32	0.16	0.11	0.9		1.86
05-Aug-93			4.51	0.4	0.15	0.2	0.57		1.52
11-Aug-93	107.5	12.7	7.33	2.46	0.64	0.14	0.7		3.56
20-Aug-93			7.32	2.41	0.84	0.13	1.5	15.1	3.02
23-Aug-93			9.5	3.47	1.17	0.14	1.05		3.86
01-Sep-93			3.59	1.51	0.5	0.17	0.86		3.82
08-Sep-93			20.1	5.94	1.61	0.61	1.21		3.65
13-Sep-93	87	7.85	4.37	2.26	0.63	0.16	0.82		3.1
22-Sep-93			11.44	3.9	1.2	0.64	1.24		3.53
29-Sep-93			7.44	3.31	1.12	0.57	0.78		3.57
04-Oct-93	241	7.56	10.3	4.47	1.35	0.68	1.64	23.1	3.08
13-Oct-93			12.7	5.11	1.49	0.63	0.72		3.33
10-Jan-94	1.6	9.98	1.09	0.32	0.11	0.03	0.37	0.37	0.79
12-Apr-94	81.2	8.28	19.56	4.81	1.89	1.54	1.14	7.75	3.78
02-May-94	189		12.6	5.27	1.67	0.55	1.34	9.5	2.73
06-Jun-94	20.4	7.78	8.17	3.32	1.56	0.19	0.67	4.44	5.53
13-Jul-94	33.2	8.07	7.88	2.07	1.37	0.219	0.9	3.55	6.72
04-Aug-94	17.6	7.46	4.88	1.9	1.36	0.9	1.61	2.32	7.63
06-Sep-94	19.2	7.58	8.42	2.69	1.68	0.275	1.58	2.43	4.49
03-Oct-94	19.2	7.93	5.48	2.21	1.79	0.382	1.58	1.77	6.77
07-Nov-94	25.6	7.67	5.83	1.89	0.796	0.641	0.54	3.12	2.07
05-Dec-94	13.6	8.34	7.03	4.83	1.84	2.7	0.98	2.94	3.41
11-Jan-95	8.8	7.69	31.3	9.22	3	2.11	1.11	2.4	6.49
08-Feb-95	23.5	7.52	25.5	6.215	2.6	1.69	2.29	3.8	6.27
09-Mar-95	4.4	9.02	73.4	5.096	3.842	15.01	1.39		10.1
13-Apr-95	14	8.56	28.8	2.26	1.98	3.52	1.25	3.45	4.52
17-May-95	160	7.68	3.99	0.689	0.57	0.29	1.08	11.47	1.5
02-Jun-95	115	11.36	3.5	0.547	0.462	0.4	1.53	7.12	2.81
05-Jul-95	24.5	7.75	3.4	0.468	0.784	0.36	1.59	3.75	4.39
11-Aug-95	84	7.23	8.75	0.708	1.84	1.017	2.68	15.39	3.68
11-Sep-95	64	6.83	4.88	0.834	1.41	0.34	2.04		4.13
02-Oct-95	12	6.79	6.6	1	1.91	0.67	1.72		6.35
08-Nov-95	56	7.34	14	1.45	1.42	1.94	1.58	4.72	4.34
04-Dec-95	26	7.1	23.4	3.31	1.94	2.27	3.23		5.79

Date	TSS	pH	Total CN	Cu	Ni	Zn	As	Fe	Ammonia
08-Jan-96	17.6		26.9	2.12	2.18	3.68			6.38
05-Feb-96	121		11.15	2.89	2.46	0.204	2.31		9.29
11-Mar-96	12.8	6.29	43.2	5.05	4.7	2.2	1.12	1.83	13.8
08-Apr-96	18.2	7.99	48.7	5.91	4.26	9	1.98	3.84	9.83
06-May-96			2.89	0.16	0.408	0.44	2		0.614
03-Jun-96	53.5		10	1.51	0.892	0.307	0.296		2.3
23-Jul-96	22.4		0.052	0.055	0.049	0.013	0.607		0.264
20-Aug-96	4		0.047	0.027	0.034	0.005	0.257	0.406	0.14
04-Sep-96	7	8	0.063	0.027	0.036	0.004	0.244		0.12
07-Oct-96	14		0.034	0.023	0.028	0.009	0.247		0.084
15-Nov-96	7	7.26	0.11	0.036	0.074	0.019	0.201	1.38	0.61
09-Dec-96	11		0.151	0.014	0.073	0.013	0.18		0.89
Jan-97	17		0.142	0.023	0.083	0.015	0.175		1.5
Feb-97	27	7.37	0.939	0.051	0.11	0.014	0.264		0.96
Mar-97	15	7.77	0.266	0.019	0.07	0.011	0.228		0.83
Apr-97	9	7.78	2.588	0.107	0.11	0.011	0.215		1.4
May-97	34	7.58	0.049	0.022	0.037	0.015	0.278		0.35
Jun-97	5	8.26	0.03	0.016	0.026	0.004	0.209	0.469	0.06
Jul-97	6	7.96	0.024	0.018	0.02	0.012	0.282	0.38	0.14
Aug-97	28	8.07	0.111	0.091	0.04	0.036	2.28	1.34	0.16
Sep-97	5	8.02	0.022	0.016	0.011	0.002	0.434		0.08
Oct-97	11	7.76	0.03	0.014	0.021	0.014	0.318		0.12
Nov-97	3	8.08	0.067	0.014	0.019	0.007	0.23	0.491	0.83
Dec-97	1	7.28	0.106	0.017	0.023	0.022	0.24	0.491	1.9
Jan-98	5	6.94	0.094	0.009	0.045	0.014	0.327	1.19	1.83
Mar-98	6	7.69	0.158	0.016	0.052	0.018	0.25	1.02	1.04
Apr-98	34	7.68	0.037	0.019	0.006	0.029	0.327	2.85	0.31
May-98	7	7.9	0.025	0.017	0.022	0.01	0.315	0.359	<0.05
Jun-98	5	8.03	0.021	0.011	0.018	0.003	0.145	0.296	0.05
Jul-98	6	7.81	0.026	0.009	0.011	0.006	0.593	0.368	0.12
Aug-98	2	7.84	0.023	0.008	0.006	0.007	1.75	0.263	0.08
Sep-98	28	8.07	0.084	0.059	0.035	0.07	4.05	0.804	<0.05
Oct-98	2	6.82	0.029	0.003	<0.002	0.002	0.44	0.141	<0.05
Nov-98	3	7.89	0.079	0.01	0.003	0.004	0.368	0.153	<0.05
Dec-98	3	7.65	0.077	0.012	0.036	0.009	0.454	0.158	0.34
Feb-99	88.00	7.47	1.950	<0.005	0.405	0.05	12.9	0.669	5.4
Apr-99	7	7.68	0.068	0.013	0.048	0.018	0.321	0.801	0.99
May-99	8	7.95	0.052	0.014	0.033	0.014	0.457	0.706	0.58
Jun-99	<2	8.07	0.040	0.015	0.027	0.007	0.444	0.562	0.17
Jul-99	6	8.02	0.032	0.016	<0.005	0.009	0.566	0.236	0.27
Aug-99	6	8.05	0.040	0.021	<0.02	0.006	0.884	0.282	0.34
Sep-99	3<T	7.79	0.047	<0.02	<0.02	0.003	0.797	0.089	0.78
Oct-99	6	7.81	0.020	<0.02	0.031	0.007	0.453	0.308	0.86
Nov-99	9	7.84	0.043	<0.02	<0.02	0.004	0.316	0.838	1.59
Dec-99	2<T	7.56	0.072	<0.02	<0.02	0.018	0.332	0.269	1.15
Feb-00	65	7.46	0.413	0.066	<0.02	0.068	0.559	1.52	3.99
Mar-00	4<T	7.49	0.225	0.046	0.041	0.029	0.53	0.912	6.38
Apr-00	12	7.7	0.035	<0.02	<0.02	0.011	0.278	0.729	1.09
May-00	11	8.21	0.029	<0.02	<0.02	0.01	0.333	0.445	0.85
Jun-00	5	7.71	0.064	0.024	<0.02	0.023	0.328	0.731	2.77
Jul-00	2<T	7.99	0.047	<0.02	<0.02	0.012	0.455	0.243	0.57

Date	TSS	pH	Total CN	Cu	Ni	Zn	As	Fe	Ammonia
Aug-00	2<T	8.33	0.181	<0.02	<0.02	0.047	0.659	0.157	0.29
Sep-00	17	7.66	0.065	0.026	<0.02	0.01	0.798	1.34	7.27
Oct-00	8	8.06	0.111	0.04	0.028	0.045	1.15	0.871	17
Nov-00		8.1	0.593	0.333	0.054	0.006	0.717	<0.005	16.5
Dec-00		7.7	1.03	0.236	0.033	0.011	0.931	<0.005	23.1
May-01	<2	7.6	1.010	0.118	0.019	0.020	1.16	0.770	20.3
Jun-01		8	0.080	0.035	0.017	0.008	1.01	0.188	14.9
Jul-01	<2	8	0.149	0.045	0.025	0.027	1.34	0.243	29.7
Aug-01	4	8.0	0.177	0.024	0.015	0.011	2.14	0.085	33.4
Sep-01	2	7.8	0.527	0.330	0.021	0.012	2.5	0.535	33.4
Oct-01	6	7.6	0.210	0.156	0.011	0.002	2.84	0.353	35.7
Nov-01	6	7.8	0.430	0.130	0.019	0.013	1.17	0.803	24.6
Dec-01	3	8.7	0.847	0.352	0.020	<0.002	1.77	0.433	39.8
Jan-02	6	7.8	2.660	0.053	0.009	0.011	1.64	1.190	52.0
Feb-02	15	8.1	1.380	0.215	0.041	0.009	1.12	0.765	37.2
May-02	11	7.9	0.166	0.102	0.011	0.007	0.98	0.415	14.0
Jun-02	6	7.8	2.680	0.074	0.016	0.026	1.12	0.191	19.8
Jul-02	3	7.4	0.025	0.036	0.013	<0.006	2.09	0.083	15.9
Aug-02	2	7.7	0.072	0.027	0.015	<0.006	3.00	0.063	24.5
Sep-02	3	7.4	0.182	0.023	0.010	<0.006	2.30	0.092	23.5
Oct-02	<2	8.0	0.188	0.029	0.010	<0.006	1.82	0.063	26.8
Nov-02	2	8.7	0.250	0.042	0.013	<0.006	1.32	0.120	31.7
Dec-02	4	8.6	0.313	0.038	0.011	<0.006	1.13	0.127	37.4

Secondary Pond Data

Date	TSS	pH	Total CN	Cu	Ni	Zn	As	Fe	Ammonia
03-Mar-93	8.4	9.1	68.8	5.12	4.48	6.6	1.78	8.64	
06-Apr-93	4.8	8.5	9.94	3.56	1.65	0.85	0.76	2.12	5.56
23-Apr-93			7.06	0.72	0.88	0.41	1.09		
29-Apr-93			5.26	1.64	1.23	0.34	1.08		
04-May-93	43.6	8.6	4.84	1.1	1.06	0.22	1.31	4.38	4.06
17-May-93			2.24	0.37	0.88	0.19	1.4	4.78	
26-May-93			2.6	0.45	1.01	0.25	0.97		
03-Jun-93	15.2	8.1	1.6	0.36	0.91	0.18	1.02	0.42	
10-Jun-93			0.25	0.64	0.98	0.12	1.26		10.8
15-Jun-93			0.85	0.83	0.96	0.11	1.32		11.3
23-Jun-93			0.61	1.04	0.96	0.09	1.44		11.9
29-Jun-93			2.7	1.36	0.96	0.1	1.37		11
05-Jul-93	109	12.1	0.29	1.31	0.85	0.14	1.14	1.52	11.6
13-Jul-93			0.87	1.04	0.71	0.1	0.84		10.7
20-Jul-93			1.15	1.16	1.03	0.08	0.93		10.82
29-Jul-93			0.75	0.82	0.46	0.09	0.77		8.71
05-Aug-93			0.38	0.28	0.17	0.06	0.62		7.36
09-Aug-93	67.5	12.4	0.47	0.46	0.17	0.06	0.52	2.17	5.67
20-Aug-93			0.8	0.42	0.25	0.04	0.86		4.51
23-Aug-93			0.61	0.55	0.28	0.03	0.93		6.03
01-Sep-93			0.86	0.76	0.38	0.06	0.89		6.13
08-Sep-93			0.97	0.8	0.35	0.07	0.91		6.45
13-Sep-93	18.5	7.76	0.88	0.84	0.38	0.08	0.86	3.31	6.97
22-Sep-93			0.95	1.15	0.47	0.15	0.83		6.73
29-Sep-93			1.3	1.37	0.56	0.19	0.69		6.88
04-Oct-93	20.8	7.37	1.74	1.54	0.61	0.23	0.78	3.06	6.49
13-Oct-93			2.13	1.79	0.72	0.27	0.66		6.32
12-Apr-94	17.6	8.02	10.65	5.62	1.61	0.88	0.69	1.54	3.69
02-May-94	13.2	8.6	8.06	3.75	1.29	0.36	0.8	2.11	3.36
06-Jun-94	12.8	7.64	0.67	2.13	1.17	0.09	0.78	1.55	8.02
12-Jul-94	16	7.92	0.45	0.833	0.657	0.068	1.42	1.15	13.8
12-Aug-94	10	7.61	0.44	0.575	0.597	0.062	1.62	2.96	14.5
06-Sep-94	12.4	7.49	0.445	0.747	0.709	0.07	1.29	1.66	12.8
03-Oct-94	8.4	7.66	0.368	0.767	0.847	0.118	0.78	0.546	10.4
07-Nov-94	41	7.41	1.6	0.99	0.63	0.28	0.59	3.74	3.87
05-Dec-94	16.4	7.41	4.29	2.05	0.83	0.44	0.5	1.97	4.77
09-Mar-95	4.4	7.3	0.34	1.688	0.848	0.162	0.86	0.696	8.38
10-Apr-95	3.6	7.57	11.8	2.7	1.47	1.04	1.14	0.955	4.09
18-May-95	31.6	7.66	2.48	1.08	0.993	0.37	0.893	3.13	5.02
07-Jun-95	41	11.21	2	0.228	0.241	0.082	0.805	2.47	4.21
05-Jul-95	4.8	7.13	0.45	0.182	0.333	0.062	1.16	1.16	2.96
11-Aug-95	10.4	6.47	0.35	0.17	0.407	0.037	1.08	6.98	3.68
11-Sep-95	12.4	6.26	0.22	0.218	0.527	0.054	1.3	0.818	2.5
02-Oct-95	10.4	6.47	0.8	0.359	0.765	0.164	1.26	0.881	3.08
08-Nov-95	10	6.2	2.52	0.49	0.95	0.262	1.05	1.56	3.24
04-Dec-95	16	6.55	6.9	1.54	1.19	0.621	1.94	2.09	4.85
08-Jan-96	51.2		24.1	2.09	1.94	2.17	3.42	17.07	8.39
30-Apr-96	6	6.18	3.72	1.21	0.621	0.553	0.332		1.59
06-May-96	112		5.38	0.945	0.65	0.305	0.782	7.51	1.87

Date	TSS	pH	Total CN	Cu	Ni	Zn	As	Fe	Ammonia
03-Jun-96	21.2		1.6	0.598	0.44	0.136	0.796	2.22	3.95
23-Jul-96	7.2		0.042	0.088	0.205	0.013	0.821	0.2	2.17
20-Aug-96	9		0.046	0.047	0.122	0.012	0.641	0.349	0.23
04-Sep-96	13	8	0.087	0.057	0.091	0.016	0.516	0.749	0.13
07-Oct-96	18		0.082	0.063	0.068	0.024	0.658	1.01	0.052
15-Nov-96	7	6.84	0.088	0.055	0.039	0.083	0.196	2.1	0.2
09-Dec-96	32		0.046	0.036	0.046	0.037	0.236	2.99	0.17
Jan-97	2.73		0.083	0.022	0.067	0.016	0.316	0.714	1
May-97	11	7.45	0.024	0.008	0.017	0.008	0.278		0.21
Jun-97	17	7.43	0.017	0.039	0.032	0.019	0.228		<0.05
Jul-97	20	7.88	0.034	0.042	0.031	0.006	0.774	0.374	0.07
Aug-97	5	8.09	0.025	0.017	0.022	0.023	0.864	..274	0.1
Sep-97	32	8.12	0.1	0.062	0.017	0.026	1.79	1	0.07
Oct-97	16	7.58	0.029	0.029	0.024	0.018	0.469	1.45	<0.05
Nov-97	4	7.53	0.017	0.013	<0.002	0.019	0.19	0.786	0.12
Dec-97	2	7.48	0.022	0.046	0.035	0.022	0.355	0.69	0.1
Jan-98	5	7.06	0.062	0.041	0.064	0.037	2.015	1.63	0.4
Mar-98	3	7.88	0.108	0.02	0.023	0.018	0.687	0.683	0.96
Apr-98	8	7.29	0.045	0.004	0.008	0.026	0.183	0.823	0.24
May-98	9	7.49	0.019	0.026	0.029	0.016	0.194	0.837	<0.05
Jun-98	3	7.85	0.015	0.021	0.011	0.006	0.204	0.318	<0.05
Jul-98	4	7.88	0.024	0.028	0.01	0.002	0.553	0.177	0.05
Aug-98	8	7.82	0.04	0.038	0.005	0.011	3.24	0.367	0.06
Sep-98	3	7.97	0.026	0.013	0.02	0.041	1.28	0.171	<0.05
Oct-98	9	7.58	0.068	0.056	0.031	0.019	0.311	0.755	0.06
Nov-98	4	7.85	0.086	0.029	0.018	0.015	0.841	0.546	<0.05
Dec-98	4	7.66	0.018	0.031	0.024	0.013	1.24	0.338	0.05
Jan-99	<2	7.43	0.028	0.043	0.040	0.065	1.67	0.370	0.22
Feb-99	4	7.30	0.037	0.082	0.073	0.045	3.05	0.683	0.50
Apr-99	3	7.23	0.047	0.013	0.028	0.014	1.60	0.602	0.94
May-99	6	7.84	0.019	0.013	0.022	0.023	0.29	0.389	0.28
Jun-99	6	8.48	0.019	0.023	0.023	0.024	0.44	0.365	0.09
Jul-99	10	8.01	0.008	0.032	0.041	0.006	0.81	0.271	0.06
Aug-99	3	7.73	0.034	0.036	0.034	0.006	1.56	0.242	0.19
Sep-99	6	7.76	0.030	0.041	<0.02	0.008	2.25	0.367	0.15
Oct-99	29	7.80	0.030	<0.02	<0.02	<0.003	0.83	0.490	0.10
Nov-99	5	7.63	0.012	0.020	<0.02	<0.003	0.37	0.666	0.17
Dec-99	4<T	7.73	0.016	<0.02	<0.02	0.007	0.36	1.200	0.23
Mar-00	<5	7.38	0.015	<0.02	<0.02	0.010	0.260	0.620	0.24
Apr-00	7.00	7.55	0.017	<0.02	<0.02	<0.008	0.210	0.421	0.24
May-00	7.79	7.58	0.016	<0.02	<0.02	<0.011	0.341	0.385	0.18
Jun-00	6.84	7.47	0.015	<0.021	<0.025	0.013	0.251	0.341	0.09
Jul-00	3<T	7.22	0.022	<0.02	<0.023	<0.012	0.586	0.399	0.07
Aug-00	7.00	7.64	0.030	<0.02	<0.024	0.050	0.851	0.329	0.19
Sep-00	6.67	7.46	0.036	<0.016	<0.014	0.016	0.467	0.387	1.09
Oct-00	7.00	7.52	0.040	0.016	<0.01	<0.032	0.354	0.189	1.93
Nov-00	9.33	7.52	0.061	0.048	0.019	0.026	0.322	0.622	4.35
Dec-00	6.00	7.54	0.065	0.049	0.019	0.009	0.292	0.653	6.22
Jan-01	4<T	7.4	0.058	0.050	0.030	0.008	4.340	0.403	5.81

Date	TSS	pH	Total CN	Cu	Ni	Zn	As	Fe	Ammonia
Feb-01	6	7.4	0.078	0.060	0.020	0.016	0.348	0.512	6.27
Mar-01	<2	7.6	0.069	0.050	0.020	0.017	0.313	0.409	6.61
Apr-01	7	7.4	0.262	0.050	0.020	0.011	0.386	0.555	7.09
May-01	<5	7.7	0.104	0.043	0.017	0.027	0.389	0.530	10.50
Jun-01	<4	7.7	0.062	0.024	0.012	0.013	0.376	0.363	6.56
Jul-01	<4	7.9	0.092	0.019	0.016	0.013	0.740	0.213	4.50
Aug-01	4	7.9	0.099	0.017	0.019	0.008	1.450	0.136	4.50
Sep-01	<3	7.4	0.084	0.023	0.018	0.009	1.285	0.158	6.62
Oct-01	<2	7.7	0.088	0.031	0.014	<0.007	1.066	0.137	8.69
Nov-01	<5	7.9	0.099	0.044	0.013	<0.004	0.886	0.181	10.08
Dec-01	6	8.0	0.097	0.048	0.011	<0.004	0.893	0.239	11.55
Jan-02	4	7.9	0.117	0.055	0.017	0.010	0.810	0.260	14.0
Feb-02	7	7.6	0.127	0.049	0.016	0.019	0.840	0.358	14.5
Mar-02	<2	7.8	0.240	0.047	0.018	<0.006	0.920	0.316	15.2
Apr-02	8	7.4	0.177	0.039	0.012	<0.007	0.515	0.371	10.10
May-02	7	7.8	0.083	0.035	0.010	<0.007	0.562	0.442	8.74
Jun-02	12	8.0	0.022	0.028	0.010	<0.006	0.602	0.428	8.28
Jul-02	<2	7.7	0.011	0.016	0.009	<0.006	1.239	0.230	3.32
Aug-02	3	7.8	0.044	0.012	0.009	<0.006	1.30	0.191	4.10
Sep-02	5	7.5	0.044	0.012	0.009	<0.006	1.00	0.208	4.47
Oct-02	4	8.0	0.032	0.016	0.015	<0.006	1.000	4.06	5.18
Nov-02	3	7.9	0.009	0.017	0.015	0.009	0.77	0.109	7.71
Dec-02	2	7.45	0.034	0.015	0.016	0.012	0.81	0.118	12.1

Appendix II: Whole Rock Analysis Results

Table All-1: Red Lake Mine Solids Results

Parameter	Units	Location															
		RLM-1-1	RLM-2-1	RLM-2-2	RLM-2-3	RLM-3-1	RLM-3-2	RLM-3-3	RLM-4	RLM-5	RLM-6-1	RLM-6-2	RLM-7	RLM-SP	RLM-PP	RLM-PP-BH	
Ag	mg/kg	0.7	0.5	0.8	0.6	0.7	0.8	<0.5	1.1	1.1	1.0	<0.5	1.0	2.1	0.8	<0.5	
Al	%	5.02	5.97	6.03	5.90	6.29	6.59	6.41	5.52	5.76	5.83	5.93	5.11	6.52	6.43	5.60	
As	mg/kg	1990	3230	4130	4100	3300	3210	2660	1180	1995	2630	2050	5690	2950	3000	2150	
Ba	mg/kg	100	90	80	90	100	110	110	100	130	100	120	100	190	180	120	
Be	mg/kg	0.8	0.8	0.8	0.8	0.8	0.9	0.8	0.9	0.9	0.8	0.8	0.8	1.0	0.9	0.8	
Bi	mg/kg	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	5	<2	<2	
Ca	%	7.33	4.28	4.43	4.32	3.51	3.90	4.14	7.39	7.27	3.88	4.16	6.56	3.63	4.85	3.90	
Cd	mg/kg	1.5	1.8	1.6	1.5	1.5	1.5	1.4	1.3	1.3	2.1	1.7	1.8	1.0	1.2	<0.5	
Co	mg/kg	28	41	50	46	43	42	41	30	30	44	44	43	49	46	31	
Cr	mg/kg	218	157	145	144	140	147	136	210	201	132	104	251	180	174	127	
Cu	mg/kg	98	104	128	125	111	119	112	111	182	121	130	133	2330	491	303	
Fe	%	7.22	9.77	10.35	9.93	9.14	9.16	8.70	7.71	8.00	9.01	9.12	8.03	7.35	7.32	6.34	
K	%	0.69	0.75	0.76	0.86	1.03	1.07	1.02	0.66	0.84	0.82	1.04	0.81	1.40	1.34	1.08	
Mg	%	3.98	2.21	2.36	2.41	2.50	2.77	2.83	3.98	4.10	2.25	3.00	3.85	2.95	3.36	2.75	
Mn	mg/kg	1820	1995	2060	2020	2080	2160	2010	1955	2030	2060	2670	1905	1860	2240	2010	
Mo	mg/kg	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	2	2	4	1	
Na	%	0.25	0.24	0.19	0.20	0.20	0.18	0.17	0.23	0.22	0.24	0.22	0.20	0.36	0.26	0.28	
Ni	mg/kg	139	174	192	176	152	142	144	138	134	171	154	168	826	320	104	
P	mg/kg	220	300	230	240	270	300	270	270	300	240	270	270	460	420	290	
Pb	mg/kg	13	68	82	114	263	347	351	146	232	66	174	142	322	393	140	
S	%	0.68	1.86	2.63	2.34	0.80	0.80	1.00	0.72	0.66	0.99	0.57	1.34	0.58	0.54	0.74	
Sb	mg/kg	40	56	55	58	78	81	72	54	73	57	80	84	104	111	57	
Sr	mg/kg	120	91	75	75	67	67	62	127	124	76	72	107	102	106	88	
Ti	%	0.32	0.37	0.37	0.37	0.38	0.39	0.39	0.35	0.38	0.37	0.39	0.34	0.33	0.35	0.37	
V	mg/kg	242	260	271	264	258	261	255	241	272	243	254	250	241	248	208	
W	mg/kg	20	80	80	80	50	50	40	20	20	40	40	20	40	70	70	
Zn	mg/kg	127	179	225	258	294	300	202	148	183	395	345	335	1860	1325	184	
IC (C)	%	2.71	0.96	1.32	1.36	1.12	1.32	1.51	2.62	2.46	1.25	1.79	2.50	1.16	1.58	1.32	
IC(CO2)	%	9.9	3.5	4.8	5.0	4.1	4.8	5.5	9.6	9.0	4.6	6.6	9.2	4.2	5.8	4.8	
Total C	%	2.97	1.14	1.39	1.45	1.30	1.50	1.81	2.73	2.68	1.50	2.09	2.52	2.82	2.22	1.50	
S	%	0.71	1.78	2.54	2.35	0.82	0.81	1.05	0.76	0.67	0.97	0.57	1.34	0.59	0.56	0.78	

Table All-1: Red Lake Mine Solids Results

Parameter	Units	Location															
		RLM-1-1	RLM-2-1	RLM-2-2	RLM-2-3	RLM-3-1	RLM-3-2	RLM-3-3	RLM-4	RLM-5	RLM-6-1	RLM-6-2	RLM-7	RLM-SP	RLM-PP	RLM-PP-BH	
Ag	mg/kg	0.7	0.5	0.8	0.6	0.7	0.8	<0.5	1.1	1.1	1.0	<0.5	1.0	2.1	0.8	<0.5	
Al	%	5.02	5.97	6.03	5.90	6.29	6.59	6.41	5.52	5.76	5.83	5.93	5.11	6.52	6.43	5.60	
As	mg/kg	1990	3230	4130	4100	3300	3210	2660	1180	1995	2630	2050	5690	2950	3000	2150	
Ba	mg/kg	100	90	80	90	100	110	110	100	130	100	120	100	190	180	120	
Be	mg/kg	0.8	0.8	0.8	0.8	0.8	0.9	0.8	0.9	0.9	0.8	0.8	0.8	1.0	0.9	0.8	
Bi	mg/kg	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	5	<2	<2	
Ca	%	7.33	4.28	4.43	4.32	3.51	3.90	4.14	7.39	7.27	3.88	4.16	6.56	3.63	4.85	3.90	
Cd	mg/kg	1.5	1.8	1.6	1.5	1.5	1.5	1.4	1.3	1.3	2.1	1.7	1.8	1.0	1.2	<0.5	
Co	mg/kg	28	41	50	46	43	42	41	30	30	44	44	43	49	46	31	
Cr	mg/kg	218	157	145	144	140	147	136	210	201	132	104	251	180	174	127	
Cu	mg/kg	98	104	128	125	111	119	112	111	182	121	130	133	2330	491	303	
Fe	%	7.22	9.77	10.35	9.93	9.14	9.16	8.70	7.71	8.00	9.01	9.12	8.03	7.35	7.32	6.34	
K	%	0.69	0.75	0.76	0.86	1.03	1.07	1.02	0.66	0.84	0.82	1.04	0.81	1.40	1.34	1.08	
Mg	%	3.98	2.21	2.36	2.41	2.50	2.77	2.83	3.98	4.10	2.25	3.00	3.85	2.95	3.36	2.75	
Mn	mg/kg	1820	1995	2060	2020	2080	2160	2010	1955	2030	2060	2670	1905	1860	2240	2010	
Mo	mg/kg	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	2	2	4	1	
Na	%	0.25	0.24	0.19	0.20	0.20	0.18	0.17	0.23	0.22	0.24	0.22	0.20	0.36	0.26	0.28	
Ni	mg/kg	139	174	192	176	152	142	144	138	134	171	154	168	826	320	104	
P	mg/kg	220	300	230	240	270	300	270	270	300	240	270	270	460	420	290	
Pb	mg/kg	13	68	82	114	263	347	351	146	232	66	174	142	322	393	140	
S	%	0.68	1.86	2.63	2.34	0.80	0.80	1.00	0.72	0.66	0.99	0.57	1.34	0.58	0.54	0.74	
Sb	mg/kg	40	56	55	58	78	81	72	54	73	57	80	84	104	111	57	
Sr	mg/kg	120	91	75	75	67	67	62	127	124	76	72	107	102	106	88	
Ti	%	0.32	0.37	0.37	0.37	0.38	0.39	0.39	0.35	0.38	0.37	0.39	0.34	0.33	0.35	0.37	
V	mg/kg	242	260	271	264	258	261	255	241	272	243	254	250	241	248	208	
W	mg/kg	20	80	80	80	50	50	40	20	20	40	40	20	40	70	70	
Zn	mg/kg	127	179	225	258	294	300	202	148	183	395	345	335	1860	1325	184	
IC (C)	%	2.71	0.96	1.32	1.36	1.12	1.32	1.51	2.62	2.46	1.25	1.79	2.50	1.16	1.58	1.32	
IC(CO2)	%	9.9	3.5	4.8	5.0	4.1	4.8	5.5	9.6	9.0	4.6	6.6	9.2	4.2	5.8	4.8	
Total C	%	2.97	1.14	1.39	1.45	1.30	1.50	1.81	2.73	2.68	1.50	2.09	2.52	2.82	2.22	1.50	
S	%	0.71	1.78	2.54	2.35	0.82	0.81	1.05	0.76	0.67	0.97	0.57	1.34	0.59	0.56	0.78	

Meilleur, D
M.A.Sc
Fall 2004
Table All-1
1 of 2

Table All-1: Red Lake Mine Solids Results

Parameter	Units	Location															
		RLM-1-1	RLM-2-1	RLM-2-2	RLM-2-3	RLM-3-1	RLM-3-2	RLM-3-3	RLM-4	RLM-5	RLM-6-1	RLM-6-2	RLM-7	RLM-SP	RLM-PP	RLM-PP-BH	
Ag	mg/Kg	0.7	0.5	0.8	0.6	0.7	0.8	<0.5	1.1	1.1	1.0	<0.5	1.0	2.1	0.8	<0.5	
Al	%	5.02	5.97	6.03	5.90	6.29	6.59	6.41	5.52	5.76	5.83	5.93	5.11	6.52	6.43	5.60	
As	mg/Kg	1990	3230	4130	4100	3300	3210	2660	1180	1995	2630	2050	5690	2950	3000	2150	
Ba	mg/Kg	100	90	80	90	100	110	110	100	130	100	120	100	190	180	120	
Be	mg/Kg	0.8	0.8	0.8	0.8	0.8	0.9	0.8	0.9	0.9	0.8	0.8	0.8	1.0	0.9	0.8	
Bi	mg/Kg	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	5	<2	<2	
Ca	%	7.33	4.28	4.43	4.32	3.51	3.90	4.14	7.39	7.27	3.88	4.16	6.56	3.63	4.85	3.90	
Cd	mg/Kg	1.5	1.8	1.6	1.5	1.5	1.5	1.4	1.3	1.3	2.1	1.7	1.8	1.0	1.2	<0.5	
Co	mg/Kg	28	41	50	46	43	42	41	30	30	44	44	43	49	46	31	
Cr	mg/Kg	218	157	145	144	140	147	136	210	201	132	104	251	180	174	127	
Cu	mg/Kg	98	104	128	125	111	119	112	111	182	121	130	133	2330	491	303	
Fe	%	7.22	9.77	10.35	9.93	9.14	9.16	8.70	7.71	8.00	9.01	9.12	8.03	7.35	7.32	6.34	
K	%	0.69	0.75	0.76	0.86	1.03	1.07	1.02	0.66	0.84	0.82	1.04	0.81	1.40	1.34	1.08	
Mg	%	3.98	2.21	2.36	2.41	2.50	2.77	2.83	3.98	4.10	2.25	3.00	3.85	2.95	3.36	2.75	
Mn	mg/Kg	1820	1995	2060	2020	2080	2160	2010	1955	2030	2060	2670	1905	1860	2240	2010	
Mo	mg/Kg	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	2	2	4	1	
Na	%	0.25	0.24	0.19	0.20	0.20	0.18	0.17	0.23	0.22	0.24	0.22	0.20	0.36	0.26	0.28	
Ni	mg/Kg	139	174	192	176	152	142	144	138	134	171	154	168	826	320	104	
P	mg/Kg	220	300	230	240	270	300	270	270	300	240	270	270	460	420	290	
Pb	mg/Kg	13	68	82	114	263	347	351	146	232	66	174	142	322	393	140	
S	%	0.68	1.86	2.63	2.34	0.80	0.80	1.00	0.72	0.66	0.99	0.57	1.34	0.58	0.54	0.74	
Sb	mg/Kg	40	56	55	58	78	81	72	54	73	57	80	84	104	111	57	
Sr	mg/Kg	120	91	75	75	67	67	62	127	124	76	72	107	102	106	88	
Ti	%	0.32	0.37	0.37	0.37	0.38	0.39	0.39	0.36	0.38	0.37	0.39	0.34	0.33	0.35	0.37	
V	mg/Kg	242	260	271	264	258	261	255	241	272	243	254	250	241	248	208	
W	mg/Kg	20	80	80	80	50	50	40	20	20	40	40	20	40	70	70	
Zn	mg/Kg	127	179	225	258	294	300	202	148	183	395	345	335	1860	1325	184	
IC (C)	%	2.71	0.96	1.32	1.36	1.12	1.32	1.51	2.62	2.46	1.25	1.79	2.50	1.16	1.58	1.32	
IC(CO2)	%	9.9	3.5	4.8	5.0	4.1	4.8	5.5	9.6	9.0	4.6	6.6	9.2	4.2	5.8	4.8	
Total C	%	2.97	1.14	1.39	1.45	1.30	1.50	1.81	2.73	2.68	1.50	2.09	2.52	2.82	2.22	1.50	
S	%	0.71	1.78	2.54	2.35	0.82	0.81	1.05	0.76	0.67	0.97	0.57	1.34	0.59	0.56	0.78	

McIlleury, D
M.A.Sc
Fall 2004
Table All-1
2 of 2

Appendix III: Rietveld Refinement Reports

***Quantitative Phase Analysis of 14 samples using the Rietveld Method
and X-ray Powder Diffraction Data.***

***Attention:
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April 23, 2003

EXPERIMENTAL METHODS

The particle size of the fourteen samples from Cochenour Mine (CM series) and from Red Lake Mine (RLM series) was further reduced to the optimum grain-size range for X-ray analysis ($<5\ \mu\text{m}$) by grinding under ethanol in a vibratory McCrone Micronising Mill (McCrone Scientific Ltd., London, UK) for 6 minutes. Fine grain-size is an important factor in reducing micro-absorption contrast between phases. Samples were pressed from the bottom of an aluminum sample holder against a ground glass slide; the cavity in the holder measures $43 \times 24 \times 1.5\ \text{mm}$. The textured surface of the glass minimizes preferred orientation of anisotropic grains in the part of the powder that is pressed against the glass.

Step-scan X-ray powder-diffraction data were collected over a range $3\text{--}70^\circ 2\theta$ with $\text{CuK}\alpha$ radiation on a standard Siemens (Bruker) D5000 Bragg-Brentano diffractometer equipped with a diffracted-beam graphite monochromator crystal, $2\ \text{mm}$ (1°) divergence and antiscatter slits, $0.6\ \text{mm}$ receiving slit and incident-beam Soller slit. The long sample holder used ($43\ \text{mm}$) ensured that the area irradiated by the X-ray beam under these conditions was completely contained within the sample. The long fine-focus Cu X-ray tube was operated at $40\ \text{kV}$ and $40\ \text{mA}$, using a take-off angle of 6° . X-ray powder-diffraction data were refined with Rietveld Topas 2.0 (Bruker AXS) running on a Pentium III $1000\ \text{MHz}$ personal computer.

RESULTS AND DISCUSSION

The X-ray diffractograms were analyzed using the International Centre for Diffraction Database PDF2 Data Sets 1-49 plus 70-86 using Search-Match software by Siemens (Bruker). The results of quantitative phase analysis by Rietveld refinement are given in Table 1. Rietveld refinement plots are given in Figures 1-14.

Table 1: Results of quantitative analysis from Rietveld refinements (wt.%)

	CM-1-1	CM-1-2	CM-2-1	CM-2-2	CM-3-1	CM-3-2	CM-4	RLM-2-1	RLM-5	RLM-6-1	RLM-6-2	RLM-7	RLM-SecP	RLM-PrP
Quartz	32.7	41.2	32.7	38.3	31.2	27.1	26.2	43.5	32.1	46.9	42.9	32.3	37.3	36.0
Plagioclase	10.2	1.9	5.9	2.2	41.1	36.1	7.3	14.1	16.4	9.7	8.3	15.3	16.6	15.0
Biotite								5.8	5.7	5.0	6.6	5.3	9.3	10.7
Muscovite	9.0	9.0	6.0	5.2	17.0	22.0	8.0	3.6		4.7	5.9			
Chlorite	5.2	5.7	7.4	7.0	2.8	4.7	10.1	8.0	7.9	10.4	12.8	8.0	18.0	15.1
Talc	3.7	3.0	9.2	6.9			9.7							
Gypsum								3.9		3.8				
Calcite	1.2	2.2	2.8	3.5	4.0	5.1	3.7		3.0		0.9	2.4		2.0
Dolomite	32.1	34.1	32.0	32.4	2.0	2.7	32.4	9.1	21.2	10.2	14.9	19.0	11.3	13.2
Siderite	2.0	0.5	2.4	0.9	0.4	0.6	1.1	0.7		3.2	2.9			
Amphibole		0.9						4.7	12.5	1.2	1.2	13.2	6.6	6.8
Pyrite	2.3													
Arsenopyrite	0.9	0.7	0.9	1.0	0.7		1.0	1.9	0.2	1.6	1.7	1.2	0.2	0.3
Pyrrhotite				0.3		0.1		0.6		0.7	0.6	2.2		
Titanite				1.0		1.2								
Hematite		0.8					0.2							
Magnetite	0.8		0.8	1.2				2.9	0.8	1.9	1.3	0.7	0.7	0.5
Goethite					0.7	0.4	0.2	1.4	0.2	0.7		0.5		0.4
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

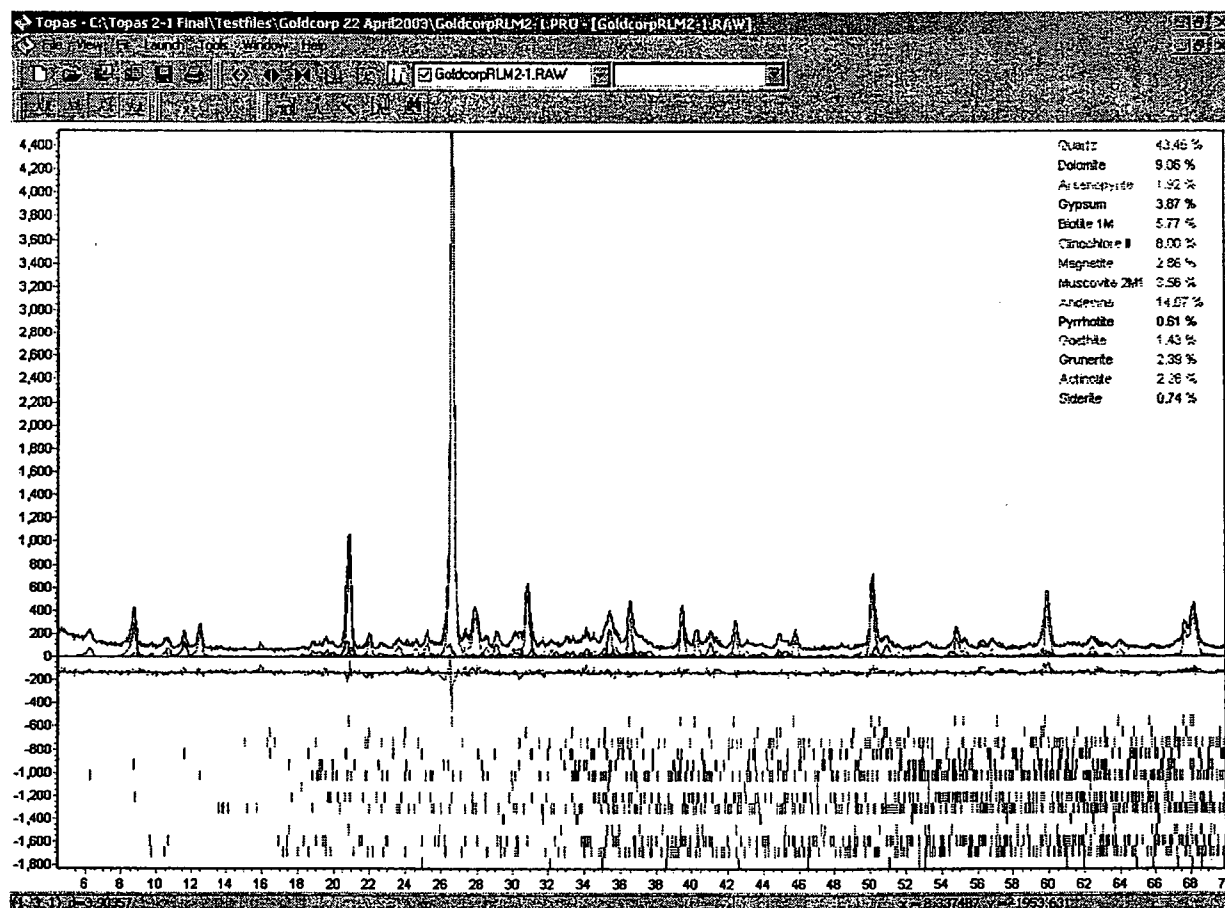


Figure 8: . Rietveld refinement plot for sample RLM-2-1 (blue line - observed intensity at each step; red line - calculated pattern, solid grey line below - difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases.

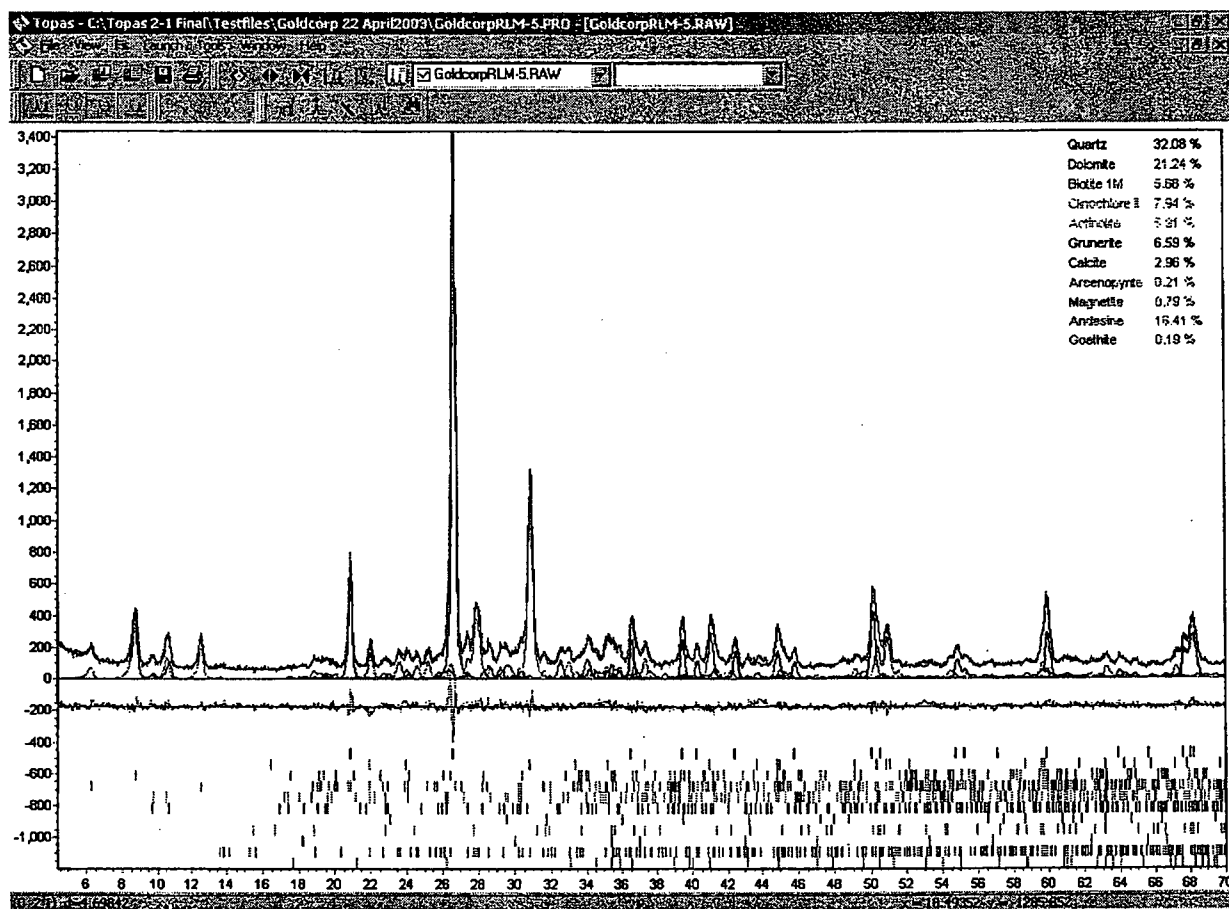


Figure 9: . Rietveld refinement plot for sample RLM-5 (blue line - observed intensity at each step; red line - calculated pattern, solid grey line below - difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases.

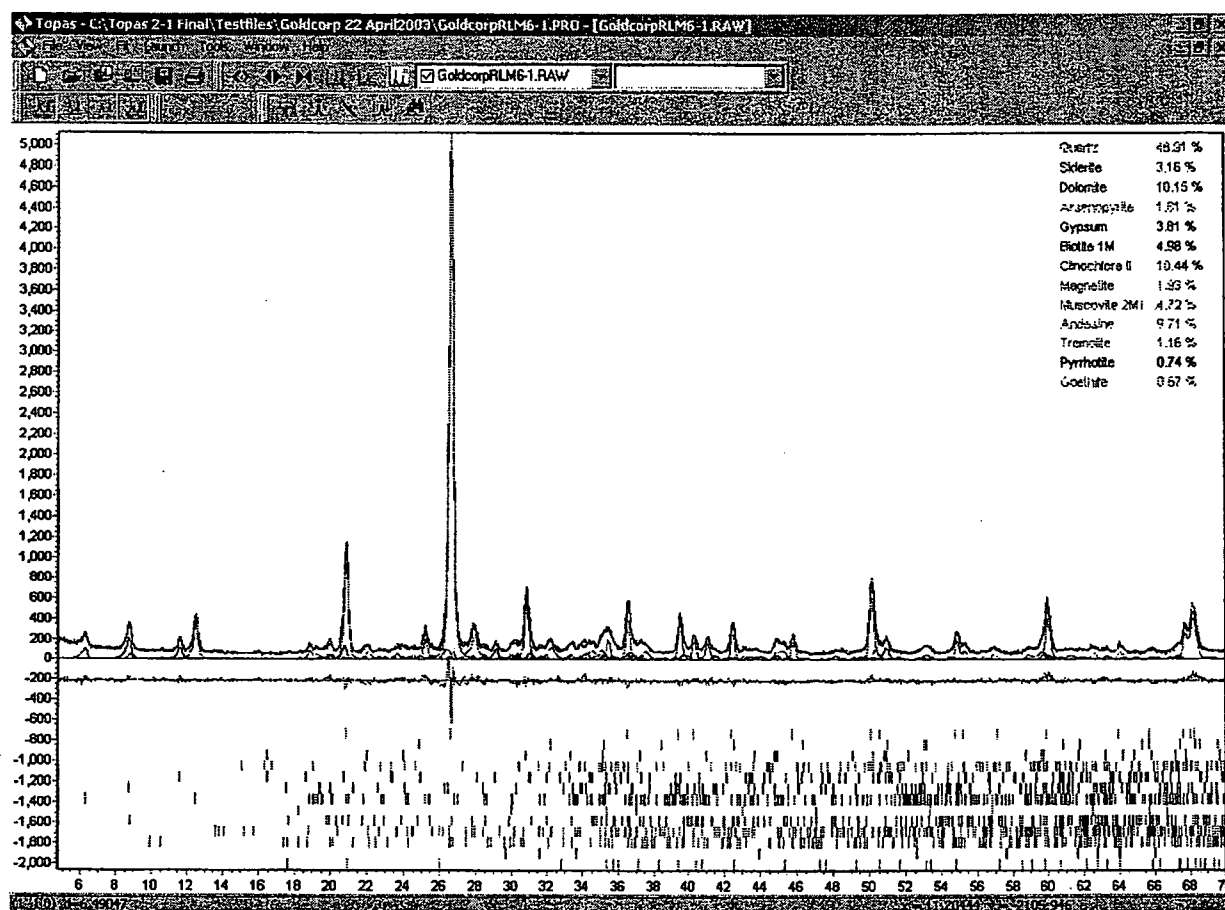


Figure 10: . Rietveld refinement plot for sample RLM-6-1 (blue line - observed intensity at each step; red line - calculated pattern, solid grey line below - difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases.

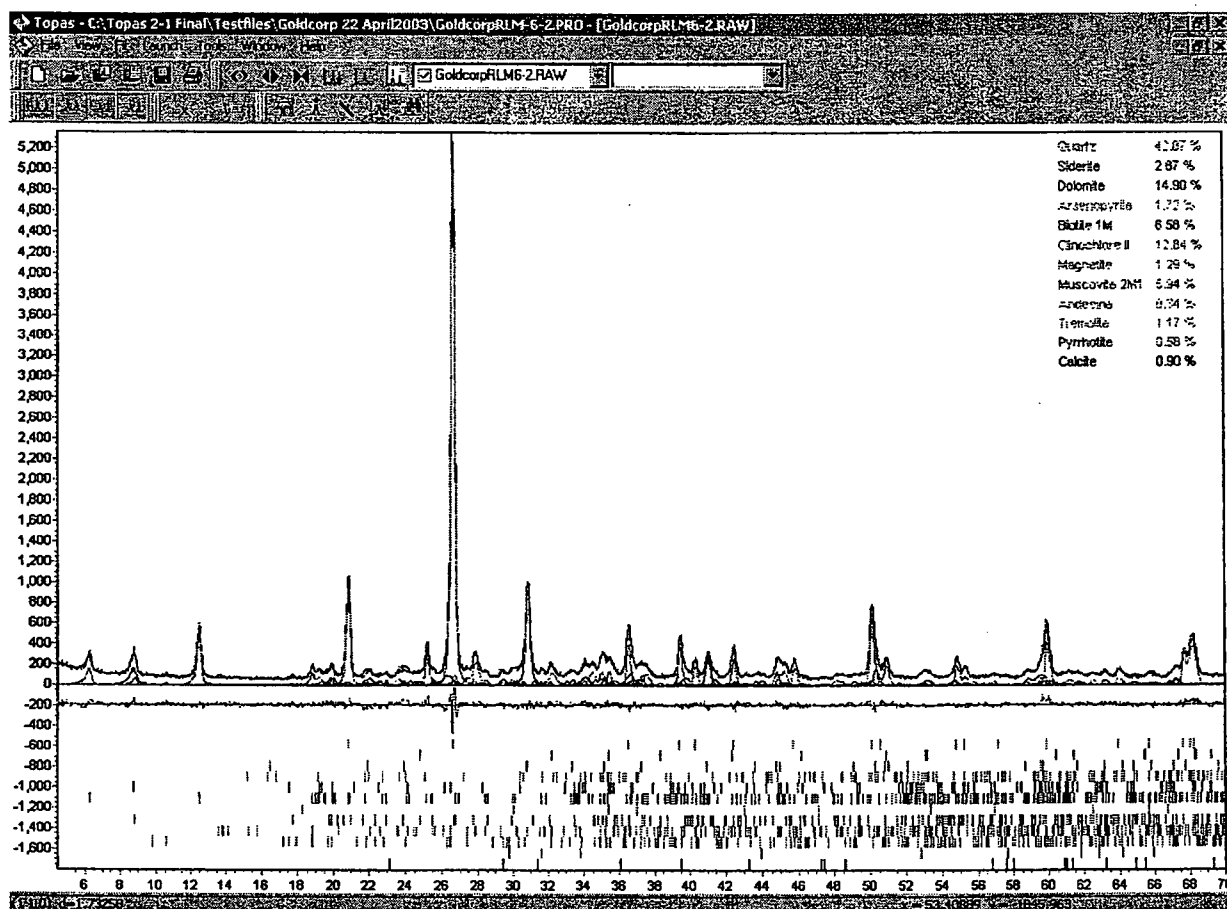


Figure 11: . Rietveld refinement plot for sample RLM-6-2 (blue line - observed intensity at each step; red line - calculated pattern, solid grey line below - difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases.

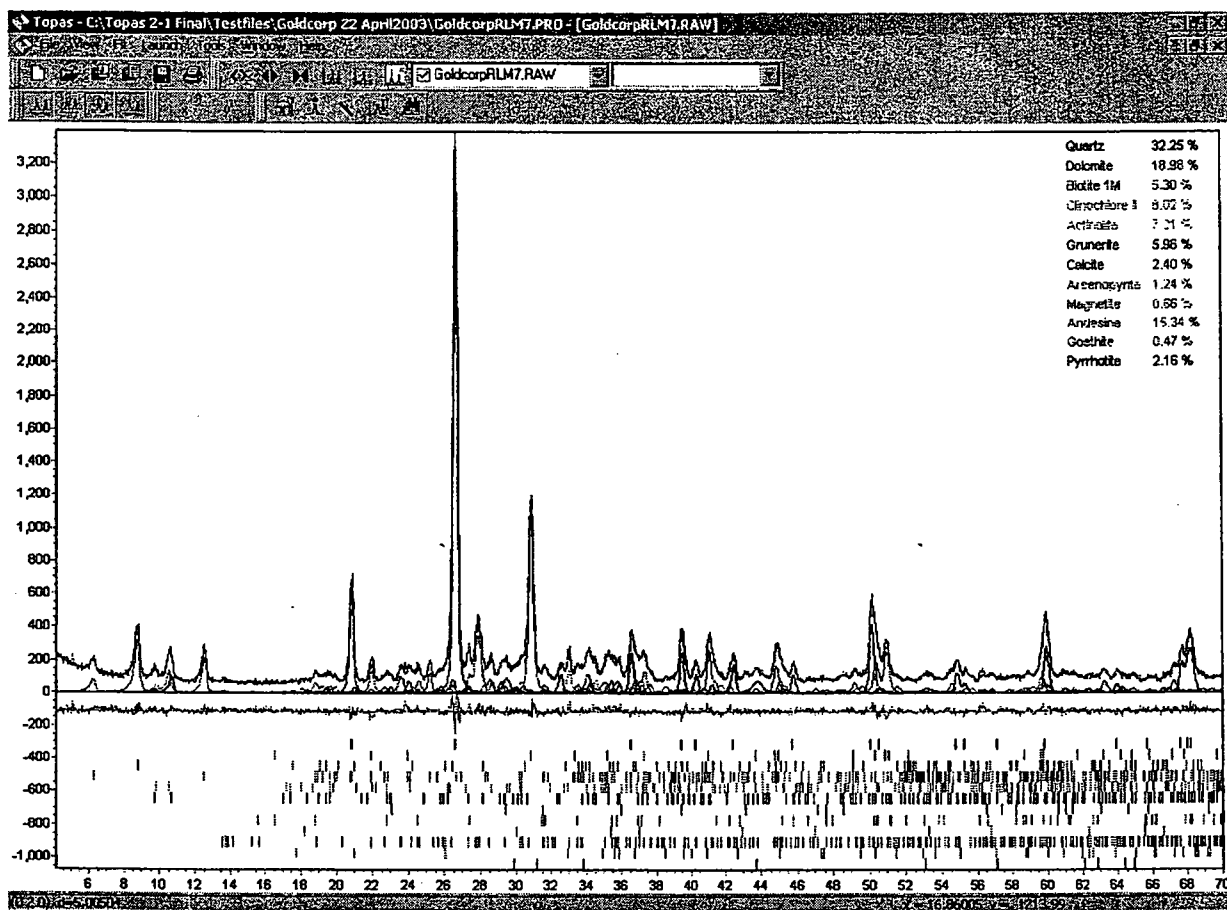


Figure 12: . Rietveld refinement plot for sample RLM-7 (blue line - observed intensity at each step; red line - calculated pattern, solid grey line below — difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases.

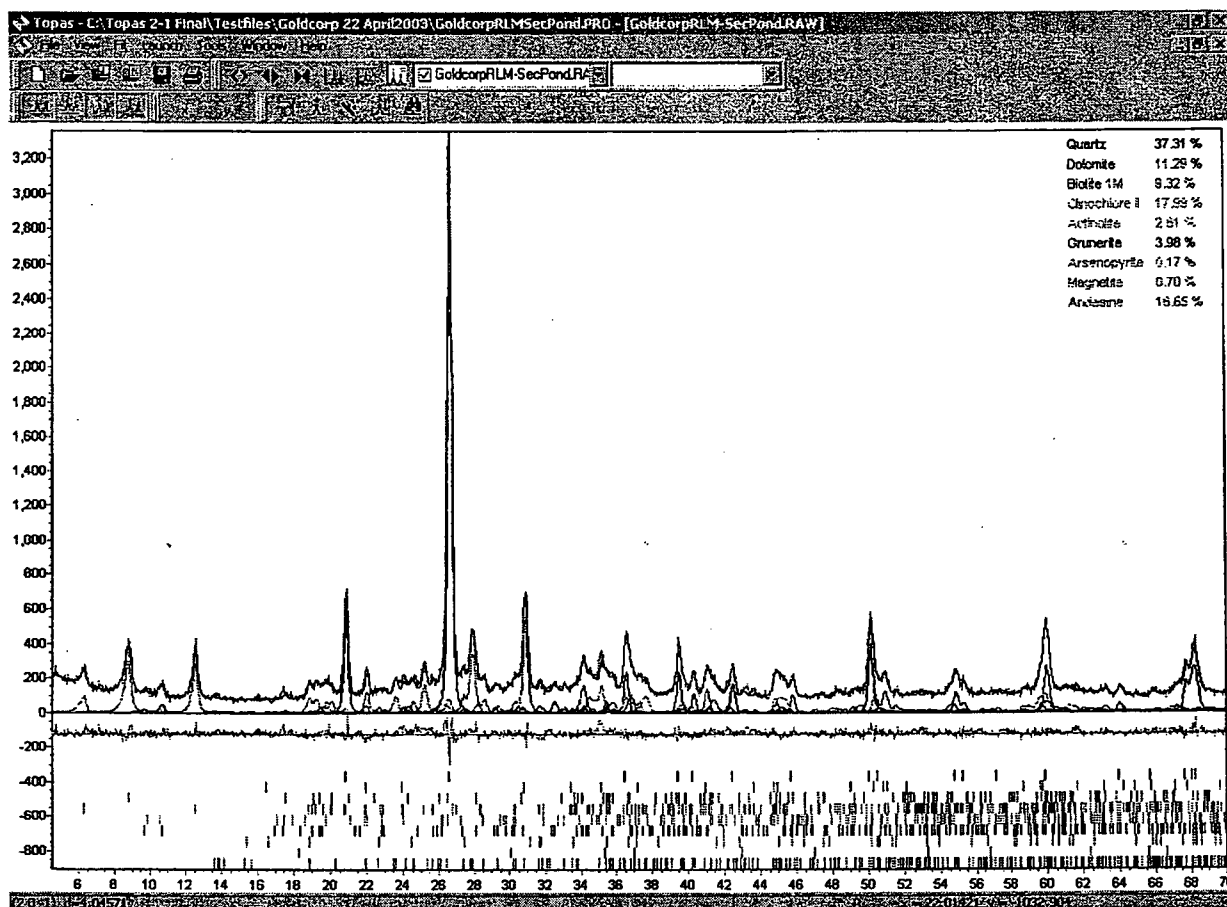


Figure 13: . Rietveld refinement plot for sample RLM-Secondary Pond (blue line - observed intensity at each step; red line - calculated pattern, solid grey line below - difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases.

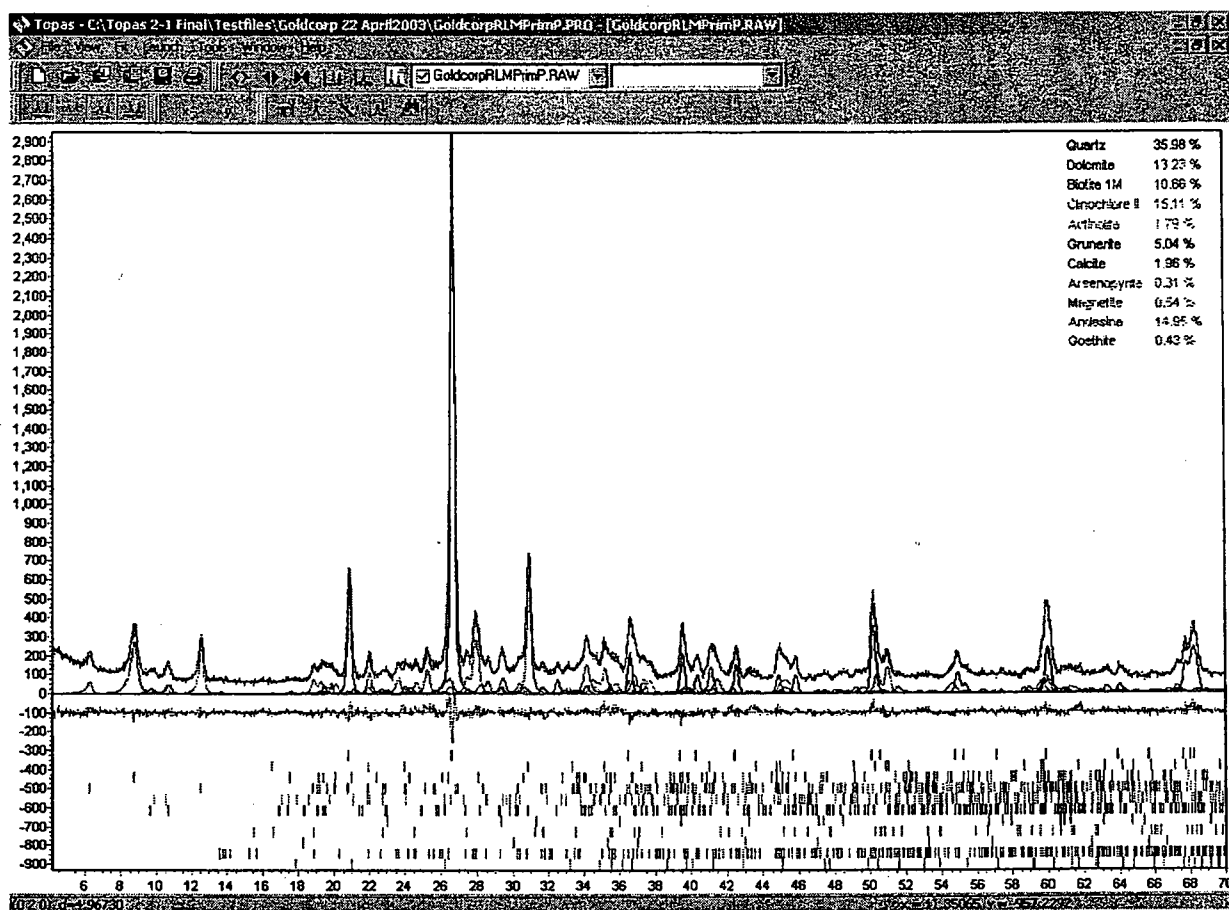


Figure 14: . Rietveld refinement plot for sample RLM-Primary Pond (blue line - observed intensity at each step; red line - calculated pattern, solid grey line below - difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases.

***Quantitative Phase Analysis of 9 samples using the Rietveld Method
and X-ray Powder Diffraction Data.***

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May 26, 2003

EXPERIMENTAL METHODS

The particle size of the nine samples **RLM-1, RLM-2-3, RLM-3-1, RLM-3-3, RLM-4, #3, #5, #24 and #29** was further reduced to the optimum grain-size range for X-ray analysis ($<5\ \mu\text{m}$) by grinding under ethanol in a vibratory McCrone Micronising Mill (McCrone Scientific Ltd., London, UK) for 6 minutes.

Step-scan X-ray powder-diffraction data were collected over a range $3\text{--}70^\circ 2\theta$ with $\text{CuK}\alpha$ radiation on a standard Siemens (Bruker) D5000 Bragg-Brentano diffractometer equipped with a diffracted-beam graphite monochromator crystal, $2\ \text{mm}$ (1°) divergence and antiscatter slits, $0.6\ \text{mm}$ receiving slit and incident-beam Soller slit. The long fine-focus Cu X-ray tube was operated at $40\ \text{kV}$ and $40\ \text{mA}$, using a take-off angle of 6° . X-ray powder-diffraction data were refined with Rietveld Topas 2.0 (Bruker AXS) running on a Pentium III $1000\ \text{MHz}$ personal computer.

RESULTS AND DISCUSSION

The X-ray diffractograms were analyzed using the International Centre for Diffraction Database PDF2 Data Sets 1-49 plus 70-86 using Search-Match software by Siemens (Bruker). The results of quantitative phase analysis by Rietveld refinement are given in Table 1. Rietveld refinement plots are given in Figures 1-9.

Table 1: Results of quantitative analysis from Rietveld refinements (wt.%)

	RLM-1	RLM-2-3	RLM-3-1	RLM-3-3	RLM-4	#3	#5	#24	#29
Quartz	36.5	48.7	49.2	50.5	33.6	32.8	32.3	37.4	41.4
Plagioclase	15.9	15.6	12.5	12.7	18.3	15.8	15.7	17.5	12.6
Biotite	4.0	4.8	6.5	7.3	3.5	5.0	5.9	8.1	7.7
Muscovite									3.8
Chlorite	3.5	5.1	14.8	8.8	4.5	7.6	6.3	17.8	10.1
Gypsum			0.8						2.4
Calcite	0.8				1.1	2.3	2.1		
Dolomite	24.1	10.6	9.1	11.9	22.0	18.8	21.7	11.0	12.3
Siderite				1.1					0.7
Amphibole	12.9	4.7	5.2	4.0	13.7	13.9	14.4	7.2	4.7
Pyrite		1.5							
Arsenopyrite		0.8				1.0	0.4	0.2	1.7
Pyrrhotite	1.5	3.2	0.4	2.3	2.1	1.6			0.6
Magnetite	0.8	2.5	1.6	1.4	0.9	0.9	1.0	0.8	1.1
Goethite						0.2	0.2		0.9
Rutile		2.4			0.2				
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

CaSO₄·2H₂OFe_(1-x)S (x=0-0.17)
α-Fe³⁺O(oh)

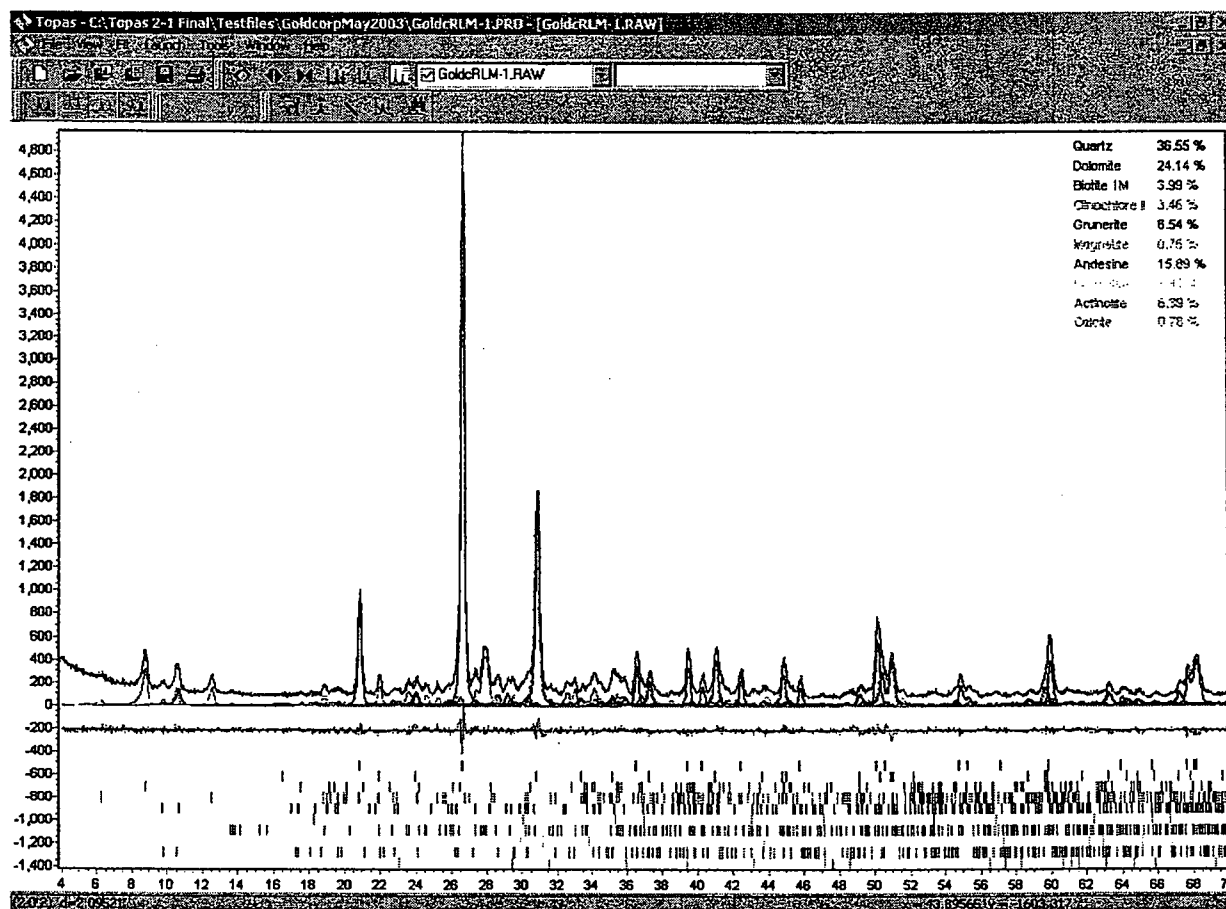


Figure 1: . Rietveld refinement plot for sample RLM-1 (blue line - observed intensity at each step; red line - calculated pattern, solid grey line below - difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases.

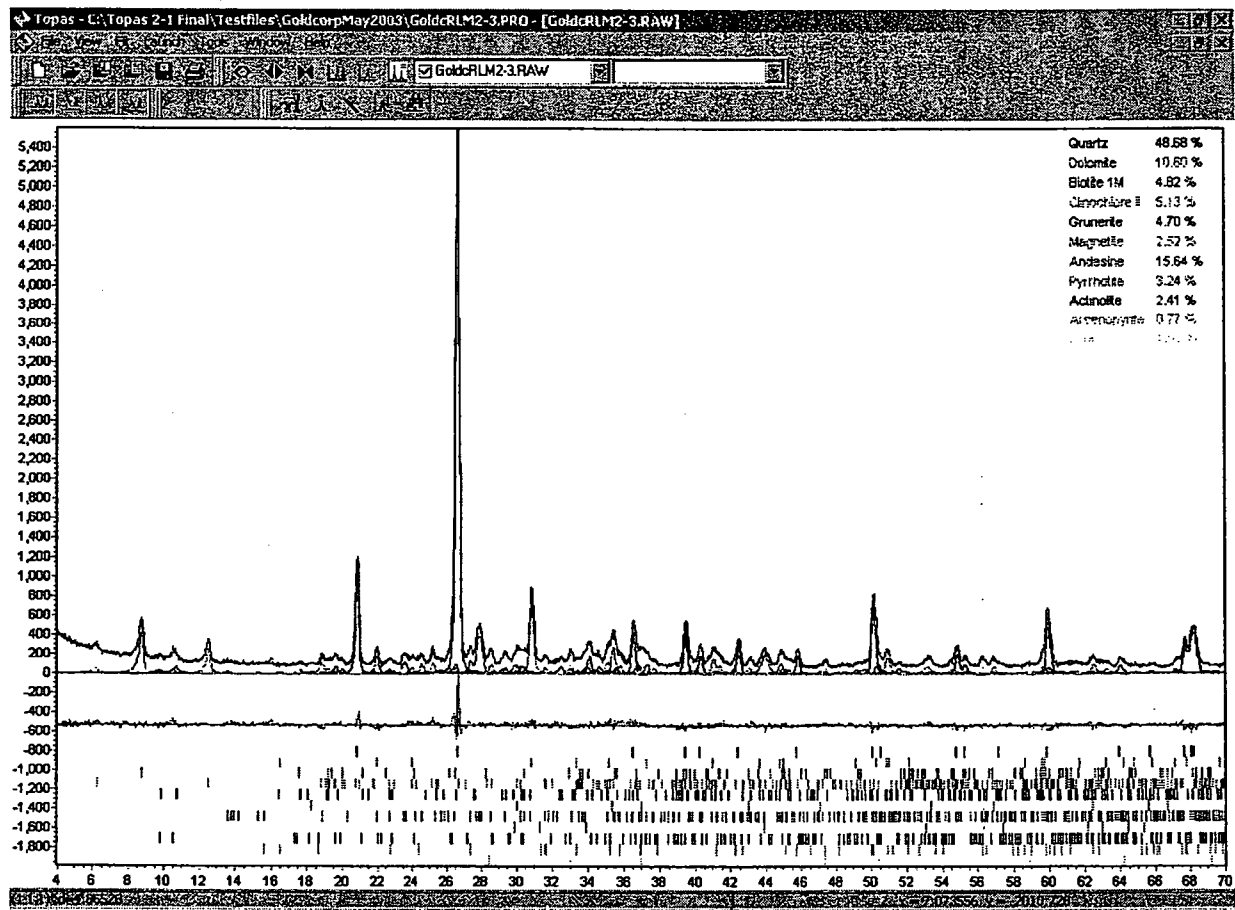


Figure 2: . Rietveld refinement plot for sample RLM-2-3 (blue line - observed intensity at each step; red line - calculated pattern, solid grey line below - difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases.

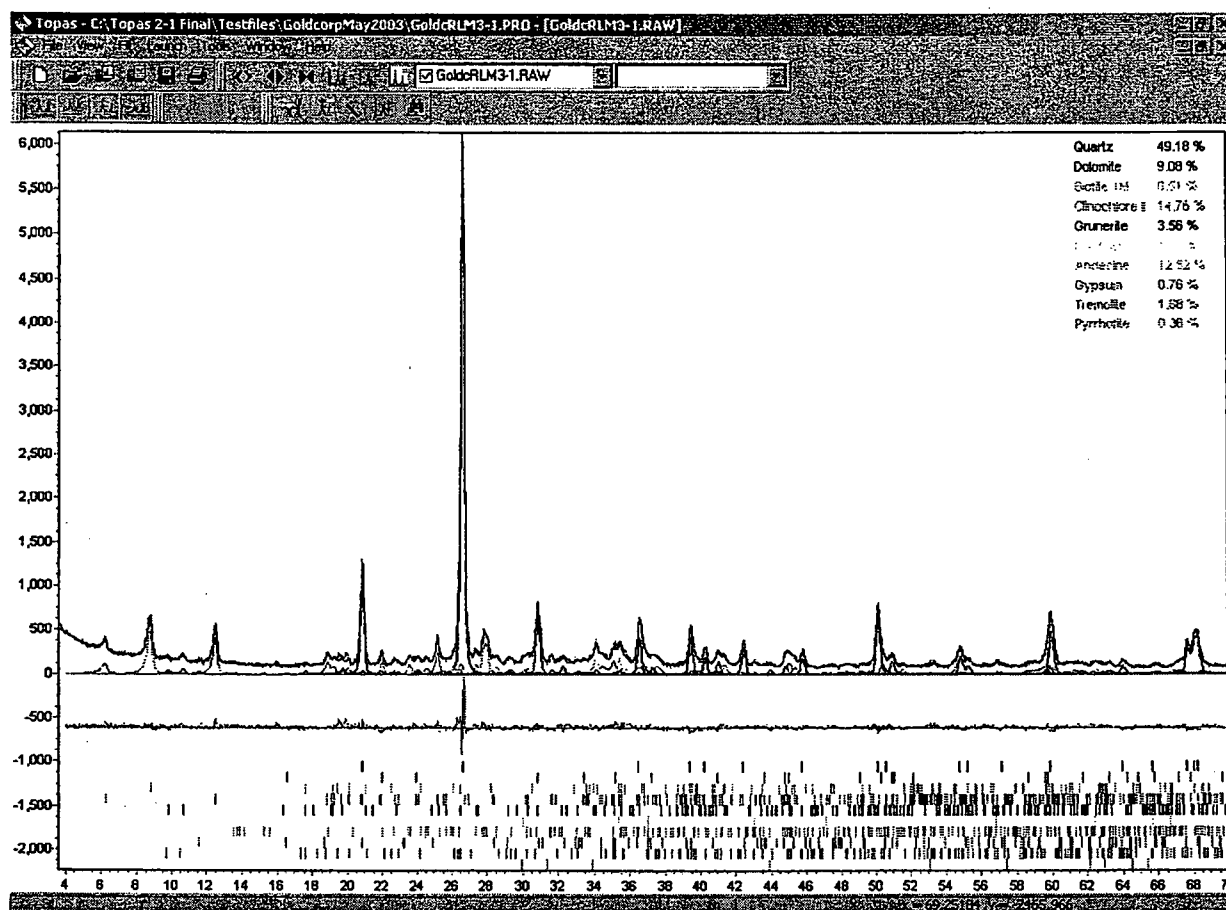


Figure 3: . Rietveld refinement plot for sample **RLM-3-1** (blue line - observed intensity at each step; red line - calculated pattern, solid grey line below - difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases.

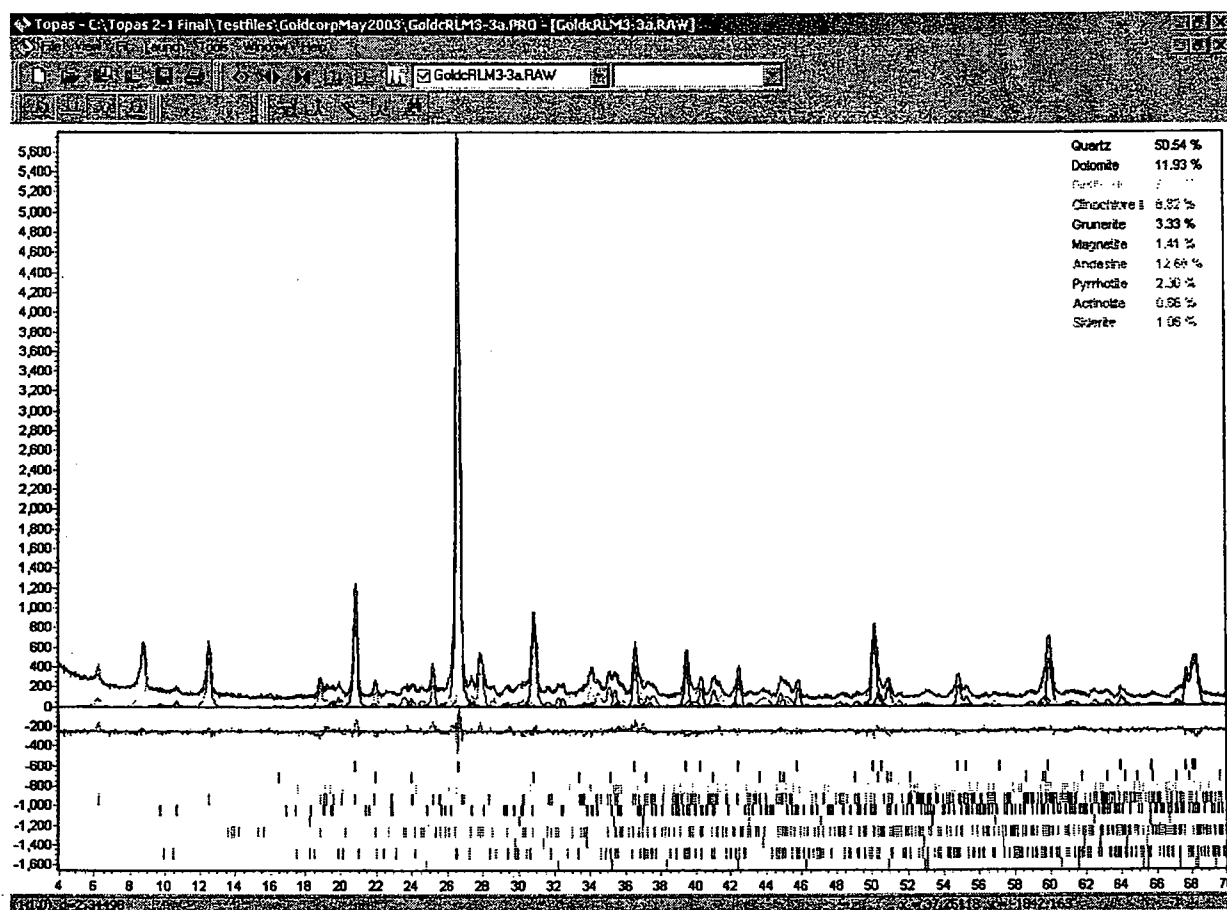


Figure 4: . Rietveld refinement plot for sample **RLM-3-3** (blue line - observed intensity at each step; red line - calculated pattern, solid grey line below - difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases.

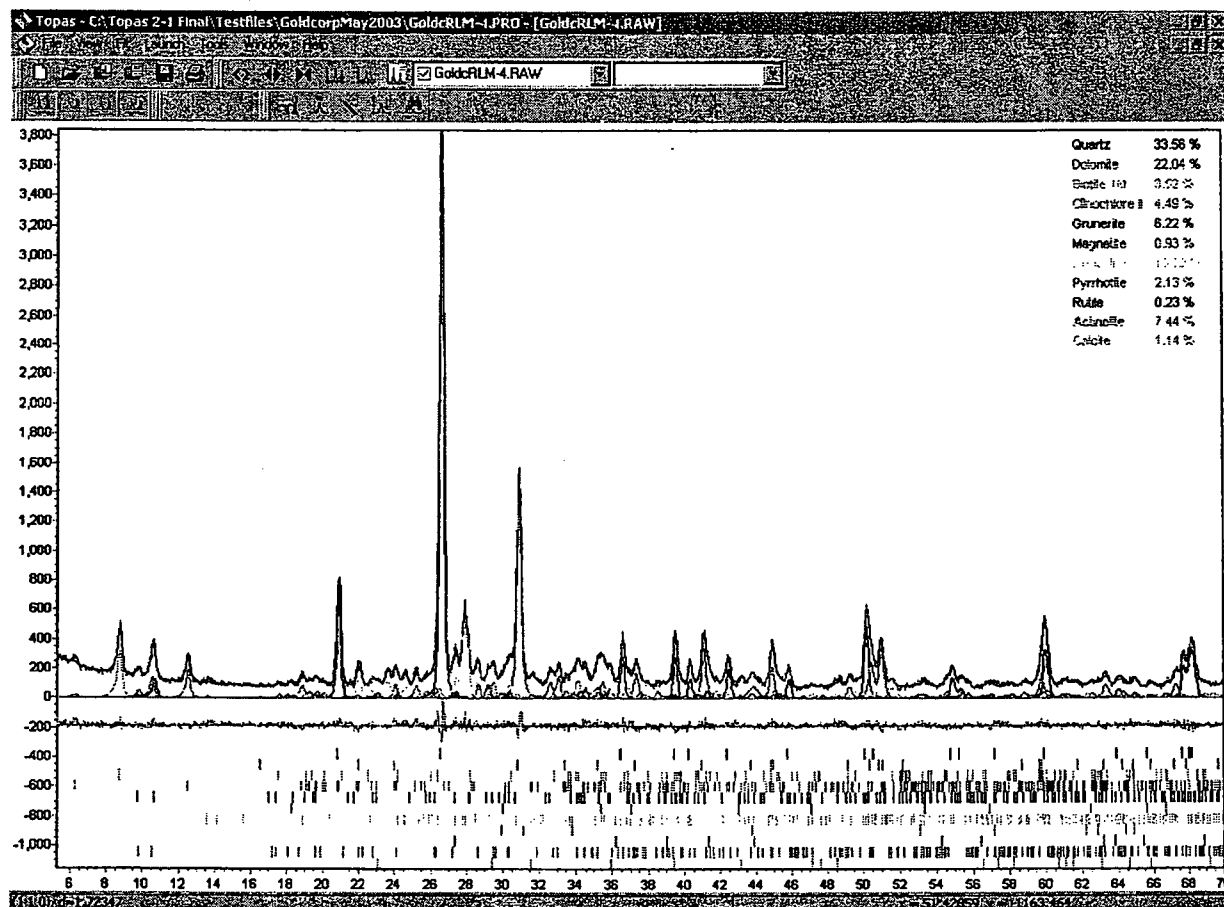


Figure 5: . Rietveld refinement plot for sample RLM-4 (blue line - observed intensity at each step; red line - calculated pattern, solid grey line below - difference between observed and calculated intensities; vertical bars, positions of all Bragg reflections. Coloured lines are individual diffraction patterns of all phases.

Appendix IV: Sequential Extraction Data and Calculations

Table AIV-1: Raw Sequential Extraction Data

Sample	Tare	Total	Liquid	[As]	Mass As	Fraction	[Fe]	Mass Fe	Fraction
		ml		mg/L	mg	As	mg/L	mg	Fe
1-1a	13.09	54.33	41.24	1.358	0.0560	0.0393	1.22	0.0503	0.0013
2-1a	13.01	55.71	42.70	0.951	0.0406	0.0290	0.58	0.0248	0.0007
3-1a	13.04	54.83	41.79	0.618	0.0258	0.0288	0	0.0000	0.0000
4-1a	13.04	54.06	41.02	0.669	0.0274	0.0301	0	0.0000	0.0000
5-1a	13.15	55.91	42.76	0.0847	0.0036	0.0023	0.23	0.0098	0.0002
6-1a	13.00	54.05	41.05	0.0866	0.0036	0.0022	0.27	0.0111	0.0003
7-1a	13.06	55.38	42.32	0.1475	0.0062	0.0067	0.05	0.0021	0.0001
8-1a	13.04	60.04	47.00	0.1485	0.0070	0.0074	0	0.0000	0.0000
1-1b	12.98	55.44	42.46	0.832	0.0353	0.0248	1.72	0.0730	0.0019
2-1b	13.13	55.17	42.04	0.594	0.0250	0.0179	0.95	0.0399	0.0011
3-1b	13.03	54.47	41.44	0.239	0.0099	0.0111	0.14	0.0058	0.0002
4-1b	13.01	55.26	42.25	0.291	0.0123	0.0135	0.25	0.0106	0.0003
5-1b	13.01	54.61	41.60	0.099	0.0041	0.0026	0.92	0.0383	0.0009
6-1b	13.00	54.97	41.97	0.124	0.0052	0.0032	1.29	0.0541	0.0013
7-1b	13.05	56.14	43.09	0.1325	0.0057	0.0062	0.26	0.0112	0.0004
8-1b	13.07	56.79	43.72	0.14	0.0061	0.0065	0.15	0.0066	0.0002
1-1w	13.14	24.17	11.03	0.76	0.0084	0.0059	1.07	0.0118	0.0003
2-1w	12.98	24.10	11.12	0.503	0.0056	0.0040	0.36	0.0040	0.0001
3-1w	13.03	22.89	9.86	0.0693	0.0007	0.0008	0.43	0.0042	0.0001
4-1w	13.07	23.25	10.18	0.094	0.0010	0.0010	0.52	0.0053	0.0002
5-1w	13.00	23.05	10.05	0.0449	0.0005	0.0003	0.38	0.0038	0.0001
6-1w	13.00	23.19	10.19	0.0611	0.0006	0.0004	0.69	0.0070	0.0002
7-1w	13.04	23.34	10.30	0.0675	0.0007	0.0008	0.24	0.0025	0.0001
8-1w	13.06	23.09	10.03	0.0663	0.0007	0.0007	0.14	0.0014	0.0000
1-2a	13.00	56.09	43.09	16.48	0.7101	0.4979	47.69	2.0550	0.0539
2-2a	13.01	56.41	43.40	12.61	0.5473	0.3912	35.7	1.5494	0.0415
3-2a	13.00	58.09	45.09	1.94	0.0875	0.0976	38.52	1.7369	0.0524
4-2a	13.08	57.95	44.87	2.605	0.1169	0.1280	49	2.1986	0.0651
5-2a	13.03	57.24	44.21	5.969	0.2639	0.1673	18.56	0.8205	0.0199
6-2a	13.04	58.30	45.26	7.414	0.3356	0.2056	22.12	1.0012	0.0235
7-2a	13.09	56.25	43.16	5.477	0.2364	0.2552	22.48	0.9702	0.0311
8-2a	13.00	57.99	44.99	6.021	0.2709	0.2861	25.45	1.1450	0.0359
1-2b	13.08	57.81	44.73	1.861	0.0832	0.0584	26.83	1.2001	0.0315
2-2b	13.03	58.05	45.02	1.526	0.0687	0.0491	21.65	0.9747	0.0261
3-2b	13.06	58.10	45.04	0.0252	0.0011	0.0013	14.75	0.6643	0.0200
4-2b	13.08	49.91	36.83	0.0627	0.0023	0.0025	17.11	0.6302	0.0187
5-2b	13.02	57.62	44.60	1.116	0.0498	0.0315	17.47	0.7792	0.0189
6-2b	13.04	58.27	45.23	1.17	0.0529	0.0324	18.19	0.8227	0.0193
7-2b	13.01	59.21	46.20	2.127	0.0983	0.1061	21.99	1.0159	0.0326
8-2b	13.13	59.11	45.98	2.383	0.1096	0.1157	37.83	1.7394	0.0546
1-2w	12.96	22.79	9.83	0.1895	0.0019	0.0013	1.38	0.0136	0.0004
2-2w	13.02	23.15	10.13	0.216	0.0022	0.0016	1.45	0.0147	0.0004
3-2w	13.07	22.86	9.79	0.0102	0.0001	0.0001	0.75	0.0073	0.0002
4-2w	13.12	31.49	18.37	0.0725	0.0013	0.0015	4.49	0.0825	0.0024
5-2w	13.02	22.35	9.33	0.12	0.0011	0.0007	0.69	0.0064	0.0002
6-2w	13.04	22.86	9.82	0.1475	0.0014	0.0009	0.83	0.0082	0.0002
7-2w	13.09	23.24	10.15	0.1685	0.0017	0.0018	0.88	0.0089	0.0003
8-2w	13.05	23.67	10.62	0.226	0.0024	0.0025	1.27	0.0135	0.0004

Table AIV-1 (Cont): Raw Sequential Extraction Data

Sample	Tare	Total	Liquid	[As]	Mass As	Fraction	[Fe]	Mass Fe	Fraction
		ml		mg/L	mg	As	mg/L	mg	Fe
1-3a	13.03	55.28	42.25	1.935	0.0818	0.0573	208.86	8.8243	0.2317
2-3a	13.04	55.13	42.09	2.325	0.0979	0.0700	245.28	10.3238	0.2764
3-3a	13.01	65.35	52.34	0.0477	0.0025	0.0028	132.76	6.9487	0.2097
4-3a	12.94	53.22	40.28	0.0851	0.0034	0.0038	199.7	8.0439	0.2383
5-3a	13.09	54.14	41.05	5.769	0.2368	0.1501	237.23	9.7383	0.2367
6-3a	13.02	54.81	41.79	7.27	0.3038	0.1862	266.26	11.1270	0.2615
7-3a	13.11	34.46	21.35	4.103	0.0876	0.0946	129.82	2.7717	0.0889
8-3a	13.05	55.18	42.13	9.186	0.3870	0.4087	197.02	8.3005	0.2605
1-3w	13.12	23.30	10.18	0.284	0.0029	0.0020	27.68	0.2818	0.0074
2-3w	12.97	23.59	10.62	0.308	0.0033	0.0023	29.54	0.3137	0.0084
3-3w	13.12	23.35	10.23	0.034	0.0003	0.0004	18.64	0.1907	0.0058
4-3w	13.04	23.02	9.98	0.17	0.0017	0.0019	23.63	0.2358	0.0070
5-3w	13.07	23.29	10.22	1.095	0.0112	0.0071	50.27	0.5138	0.0125
6-3w	13.07	23.40	10.33	1.297	0.0134	0.0082	47.26	0.4882	0.0115
7-3w	13.02	23.32	10.30	1.03	0.0106	0.0115	23.12	0.2381	0.0076
8-3w	13.13	22.98	9.85	2.211	0.0218	0.0230	40.3	0.3970	0.0125
1-4a	13.09	55.01	41.92	0.208	0.0087	0.0061	18.83	0.7894	0.0207
2-4a	13.02	55.15	42.13	0.236	0.0099	0.0071	16.89	0.7116	0.0190
3-4a	12.97	54.63	41.66	0.0112	0.0005	0.0005	43.21	1.8001	0.0543
4-4a	13.02	55.43	42.41	0.0143	0.0006	0.0007	52.37	2.2210	0.0658
5-4a	12.99	55.50	42.51	3.833	0.1629	0.1033	191.02	8.1203	0.1974
6-4a	13.06	55.14	42.08	3.972	0.1671	0.1024	194.5	8.1846	0.1923
7-4a	13.08	54.82	41.74	2.081	0.0869	0.0938	130.2	5.4345	0.1744
8-4a	13.04	55.06	42.02	3.731	0.1568	0.1656	198.74	8.3511	0.2621
1-4w	13.06	23.15	10.09	0.139	0.0014	0.0010	16.11	0.1625	0.0043
2-4w	13.13	23.26	10.13	0.1455	0.0015	0.0011	12.92	0.1309	0.0035
3-4w	13.04	23.14	10.10	0.0023	0.0000	0.0000	5.95	0.0601	0.0018
4-4w	12.97	23.24	10.27	0.0037	0.0000	0.0000	7.06	0.0725	0.0021
4-5w	13.08	23.22	10.14	0.26	0.0026	0.0017	25.87	0.2623	0.0064
4-6w	13.01	23.09	10.08	0.279	0.0028	0.0017	31.83	0.3208	0.0075
4-7w	13.02	23.32	10.30	0.1945	0.0020	0.0022	24.23	0.2496	0.0080
4-8w	13.01	22.99	9.98	0.376	0.0038	0.0040	34.29	0.3422	0.0107
1-5a	13.08	55.78	42.70	0.587	0.0251	0.0176	48.81	2.0842	0.0547
2-5a	13.00	55.44	42.44	0.673	0.0286	0.0204	60	2.5464	0.0682
3-5a	13.00	55.44	42.44	0.012	0.0005	0.0006	34.3	1.4557	0.0439
4-5a	13.03	55.49	42.46	0.0138	0.0006	0.0006	40.21	1.7073	0.0506
5-5a	13.07	56.18	43.11	0.0245	0.0011	0.0007	31.65	1.3644	0.0332
6-5a	13.09	55.13	42.04	0.0342	0.0014	0.0009	38.74	1.6286	0.0383
7-5a	13.05	55.88	42.83	0.0854	0.0037	0.0039	34.34	1.4708	0.0472
8-5a	13.01	57.04	44.03	0.106	0.0047	0.0049	41.25	1.8162	0.0570
1-5w	13.11	23.48	10.37	0.1185	0.0012	0.0009	18.82	0.1952	0.0051
2-5w	13.15	23.90	10.75	0.086	0.0009	0.0007	12.72	0.1367	0.0037
3-5w	13.05	24.12	11.07	0.0093	0.0001	0.0001	8.39	0.0929	0.0028
4-5w	13.01	23.20	10.19	0.0093	0.0001	0.0001	10.28	0.1048	0.0031
5-5w	13.08	24.10	11.02	0.0147	0.0002	0.0001	7.98	0.0879	0.0021
6-5w	13.01	23.59	10.58	0.0144	0.0002	0.0001	7.16	0.0758	0.0018
7-5w	13.02	23.66	10.64	0.0281	0.0003	0.0003	5.49	0.0584	0.0019
8-5w	12.98	23.61	10.63	0.0377	0.0004	0.0004	5.97	0.0635	0.0020

Table AIV-2: Percent Solids Data for Sequential Extractions

Sample	Tare	Total Wet	Total Dry	% Solids	Average
RLM-5	2.56	20.75	17.57	82.5	82.4
RLM-5	1.61	23.83	19.88	82.2	
RLM-2a	2.12	27.9	22.45	78.9	79.1
RLM-2b	1.68	27.55	22.19	79.3	
RLM-6a	1.83	21.21	17.47	80.7	80.7
RLM-6b	3.82	23.3	19.55	80.7	
Secondary Pond a	1.44	18.69	10.35	51.7	51.4
Secondary Pond b	2.07	25.15	13.86	51.1	

Table AIV-3: Summary Data for Sequential Extractions

Location	% Total Arsenic					
	Step 1	Step 2	Step 3	Step 4	Step 5	Residual
Secondary Pond Sediment	6.99	55.75	5.93	0.71	1.84	28.77
Secondary Pond Sediment	5.09	44.19	7.23	0.82	2.11	40.57
RLM-5	4.06	9.90	0.32	0.05	0.07	85.60
RLM-5	4.46	13.20	0.56	0.07	0.07	81.63
RLM-2-1	0.52	19.95	15.72	10.50	0.08	53.23
RLM-2-1	0.57	23.89	19.44	10.41	0.10	45.58
RLM-6-1	1.37	36.31	10.60	9.59	0.43	41.70
RLM-6-1	1.45	40.43	43.17	16.95	0.54	-2.54

Location	% Total Iron					
	Step 1	Step 2	Step 3	Step 4	Step 5	Residual
Secondary Pond Sediment	0.35	8.58	23.91	2.50	5.98	58.67
Secondary Pond Sediment	0.18	6.80	28.47	2.26	7.18	55.11
RLM-5	0.03	7.27	21.54	5.61	4.67	60.87
RLM-5	0.05	8.63	24.53	6.80	5.37	54.63
RLM-2-1	0.13	3.90	24.92	20.38	3.53	47.14
RLM-2-1	0.17	4.31	27.29	19.99	4.01	44.24
RLM-6-1	0.05	6.40	9.66	18.24	4.91	60.75
RLM-6-1	0.02	9.10	27.30	27.29	5.90	30.40

Location	mg As/Kg dry sediment					
	Step 1	Step 2	Step 3	Step 4	Step 5	Residual
Secondary Pond Sediment	187	1489	158	19	49	768
Secondary Pond Sediment	136	1180	193	22	56	1083
RLM-5	82	199	6	1	1	1725
RLM-5	90	266	11	1	2	1645
RLM-2-1	18	686	541	361	3	1831
RLM-2-1	20	822	669	358	3	1568
RLM-6-1	35	926	270	245	11	1063
RLM-6-1	37	1031	1101	432	14	-65

Location	mg Fe/Kg dry sediment					
	Step 1	Step 2	Step 3	Step 4	Step 5	Residual
Secondary Pond Sediment	253	6118	17046	1782	4267	41835
Secondary Pond Sediment	131	4845	20303	1608	5121	39292
RLM-5	23	5415	16051	4182	3481	45348
RLM-5	35	6426	18276	5063	4000	40700
RLM-2-1	113	3502	22355	18278	3167	42285
RLM-2-1	152	3862	24483	17928	3593	39683
RLM-6-1	43	5492	8285	15647	4210	52122
RLM-6-1	21	7804	23422	23411	5062	26080

Appendix V: Column Experiment Results

July 4th Probe Readings (before addition)

Location	Depth m	Temp Celcius	SPC	DO mg/L	pH units	ORP	Water Level inches
Column 1	0	19.66	1.441	4.63	7.72	102	60.5
	0.4	19.35	1.439	4.35	7.71	102	
	0.8	19.14	1.44	4.67	7.7	101	
	1.2	18.75	1.443	5.31	7.69	101	
Column 2	0	20.18	1.447	4.7	7.73	103	65.0
	0.4	19.64	1.444	4.56	7.73	101	
	0.8	19.18	1.443	4.49	7.73	99	
	1.4	18.5	1.445	4.66	7.73	92	
Column 3	0	21.33	1.444	5.12	7.73	100	70.5
	0.3	20.65	1.441	4.8	7.73	101	
	0.8	19.58	1.441	4.67	7.72	98	
	1.5	18.6	1.446	4.76	7.72	88	
Column 4	0	20	1.44	5.63	7.73	100	63.0
	0.4	19.51	1.44	5.52	7.73	99	
	0.8	19.19	1.439	5.5	7.73	97	
	1.4	18.62	1.438	6.01	7.72	92	

July 6th Probe Readings

Location	Depth m	Temp Celcius	SPC	DO mg/L	pH units	ORP	Water Level inches
Column 1	0	20.29	1.47	4.35	7.68	117	59.0
	0.4	19.64	1.47	4.17	7.65	99	
	0.8	19.07	1.47	4.45	7.64	88	
	1.3	18.63	1.47	4.78	7.64	82	
Column 2	0	22.96	1.359	3.93	5.35	186	69.0
	0.4	20.43	1.368	3.99	5.56	148	
	0.8	19.31	1.371	4.06	5.57	143	
	1.5	18.73	1.375	4.39	5.61	143	
Column 3	0	23.54	2.01	3.8	5.55	215	75.5
	0.4	22.43	2.02	3.8	5.63	197	
	0.9	19.97	2.03	3.68	5.69	151	
	1.7	18.6	1.94	2.02	5.77	148	
Column 4	0	22.42	2.12	2.37	6	154	69.0
	0.4	20.74	2.12	2.3	5.99		
	0.8	19.45	2.13	2.61	5.98	108	
	1.5	18.82	2.13	2.54	6.02	110	

July 8th Probe Readings

Location	Depth m	Temp Celcius	SPC	DO mg/L	pH units	ORP	Water Level inches
Column 1	0	23.39	1.455	3.8	7.81	134	58.5
	0.3	23.09	1.454	4.26	7.8	132	
	0.8	22.74	1.455	3.88	7.79	129	
	1.3	21.59	1.461	3.39	7.71	128	
Column 2	0	25.74	1.375	2.56	5.46	216	68.5
	0.4	23.85	1.37	2.55	5.54	193	
	0.9	22.68	1.374	2.59	5.56	181	
	1.5	21.75	1.378	2.6	5.58	182	
Column 3	0	27.68	2.03	2.94	5.61	64	74.5
	0.4	24.33	2.03	2.82	5.69	235	
	1	22.99	2.03	2.95	5.71	244	
	1.6	21.67	2.03	2.91	5.76	231	
Column 4	0	26.02	2.14	1.92	6.11	-50	68.5
	0.3	23.54	2.13	1.62	6.06	122	
	0.8	22.88	2.13	1.76	6.06	109	
	1.4	21.91	2.14	1.9	6.12	97	

July 10th Probe Readings

Location	Depth m	Temp Celcius	SPC	DO mg/L	pH units	ORP	Water Level inches
Column 1	0	23.06	1.449	5.56	7.89	136	58.5
	0.4	22.52	1.448	5.32	7.87	139	
	0.9	22.08	1.451	4.97	7.84	144	
	1.3	21.93	1.453	5.48	7.79	164	
Column 2	0	24.85	1.384	3	5.38	220	67.5
	0.4	23.36	1.379	2.66	5.42	188	
	0.8	22.52	1.379	2.69	5.47	198	
	1.4	22.02	1.378	1.56	5.58	193	
Column 3	0	26.43	2.05	5.06	5.6	225	73.0
	0.4	23.63	2.05	5.09	5.59	178	
	1	22.47	2.06	4.91	5.59	175	
	1.6	22.11	2.06	2.52	5.64	170	
Column 4	0	24.48	2.14	1.99	5.99	137	68.0
	0.4	23.71	2.14	1.9	5.97	125	
	0.8	22.74	2.14	1.69	5.96	117	
	1.4	22.13	2.14	1.71	5.96	123	
Pond	0	24.09	1.8	6.5	7.81	135	63.0
	0.3	23.82	1.8	6.75	7.82	100	
	0.8	22.24	1.79	6.4	7.81	86	
	1.3	21.85	1.81	6.03	7.79	86	

July 11th Sampling

Location	Water level		Volume Removed ml
	Before inches	After inches	
Column 1	58.5	56.0	2060
Column 2	67.5	64.0	2883
Column 3	73.0	69.5	2883
Column 4	68.0	64.0	3295

Water level		Volume Evaporated ml
Initial inches	July 10th inches	
60.5	58.5	1648
70.0	67.5	2060
76.5	73.0	2883
70.0	68.0	1648

July 18th Probe Readings

Location	Depth m	Temp Celcius	SPC	DO mg/L	pH units	ORP	Water Level inches
Column 1	0	25.13	1.324	7.04	8.27	134	55.0
	0.4	25.05	1.323	6.73	8.27	134	
	0.8	24.97	1.322	7	8.27	133	
	1.2	24.67	1.324	6.84	8.24	133	
Column 2	0	22.03	1.286	4.7	5.71	184	62.0
	0.4	22.05	1.285	4.54	5.71	183	
	0.8	22.03	1.285	4.57	5.71	185	
	1.2	21.96	1.286	4.84	5.73	183	
Column 3	0	21.95	1.92	6.5	5.96	192	65.5
	0.4	21.92	1.92	6.1	5.96	194	
	0.9	21.88	1.92	6.31	5.97	197	
	1.4	21.86	1.92	6.42	5.97	189	
Column 4	0	25.1	1.96	3.49	6.21	-37	63.0
	0.4	25.01	1.96	3.68	6.21	-50	
	0.8	24.86	1.96	3.47	6.22	-59	
	1.2	24.51	1.97	3.79	6.3	-85	
Pond	0	21.97	2.08	4.88	7.61	145	62.0
	0.4	21.96	2.08	4.93	7.62	147	
	0.8	21.9	2.08	4.99	7.61	152	
	1.2	21.82	2.08	5.1	7.6	159	

July 24th Probe Readings

Location	Depth m	Temp Celcius	SPC	DO mg/L	pH units	ORP	Water Level inches
Column 1	0	21.62	1.325	5.54	7.98	79	55.0
	0.4	21.55	1.325	5.55	7.97	73	
	0.7	21.45	1.325	5.34	7.95	77	
	1.1	21.36	1.325	5	7.93	83	
Column 2	0	21.83	1.298	4.26	6.07	100	61.0
	0.4	21.68	1.297	5.00	6.07	105	
	0.8	21.61	1.297	4.17	6.15	104	
	1.1	21.46	1.296	4.76	6.33	100	
Column 3	0	21.77	1.95	5.85	6.39	118	64.5
	0.5	21.5	1.95	6.61	6.37	124	
	0.9	21.38	1.94	5.91	6.37	124	
	1.3	21.29	1.95	6.6	6.44	135	
Column 4	0	21.67	1.98	5.25	6.22	101	62.0
	0.4	21.54	1.98	4.95	6.6	105	
	0.8	21.43	1.97	4.48	6.61	105	
	1.2	21.31	1.98	5.06	6.65	107	
Pond	0	22.02	2.36	6.24	7.76	91	62.0
	0.4	21.98	2.36	6.26	7.76	90	
	0.9	21.9	2.36	6.15	7.76	90	
	1.3	21.84	2.36	6.04	7.75	90	

July 26th Sampling

Location	Water level		Volume Removed ml
	Before inches	After inches	
Column 1	55.0	52.0	2472
Column 2	61.0	57.5	2883
Column 3	64.0	61.0	2472
Column 4	62.0	58.0	3295

Water level		Volume Evaporated ml
July 11th inches	July 26th inches	
56.0	55.0	824
64.0	61.0	2472
69.5	64.0	4531
64.0	62.0	1648

August 1st Probe Readings

Location	Depth m	Temp Celcius	SPC	DO mg/L	pH units	ORP	Water Level inches
Column 1	0	18.11	1.332	4.52	7.62	118	52.5
	0.5	17.99	1.331	3.73	7.61	120	
	0.8	17.86	1.331	3.77	7.6	122	
	1.2	17.73	1.331	4.51	7.55	132	
Column 2	0	17.77	1.317	7.47	6.48	153	57.0
	0.4	17.68	1.316	6.75	6.53	137	
	0.8	17.63	1.315	6.9	6.69	136	
	1.2	17.54	1.313	7.04	6.96	134	
Column 3	0	17.87	1.96	8.16	6.95	170	60.3
	0.4	17.79	1.96	7.45	6.98	168	
	0.8	17.71	1.96	7.12	7.04	160	
	1.2	17.59	1.96	7.9	7.22	154	
Column 4	0	17.99	1.98	6.4	7	152	57.5
	0.4	17.87	1.99	6.43	6.99	170	
	0.8	17.83	1.98	6.42	6.98	171	
	1.1	17.68	1.99	6.35	6.93	169	
Pond	0	18.12	2.4	8.21	7.79	162	
	0.4	18.09	2.4	8.21	7.8	162	
	0.8	18.07	2.4	8.29	7.79	163	
	1.1	18.06	2.4	8.3	7.74	160	

August 7th Probe Readings

Location	Depth m	Temp Celcius	SPC	DO mg/L	pH units	ORP	Water Level inches
Column 1	0	21	1.337	6.36	7.54	117	52.0
	0.4	20.46	1.336	5.41	7.51	119	
	0.7	20.13	1.338	5.61	7.51	122	
	1.1	19.84	1.336	5.75	7.53	124	
Column 2	0	21.1	1.323	6.85	6.4	123	57.0
	0.4	20.87	1.32	5.65	6.35	123	
	0.7	20.58	1.32	7.13	6.23	122	
	1.2	20.1	1.316	4.54	5.82	136	
Column 3	0	21.21	1.97	9.51	7.18	97	60.0
	0.4	21.02	1.97	8.61	7.15	98	
	0.7	20.64	1.97	8.61	7.15	98	
	1.2	20.18	1.97	8.55	7.05	110	
Column 4	0	21.23	1.99	5.87	7.18	97	57.0
	0.4	20.8	1.99	6.65	7.14	114	
	0.7	20.32	1.99	6.99	7.09	120	
	1.2	20.13	1.99	5.87	7.17	117	
Pond	0	21.56	2.49	8.24	7.72	101	
	0.4	21.57	2.5	7.93	7.71	99	
	0.7	21.25	2.49	7.53	7.71	109	
	1.2	20.16	2.49	7.2	7.68	132	

August 9th Sampling (just metals)

Location	Water level		Volume Removed ml
	Before inches	After inches	
Column 1	52.0	51.5	412
Column 2	57.0	56.5	412
Column 3	60.0	59.5	412
Column 4	57.0	56.5	412

Water level		Volume Evaporated ml
July 26th inches	Aug 9th inches	
52.0	52.0	0
57.5	57.0	412
61.0	60.0	824
58.0	57.0	824

August 20th Probe Readings

Location	Depth m	Temp Celcius	SPC	DO mg/L	pH units	ORP	Water Level inches
Column 1	0	19.87	1.27	2.82	7.35	113	54.0
	0.4	19.59	1.27	2.7	7.34	115	
	0.8	19.42	1.271	2.54	7.36	105	
	1.1	19.41	1.266	3.35	7.4	104	
Column 2	0	19.77	1.257	4.02	5.37	132	57.5
	0.3	19.56	1.256	3.73	5.38	128	
	0.7	19.43	1.256	3.94	5.46	123	
	1.1	19.2	1.256	4.22	5.68	111	
Column 3	0	20.1	1.88	4.64	7.11	117	60.3
	0.4	19.74	1.9	4.75	7.03	124	
	0.8	19.58	1.9	4.81	6.94	123	
	1.1	19.35	1.9	5.14	6.93	121	
Column 4	0	20.07	1.88	3.83	7.09	107	59.0
	0.4	19.83	1.92	3.96	6.98	112	
	0.8	19.61	1.93	3.76	6.95	113	
	1.1	19.42	1.94	3.95	7.01	116	
Pond	0	20.2	2.21	5.26	7.49	102	
	0.4	19.96	2.2	4.89	7.48	104	
	0.8	19.68	2.21	4.54	7.47	107	
	1.2	19.55	2.21	5.02	7.45	111	

August 22nd Sampling (just metals)

Location	Water level		Volume Removed ml
	Before inches	After inches	
Column 1	53.5	51.5	1648
Column 2	57.0	54.5	2060
Column 3	59.5	57.0	2060
Column 4	57.5	56.0	1236

Water level		Volume Evaporated ml
Aug 9th inches	Aug 22nd inches	
51.5	53.5	-1648
56.5	57.0	-412
59.5	59.5	0
56.5	57.5	-824

August 27th Probe Readings

Location	Depth m	Temp Celcius	SPC	DO mg/L	pH units	ORP	Water Level inches
Column 1	0	17.93	1.287	3.16	7.51	143	51.8
	0.4	17.89	1.286	3.15	7.46	149	
	0.8	17.73	1.287	3.66	7.39	164	
	1.2	17.63	1.286	3.61	7.21	179	
Column 2	0	17.94	1.276	3.29	4.91	194	54.5
	0.4	17.92	1.276	3.27	4.96	200	
	0.8	17.84	1.276	3.27	4.96	200	
	1.1	17.75	1.275	3.84	5.23	190	
Column 3	0	17.98	1.92	6.01	7.06	177	57.0
	0.4	17.98	1.92	5.29	7.02	175	
	0.8	17.94	1.93	5.81	6.95	168	
	1.1	17.76	1.93	6.35	6.91	166	
Column 4	0	17.96	1.94	4.61	7.2	131	55.8
	0.4	17.89	1.94	3.94	7.19	130	
	0.8	17.84	1.94	3.86	7.17	128	
	1	17.75	1.94	4.93	7.18	132	
Pond	0	18.11	2.3	6.72	7.73	124	
	0.4	18.11	2.31	6.42	7.73	120	
	0.9	18.1	2.31	6.32	7.73	120	
	1.2	18.1	2.31	6.52	7.73	129	

Sept. 17-18th Sampling

Location	Water level		Volume Removed ml
	Before inches	After inches	
Column 1	52.8	50.5	1854
Column 2	55.0	52.0	2472
Column 3	58.0		
Column 4	57.0	54.0	2472

Water level		Volume Evaporated ml
Aug 22nd inches	Sep 17th inches	
51.5	52.8	-1071
54.5	55.0	-412
57.0	58.0	-824
56.0	57.0	-824

Parameter	Units	Column 1 (Control)											
		4-Jul (Before Addition)				26-Jul				9-Aug			
		C1-Bottom	C1-Top	C1-Bottom	C1-Top	C1-Bottom	C1-Top	C1-Bottom	C1-Top	C1-Bottom	C1-Top	C1-Bottom	C1-Top
As	mg/L	1.1	1.19	1.07	1.09	1.14	1.1	0.99	0.98	1.08	1.05		
Ammonia	mg/L			8.53	8.89			5.44	11.4	4.15	3.97		
Cl	mg/L		132	131	132			123	124	129	125		
DOC	mg/L			11	11			10	11	11	9		
Nitrate	mg/L		5.5	4.9	4.96			6.27	6.33	7.75	7.79		
Phosphate	mg/L			<0.04	<0.04			<0.04	0.04	<0.04	<0.04		
Sulphate	mg/L		445	457	456			424	429	440	435		
Ag	mg/L	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001		
Al	mg/L	0.482	0.726	0.072	0.083	0.053	0.065	0.054	0.039	0.026	0.025		
B	mg/L	0.14	0.14	0.14	0.14	0.16	0.16	0.14	0.14	0.14	0.14		
Ba	mg/L	0.0293	0.0319	0.0319	0.0307	0.0312	0.0308	0.028	0.0288	0.0304	0.0286		
Be	mg/L	<0.0002	<0.0002	<0.0002	<0.0002	0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002		
Cd	mg/L	0.013	0.014	0.016	0.017	0.009	0.009	0.008	0.009	0.025	0.026		
Co	mg/L	0.067	0.07	0.065	0.069	0.064	0.063	0.059	0.059	0.058	0.06		
Cr	mg/L	0.0014	0.0026	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007		
Cu	mg/L	0.0351	0.0544	0.0288	0.0317	0.025	0.0283	0.0192	0.024	0.0188	0.0211		
Mo	mg/L	0.034	0.031	0.036	0.025	0.026	0.027	0.024	0.025	0.042	0.031		
Ni	mg/L	0.016	0.021	0.013	0.013	0.011	0.015	0.011	0.012	0.012	0.01		
Pb	mg/L	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006		
Sn	mg/L	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006		
Sr	mg/L	0.786	0.794	0.821	0.817	0.822	0.826	0.77	0.765	0.8	0.805		
Ti	mg/L	<0.006	0.011	<0.006	<0.006	<0.006	0.011	<0.006	<0.006	<0.006	<0.006		
Tl	mg/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05		
V	mg/L	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.007	0.012		
Zn	mg/L	0.019	0.045	<0.006	0.009	<0.006	0.009	0.007	<0.006	0.01	0.012		
Ca	mg/L	167	168	176	174	177	177	170	165	169	171		
K	mg/L	23.9	23.8	24.8	24.5	24.6	24.6	23	23.5	23.4	23.7		
Mg	mg/L	22.5	23	22.6	22.2	23	23	21.7	21.5	21.8	21.9		
Na	mg/L	73.1	73.3	76.1	74.3	74.5	75	71.3	70.3	69.9	69.7		
Fe	mg/L	0.44	0.726	0.015	0.012	0.042	0.027	0.032	0.022	0.018	0.007		
Mn	mg/L	0.107	0.124	0.0111	0.0038	0.0187	0.0078	0.0169	0.0035	0.0063	0.0014		

Parameter	Units	Column 2 (Peat)											
		4-Jul (Before Addition)			26-Jul			9-Aug					
		C2-Bottom	C2-Middle	C2-Top	C2-Bottom	C2-Middle	C2-Top	C2-Bottom	C2-Middle	C2-Top	C2-Bottom	C2-Middle	C2-Top
As	mg/L	1.23		1.22	1.36	1.03	1.18	1.21	0.73		1.21	0.73	1.21
Ammonia	mg/L				14	14.8	14.5						
Cl	mg/L			132	129	128	138						
DOC	mg/L				22	26	18						
Nitrate	mg/L			5.43	5.15	3.16	5.49						
Phosphate	mg/L				<0.04	0.09	<0.04						
Sulphate	mg/L			444	478	435	480						
Ag	mg/L	<0.0001		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Al	mg/L	0.33		0.448	0.045	0.057	0.044	0.049	0.078	0.045	0.049	0.078	0.045
B	mg/L	0.14		0.14	0.16	0.12	0.14	0.15	0.1	0.15	0.15	0.1	0.15
Ba	mg/L	0.0295		0.0313	0.473	0.0483	0.0546	0.0582	0.0333	0.0523	0.0582	0.0333	0.0523
Be	mg/L	<0.0002		<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	0.0003	0.0005	<0.0002	0.0003	0.0005
Cd	mg/L	0.013		0.014	0.02	0.014	0.017	0.009	0.007	0.01	0.009	0.007	0.01
Co	mg/L	0.067		0.068	0.069	0.059	0.072	0.064	0.05	0.066	0.064	0.05	0.066
Cr	mg/L	0.0008		0.0017	<0.0007	<0.0007	<0.0007	<0.0007	0.0007	0.0009	<0.0007	0.0007	0.0009
Cu	mg/L	0.0392		0.0469	0.0067	0.0027	0.0094	0.0052	0.0028	0.0053	0.0052	0.0028	0.0053
Mo	mg/L	0.032		0.031	0.018	0.019	0.015	0.01	0.0007	0.017	0.01	0.0007	0.017
Ni	mg/L	0.016		0.021	0.003	<0.002	0.002	<0.002	0.003	0.005	<0.002	0.003	0.005
Pb	mg/L	<0.006		<0.006	<0.006	0.027	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Sn	mg/L	<0.006		<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Sr	mg/L	0.785		0.801	0.617	0.546	0.608	0.599	0.497	0.6	0.599	0.497	0.6
Ti	mg/L	<0.006		0.006	<0.006	<0.006	<0.006	<0.006	<0.006	0.006	<0.006	<0.006	0.006
Tl	mg/L	<0.05		<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
V	mg/L	<0.002		<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Zn	mg/L	0.021		0.037	0.017	0.028	0.033	0.013	0.011	0.02	0.013	0.011	0.02
Ca	mg/L	172		174	149	131	145	143	119	146	143	119	146
K	mg/L	24.1		24.3	26.6	24.8	25.5	25.2	25.8	25.4	25.2	25.8	25.4
Mg	mg/L	22.6		23.1	26.7	24.4	25.6	26.1	23.5	26.4	26.1	23.5	26.4
Na	mg/L	73.2		75	81.3	75.4	77.1	78.3	76.3	77.7	78.3	76.3	77.7
Fe	mg/L	0.294		0.43	0.274	0.705	0.061	0.046	1.3	0.037	0.046	1.3	0.037
Mn	mg/L	0.104		0.111	0.149	0.127	0.134	0.125	0.118	0.126	0.125	0.118	0.126

Parameter	Units	Column 2											
		22-Aug			18-Sep			17-Oct			C2-Bottom	C2-Middle	C2-Top
		C2-Bottom	C2-Middle	C2-Top	C2-Bottom	C2-Middle	C2-Top	C2-Bottom	C2-Middle	C2-Top			
As	mg/L	0.96	0.68	1.17	1.72	1.26	1.14	4.68	1.71	1.08			
Ammonia	mg/L	12	14.1	5.34	12.3	13.9	10.5	13.4	11.2	10.3			
Cl	mg/L	132	132	133	140	137	136	125	127	122			
DOC	mg/L	21	26	18	21	24	17	21	19	20			
Nitrate	mg/L	3.18	1.14	4.85	4.49	2.92	7.01	4.14	5.82	6.59			
Phosphate	mg/L	0.05	0.28	<0.04	<0.04	0.1	<0.04	<0.04	<0.04	0.26			
Sulphate	mg/L	437	396	453	441	412	470	414	447	443			
Ag	mg/L	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.001	<0.001	<0.001			
Al	mg/L	0.042	0.059	0.042	0.055	0.042	0.069	0.035	0.051	0.076			
B	mg/L	0.11	0.09	0.13	0.12	0.1	0.14	0.1	0.12	0.13			
Ba	mg/L	0.0363	0.0471	0.0603	0.049	0.0367	0.0631	0.0846	0.0453	0.0535			
Be	mg/L	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002			
Cd	mg/L	0.007	0.006	0.01	0.041	0.03	0.026	0.114	0.041	0.025			
Co	mg/L	0.055	0.047	0.064	0.054	0.048	0.067	0.047	0.055	0.058			
Cr	mg/L	0.0009	0.0009	<0.0007	0.0008	0.0007	0.001	<0.0007	<0.0007	<0.0007			
Cu	mg/L	0.0019	0.0013	0.0057	0.0023	0.0018	0.0044	0.0071	0.0033	0.0046			
Mo	mg/L	0.008	<0.006	0.009	0.009	0.008	0.012	0.012	0.006	0.017			
Ni	mg/L	0.002	<0.002	0.003	0.013	0.003	0.004	0.003	0.004	0.004			
Pb	mg/L	0.009	0.014	<0.006	<0.006	<0.006	0.022	0.025	0.151	<0.006			
Sn	mg/L	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006			
Sr	mg/L	0.531	0.482	0.583	0.548	0.516	0.595	0.507	0.541	0.557			
Ti	mg/L	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.008	<0.008	<0.008			
Tl	mg/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05			
V	mg/L	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	0.022	<0.001	<0.001			
Zn	mg/L	0.008	0.008	0.027	0.031	0.027	0.033	0.031	0.032	0.034			
Ca	mg/L	131	119	139	129	121	139	124	131	131			
K	mg/L	24.4	24.9	24.2	25	25.4	24.4	25	24.1	23.4			
Mg	mg/L	24.6	23.1	24.8	23.9	23.9	24.7	24.8	24.8	23.6			
Na	mg/L	74.7	75.6	75.2	73.9	73.5	74.6	72.7	72.5	70.4			
Fe	mg/L	0.769	1.26	0.041	0.664	1.18	0.042	0.454	0.147	0.039			
Mn	mg/L	0.129	0.116	0.129	0.132	0.129	0.136	0.14	0.138	0.132			

Parameter	Units	Column 3 (Peat + Gypsum)											
		4-Jul (Before Addition)			26-Jul			9-Aug					
		C3-Bottom	C3-Middle	C3-Top	C3-Bottom	C3-Middle	C3-Top	C3-Bottom	C3-Middle	C3-Top	C3-Bottom	C3-Middle	C3-Top
As	mg/L	1.16		1.18	2.65	0.78	1.21	3.15	0.49	1.27			
Ammonia	mg/L				16.6	15.9	13.7						
Cl	mg/L			133	130	137	139						
DOC	mg/L				39	27	18						
Nitrate	mg/L			5.4	<0.03	2.42	5.61						
Phosphate	mg/L				<0.04	<0.04	<0.04						
Sulphate	mg/L			449	1540	1120	1060						
Ag	mg/L	<0.0001		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Al	mg/L	0.595		0.261	0.032	0.028	0.028	0.06	0.036	0.043			
B	mg/L	0.14		0.13	0.1	0.15	0.25	0.07	0.14	0.27			
Ba	mg/L	0.0307		0.0298	0.115	0.0669	0.073	0.227	0.0314	0.0712			
Be	mg/L	<0.0002		<0.0002	<0.0002	<0.0002	<0.0002	0.0003	0.0003	<0.0002			
Cd	mg/L	0.014		0.013	0.04	0.012	0.018	0.024	0.004	0.01			
Co	mg/L	0.069		0.068	0.041	0.054	0.069	0.028	0.043	0.066			
Cr	mg/L	0.002		0.0014	<0.0007	<0.0007	<0.0007	<0.0007	0.0008	<0.0007			
Cu	mg/L	0.0374		0.046	0.0006	0.0014	0.0083	<0.0005	0.0018	0.006			
Mo	mg/L	0.028		0.037	0.023	0.022	0.026	0.024	0.026	0.017			
Ni	mg/L	0.021		0.017	0.011	<0.002	<0.002	0.011	0.003	0.004			
Pb	mg/L	<0.006		<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006			
Sn	mg/L	<0.006		<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006			
Sr	mg/L	0.787		0.797	2.47	2.9	1.16	3.63	3.46	1.26			
Ti	mg/L	0.008		<0.006	<0.006	<0.006	<0.006	0.008	<0.006	<0.006			
Tl	mg/L	<0.05		<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05			
V	mg/L	<0.002		<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002			
Zn	mg/L	0.011		0.017	<0.006	0.017	0.012	<0.006	<0.006	0.008			
Ca	mg/L	173		173	638	337	348	615	347	346			
K	mg/L	24.3		24.4	27.9	25.7	26.3	28.8	26.9	26.8			
Mg	mg/L	22.9		22.9	88.2	40	29.9	72	43.3	31.2			
Na	mg/L	74.3		74.7	75.7	77.9	79.5	77.8	80.6	80.6			
Fe	mg/L	0.584		0.244	8.49	0.721	0.035	10.3	0.845	0.03			
Mn	mg/L	0.109		0.101	0.345	0.153	0.149	0.32	0.151	0.141			

Parameter	Units	Column 3											
		22-Aug			18-Sep			17-Oct					
		C3-Bottom	C3-Middle	C3-Top	C3-Bottom	C3-Middle	C3-Top	C3-Bottom	C3-Middle	C3-Top	C3-Bottom	C3-Middle	C3-Top
As	mg/L	3.33	0.96	1.15	3.04	1.17	1.13	5.75	1.11	1.1	5.75	1.11	1.1
Ammonia	mg/L	18	13.3	13.3	18.7	12.5	11.7	16.2	10.9	10.9	16.2	10.9	10.9
Cl	mg/L	135	139	136	140	138	140	131	129	124	131	129	124
DOC	mg/L	30	17	18	30	16	15	23	18	19	23	18	19
Nitrate	mg/L	<0.03	4.83	4.97	0.03	4.62	4.66	<0.3	4.97	4.77	<0.3	4.97	4.77
Phosphate	mg/L	<0.04	0.05	0.07	0.08	<0.04	<0.04	<0.4	<0.04	<0.04	<0.4	<0.04	<0.04
Sulphate	mg/L	1890	1060	1050	1520	1050	1050	1710	1050	1010	1710	1050	1010
Ag	mg/L	<0.0001	<0.0001	<0.0001	0.0001	<0.0001	<0.0001	0.001	<0.001	<0.001	0.001	<0.001	<0.001
Al	mg/L	0.033	0.024	0.03	0.017	0.015	0.017	0.012	0.019	0.021	0.012	0.019	0.021
B	mg/L	<0.05	0.23	0.24	0.06	0.23	0.23	<0.05	0.21	0.22	<0.05	0.21	0.22
Ba	mg/L	0.248	0.0816	0.0668	0.0426	0.0745	0.0715	0.0728	0.0657	0.0655	0.0728	0.0657	0.0655
Be	mg/L	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Cd	mg/L	0.027	0.007	0.01	0.075	0.025	0.027	0.138	0.026	0.025	0.138	0.026	0.025
Co	mg/L	0.023	0.059	0.062	0.023	0.059	0.06	0.016	0.053	0.056	0.016	0.053	0.056
Cr	mg/L	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007	0.0007	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007
Cu	mg/L	<0.0005	0.0032	0.0055	<0.0005	0.0032	0.0035	<0.0005	0.0047	0.0036	<0.0005	0.0047	0.0036
Mo	mg/L	0.028	0.015	0.016	0.007	0.014	0.018	0.01	0.016	0.012	0.01	0.016	0.012
Ni	mg/L	0.006	<0.002	<0.002	0.006	0.004	0.005	0.009	0.007	0.004	0.009	0.007	0.004
Pb	mg/L	<0.006	0.336	<0.006	<0.006	0.092	<0.006	<0.006	0.049	<0.006	<0.006	0.049	<0.006
Sn	mg/L	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Sr	mg/L	3.25	1.87	1.32	3.12	1.68	1.67	3.57	1.79	1.77	3.57	1.79	1.77
Ti	mg/L	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008
Tl	mg/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
V	mg/L	<0.002	<0.002	<0.002	<0.002	0.005	<0.002	<0.001	0.004	0.002	<0.001	0.004	0.002
Zn	mg/L	<0.006	<0.006	0.008	0.015	0.016	0.024	0.018	0.023	0.018	0.018	0.023	0.018
Ca	mg/L	613	329	334	592	333	329	565	326	325	565	326	325
K	mg/L	28.8	25.9	26.3	28.2	25.9	25.9	27.1	24.9	25.1	27.1	24.9	25.1
Mg	mg/L	68.5	30.8	29.9	61.4	30.2	30	83.5	29.6	29.6	83.5	29.6	29.6
Na	mg/L	78.7	77.7	78.8	74.4	75.6	76.2	72	73.7	73	72	73.7	73
Fe	mg/L	11	0.053	0.043	11.4	0.03	0.011	18.8	0.029	0.029	18.8	0.029	0.029
Mn	mg/L	0.374	0.11	0.102	0.364	0.0246	0.023	0.684	0.0518	0.0518	0.684	0.0518	0.0518

Parameter	Units	Column 4 (Peat + Gypsum + Iron Fillings)											
		4-Jul (Before Addition)			26-Jul			9-Aug					
		C4-Bottom	C4-Middle	C4-Top	C4-Bottom	C4-Middle	C4-Top	C4-Bottom	C4-Middle	C4-Top	C4-Bottom	C4-Middle	C4-Top
As	mg/L	1.21		1.17	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ammonia	mg/L				17.9	13.2	13.3						
Cl	mg/L			132	159	134	135						
DOC	mg/L				16	12	13						
Nitrate	mg/L			5.37	0.06	4.86	4.88						
Phosphate	mg/L				<0.04	<0.04	0.04						
Sulphate	mg/L			442	1550	1090	1080						
Ag	mg/L	<0.0001		<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Al	mg/L	0.096		0.437	0.01	0.011	0.013	0.067	0.037	0.037	0.067	0.037	0.242
B	mg/L	0.14		0.14	0.64	0.27	0.27	0.69	0.29	0.29	0.69	0.29	0.24
Ba	mg/L	0.0319		0.0293	0.0593	0.0607	0.06	0.0583	0.0539	0.0539	0.0583	0.0539	0.0581
Be	mg/L	<0.0002		<0.0002	<0.0002	<0.0002	<0.0002	0.0002	0.0004	0.0004	0.0002	0.0004	0.0003
Cd	mg/L	0.014		0.013	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Co	mg/L	0.069		0.07	0.006	0.064	0.063	<0.003	0.054	0.054	<0.003	0.054	0.063
Cr	mg/L	<0.0007		0.0019	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007	<0.0007	0.0037
Cu	mg/L	0.0268		0.0443	<0.0005	0.0068	0.0127	<0.0005	0.0068	0.0284	<0.0005	0.0068	0.0284
Mo	mg/L	0.028		0.025	0.074	0.036	0.035	0.065	0.032	0.03	0.065	0.032	0.03
Ni	mg/L	0.016		0.017	0.002	0.02	0.019	<0.002	0.017	0.047	<0.002	0.017	0.047
Pb	mg/L	<0.006		<0.006	<0.006	<0.006	<0.006	<0.006	0.017	0.036	<0.006	0.017	0.036
Sn	mg/L	<0.006		<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Sr	mg/L	0.826		0.786	3.13	1.52	1.5	3.75	1.73	1.64	3.75	1.73	1.64
Ti	mg/L	<0.006		<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Tl	mg/L	<0.05		<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
V	mg/L	<0.002		<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Zn	mg/L	0.012		0.019	<0.006	0.018	0.027	<0.006	0.01	0.024	<0.006	0.01	0.024
Ca	mg/L	178		172	608	372	372	591	362	353	591	362	353
K	mg/L	25		24	33.6	25.7	25.6	31.9	25.6	25.3	31.9	25.6	25.3
Mg	mg/L	23.3		22.7	26.3	26.2	26.2	23.4	27.2	26.3	23.4	27.2	26.3
Na	mg/L	76.1		74.7	84.6	76.6	77.2	82.2	76.1	74.8	82.2	76.1	74.8
Fe	mg/L	0.052		0.441	0.043	0.525	0.489	0.318	0.816	8.19	0.318	0.816	8.19
Mn	mg/L	0.0977		0.106	0.491	0.672	0.668	0.435	0.636	0.679	0.435	0.636	0.679

Parameter	Units	Column 4						
		22-Aug			18-Sep			
		C4-Bottom	C4-Middle	C4-Top	C4-Bottom	C4-Middle	C4-Top	C4-Top
As	mg/L	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ammonia	mg/L	16.6	12	12.3	18.5	12.6	12.1	12.1
Cl	mg/L	150	130	128	151	128	129	129
DOC	mg/L	12	12	13	11	10	11	11
Nitrate	mg/L	<0.03	4.83	3.84	<0.03	3.29	3.46	3.46
Phosphate	mg/L	<0.04	0.05	0.04	<0.04	0.1	<0.04	<0.04
Sulphate	mg/L	1770	1060	1090	1400	1080	1080	1080
Ag	mg/L	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Al	mg/L	0.045	0.02	0.018	0.013	0.014	0.017	0.017
B	mg/L	0.61	0.26	0.25	0.47	0.24	0.25	0.25
Ba	mg/L	0.0528	0.0532	0.0534	0.0495	0.0528	0.0533	0.0533
Be	mg/L	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002
Cd	mg/L	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002	<0.002
Co	mg/L	0.004	0.052	0.05	0.004	0.046	0.044	0.044
Cr	mg/L	<0.0007	<0.0007	<0.0007	0.0011	<0.0007	<0.0007	<0.0007
Cu	mg/L	0.0005	0.0055	0.0055	<0.0005	0.0044	0.0043	0.0043
Mo	mg/L	0.06	0.026	0.029	0.034	0.025	0.029	0.029
Ni	mg/L	<0.002	0.013	0.014	<0.002	0.014	0.013	0.013
Pb	mg/L	<0.006	<0.006	<0.006	<0.006	<0.006	0.013	0.013
Sn	mg/L	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Sr	mg/L	3.33	1.76	1.72	2.86	2.16	2.14	2.14
Ti	mg/L	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006
Tl	mg/L	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
V	mg/L	<0.002	<0.002	<0.002	<0.002	<0.002	0.005	0.005
Zn	mg/L	<0.006	0.011	<0.006	0.006	0.024	0.028	0.028
Ca	mg/L	563	344	342	572	355	359	359
K	mg/L	31	24.5	23.8	29.5	24.3	24.4	24.4
Mg	mg/L	23.4	25.9	25.4	21.9	25.7	25.8	25.8
Na	mg/L	79.3	71.6	72.4	78	71	72.5	72.5
Fe	mg/L	0.119	0.16	0.126	0.048	0.097	0.088	0.088
Mn	mg/L	0.42	0.561	0.559	0.603	0.425	0.424	0.424

Appendix VI: Designed Laboratory Experiment Results

Date: Feb 24/25

 Temperature: 20.2 C
 Volume Removed: 20 ml

Trial Number	pH	Int. Wt.	Final Wt.	[As] mg/L	[Fe] mg/L	[DOC] mg/L	[Sulphate] mg/L	Comments
1	8.55		387.7	19.96	0.09	22.6		
2	8.93		388.8	12.72	0.02	13.4		
3	8.87		390.1	27.55	1.03	10.9		
4	8.85		406	0.66	1.20	7.9		
5	8.49		391.7	1.74	0.09	15.0		
6	9.01		403.2	2.78	0.02	9.7		
7	8.51		399.5	1.56	1.43	21.6		
8	8.75		386.1	9.80	0.05	19.4		
9	8.96		398.9	8.66	0.60	27.9		
10	8.87		375.4	6.24	3.04	17.8		
11	8.94		404.2	2.77	1.21	15.1		
12	8.61		388.2	1.42	0.95	17.3		
13	8.69			1.20	0.03	10.8		broke flask, new one made on 25th
14	8.6		385.2	2.59	0.04	20.6		
15	8.85		398	8.60	0.09	11.1		
16	8.66		387.1	2.50	0.58	6.7		
17	7.69		380	0.41	0.08	10.8		
18	7.23		391.7	5.05	0.03	33.5		
19	6.65		386.1	11.48	1.02	352.9		
20	7.4		396.1	0.14	3.30	8.3		
21	7.33		396.8	2.04	0.67	24.6		
22	7.46		383	0.35	1.82	9.9		
23	7.34		383.2	0.41	0.08	22.2		
24	7.37		387	5.72	0.05	24.2		
25	7.62		393.9	0.14	0.81	18.6		
26	7.68		393.2	0.12	0.69	9.4		
27	7.46		400.6	1.67	0.40	31.2		
28	7.24		381.9	5.06	1.89	35.9		
29	7.87		383.4	0.35	2.22	21.7		
30	7.39		394.2	3.84	0.10	22.3		
31	7.56		385.1	0.07	0.70	22.7		
32	7.31		381.3	7.48	1.15	22.7		

Date: Mar-04

Temperature: C
Volume Removed: 10 ml

Trial Number	pH	Int. Wt.	Final Wt.	[As] mg/L	[Fe] mg/L	[DOC] mg/L	[Sulphate] mg/L	Comments
1	7.7			2.29			619	
2	7.44			10.56			678	
3	8.18	384	374.2	14.96			2647	
4	8.28	399.8	390.1	1.80			1868	
5	8.04	385.6	375	2.04			709	
6	7.47			1.15			1959	
7	8.2	393.8	387.1	2.69			640	
8	8.29	380.3	371.4	15.32			714	
9	7.43			5.32			674	
10	7.68			8.44			1980	
11	8.31	398.2	389.4	7.28			2171	
12	7.75			1.69			589	
13	7.73			0.90			1807	
14	8.41	379.78	370.81	3.04			2065	
15	8.19	392.4	382.3	11.76			664	cloudy (others clear)
16	7.3			0.50			1961	
17	7.78	374.6	364.6	0.25			2001	
18	6.8			0.85			771	
19	7.61	381.2	371.73	6.44			719	
20	7.14			0.10			1829	
21	6.93			0.54			2029	
22	7.02			0.18			916	
23	7			0.23			947	
24	7.18	382.1	371.6	0.71			2103	
25	8.06	388.7	380.1	0.22			1939	
26	8.11	388.6	378.95	0.17			3217	
27	7.3	395.6	385.7	0.57			2290	
28	6.57			0.46			2248	
29	8.08	378.6	371.2	0.38			3517	
30	6.7	388.8	377.95	0.21			219	
31	7.17			0.15				
32	6.6			1.06			825	

Date: Mar-18

Temperature: 22.6 C
Volume Removed: 10 ml

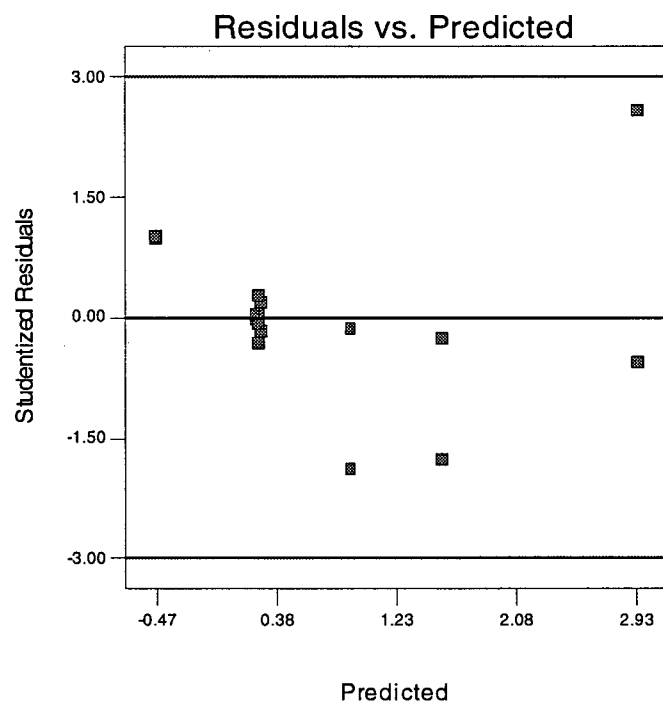
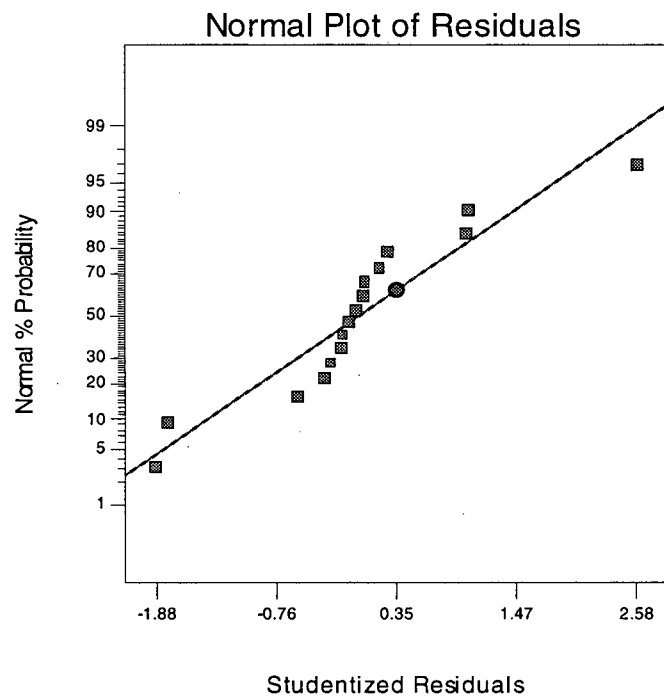
Trial Number	pH	Int. Wt.	Final Wt.	[As] mg/L	[Fe] mg/L	[DOC] mg/L	[Sulphate] mg/L	Comments
1	7.51			2.03		8.0		no black, all grey
2	7.55			4.81		8.3		no black, all grey
3	7.71	366.96	358.52	7.72		9.3		no dark spots, grey brown throughout
4	7.88	383.08	373.25	1.51		8.6		darker shading on bottom, likely just Fe0
5	7.7	368.03	357.52	0.29		10.1		no dark spots, grey brown throughout
6	8.12			0.04		3.8		orange water, lots of black/shiny
7	8.02	380.43	370.41	2.64		8.9		darker shading on bottom, likely just Fe0
8	8.11	364.54	354.53	9.68		12.5		no dark spots, grey brown throughout
9	7.18			0.05		4.5		black/shiny
10	7.93			5.24		8.1		no black, all grey
11	7.9	382.76	372.41	1.50		6.7		black/shiny on bottom (some), and some orange spots on top
12	7.63			1.57		7.5		darker shading on bottom, likely just Fe0
13	8.1			1.32		8.9		darker shading on bottom, likely just Fe0
14	8.16	364.11	354.94	1.74		8.6		no dark spots, grey brown throughout
15	7.9	375.07	364.88	6.20		8.8		black/shiny on bottom
16	7.38			0.50		11.1		darker shading on bottom, likely just Fe0
17	7.31	357.53	346.87	0.12		8.8		pure brown, no black
18	6.43			0.09		9.5		tonnes of black/shiny, layering and bubbles
19	6.59	365.01	354.58	4.64		769.3		no black, still colloidal, bubbles in solids
20	7.27			0.14		7.0		darker shading on bottom, likely just Fe0
21	6.48			0.12		9.0		darker shading on bottom, likely just Fe0, layering and bubbles
22	7.1			0.16		6.9		darker shading on bottom, likely just Fe0
23	7.04			0.19		11.3		darker shading on bottom, likely just Fe0
24	7.06	365.28	354.84	0.23		20.9		really murky water, no black, layering and bubbles
25	7.69	373.9	365.59	0.27		6.2		darker shading on bottom, likely just Fe0
26	7.25	373.06	363.58	0.19		7.1		darker shading on bottom, likely just Fe0
27	6.91	379.76	369.01	0.09		10.8		orange precip. On top of solids, layering with bubbles, then black/shiny
28	6.72			0.24		15.2		no black, layering and bubbles
29	7.57	364.31	354.35	0.27		9.5		pure brown, no black
30	6.84	371.84	361.04	0.22		13.4		green layer, brown layer with bubbles, black layer, grey layer
31	7.4			0.11		7.6		darker shading on bottom, likely just Fe0
32	6.62			0.24		15.2		layering and bubbles, no black

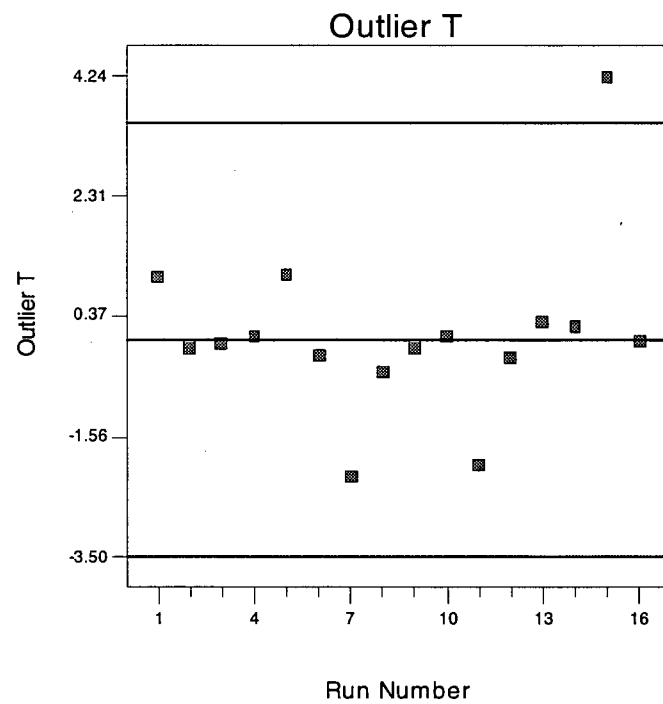
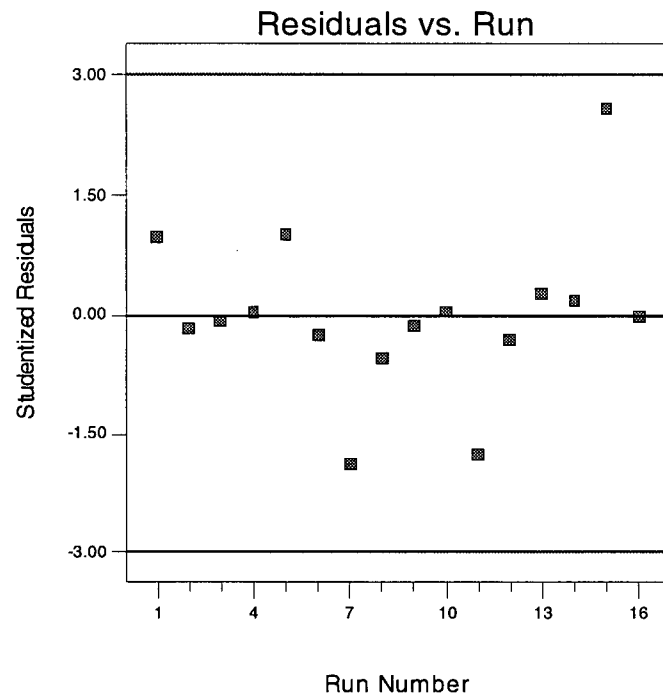
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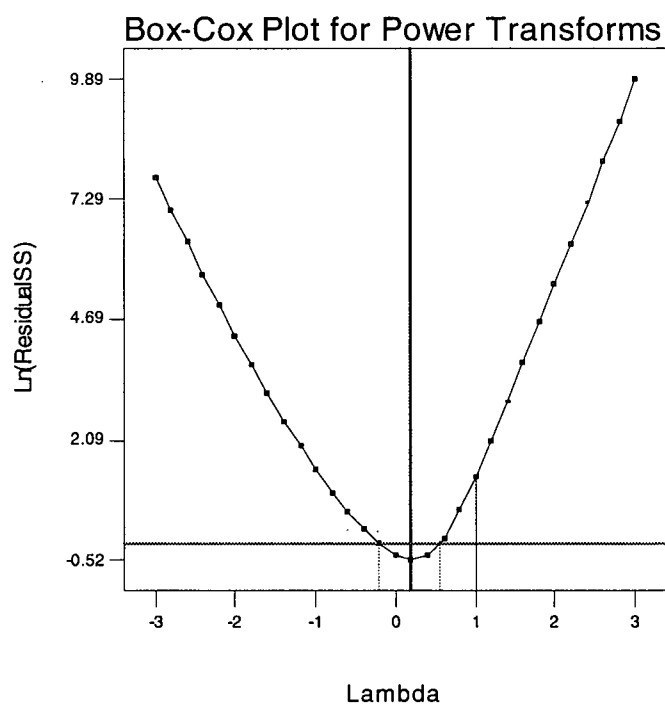
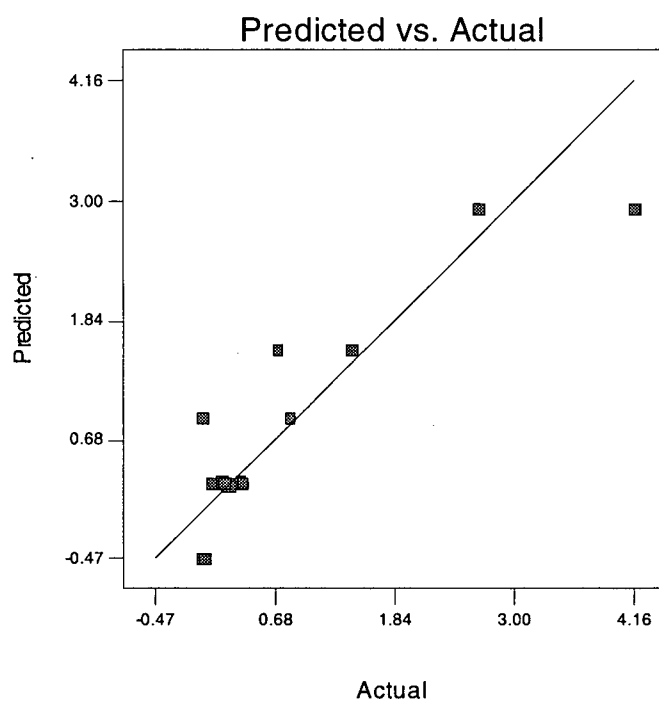
Temperature: C
Volume Removed: 30 ml

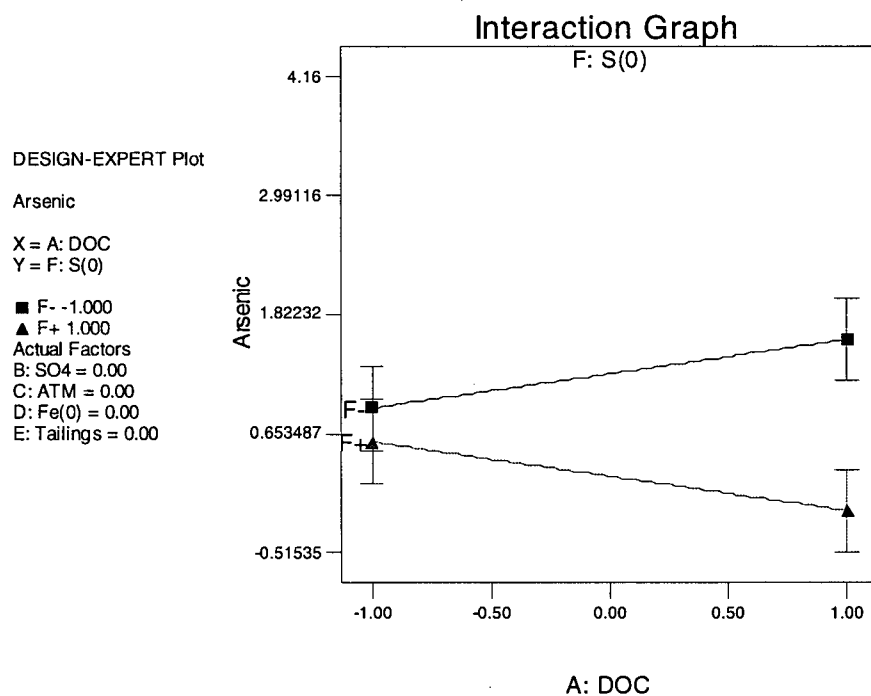
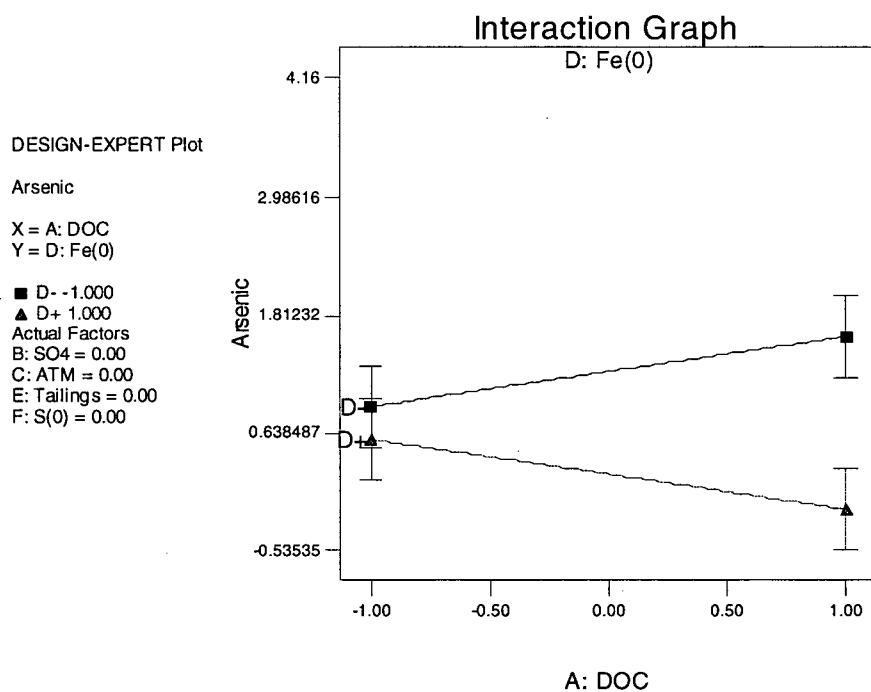
Trial Number	pH	Int. Wt.	Final Wt.	[As] mg/L	[Fe] mg/L	[DOC] mg/L	[Sulphate] mg/L	Comments
1				0.36	0.006	10.2	1240	no black, all grey
2				0.71	0.033	5.8	839	no black, all grey
3				1.43	0.560	10.2	2482	no dark spots, grey brown throughout
4				0.21	0.119	7.0	2260	darker shading on bottom, likely just Fe0
5				0.10	0.065	9.4	424	no dark spots, grey brown throughout
6				0.00	0.004	4.5	581	orange water, lots of black/shiny
7				0.25	0.042	5.3	312	darker shading on bottom, likely just Fe0
8				2.66	0.142	8.0	933	no dark spots, grey brown throughout
9				0.00	0.021	3.1	1321	black/shiny
10				4.16	0.008	8.8	2270	no black, all grey
11				0.02	0.039	2.9		black/shiny on bottom (some), and some orange spots on top
12				0.28	0.080	6.2	728	darker shading on bottom, likely just Fe0
13				0.22	0.019	4.5	2126	darker shading on bottom, likely just Fe0
14				0.19	0.127	10.9	3064	no dark spots, grey brown throughout
15				0.83	0.070	4.8	1500	black/shiny on bottom
16				0.38	0.012	10.9	2749	darker shading on bottom, likely just Fe0
17				0.06	0.007	9.7	2720	pure brown, no black
18				1.25	0.038	6.4	2081	tonnes of black/shiny, layering and bubbles
19								no black, still colloidal, bubbles in solids
20				0.13	0.008	3.2	2327	darker shading on bottom, likely just Fe0
21				0.17	0.093	8.1	3706	darker shading on bottom, likely just Fe0, layering and bubbles
22				0.09	0.011	4.4	4066	darker shading on bottom, likely just Fe0
23				0.11	0.025	9.8	2614	darker shading on bottom, likely just Fe0
24				0.58	0.040	16.2	2936	really murky water, no black, layering and bubbles
25				0.13	0.019	4.4	2482	darker shading on bottom, likely just Fe0
26				0.17	0.050	6.1	4054	darker shading on bottom, likely just Fe0
27				0.10	0.294	6.9	3675	orange precip. On top of solids, layering with bubbles, then black/shiny
28				0.66	0.100	18.7	2964	no black, layering and bubbles
29				0.14	0.074	9.5	2261	pure brown, no black
30				5.12	1.220	14.2	2049	green layer, brown layer with bubbles, black layer, grey layer
31				0.16	0.016	5.9	3984	darker shading on bottom, likely just Fe0
32				0.63	0.049	16.5	1148	layering and bubbles, no black

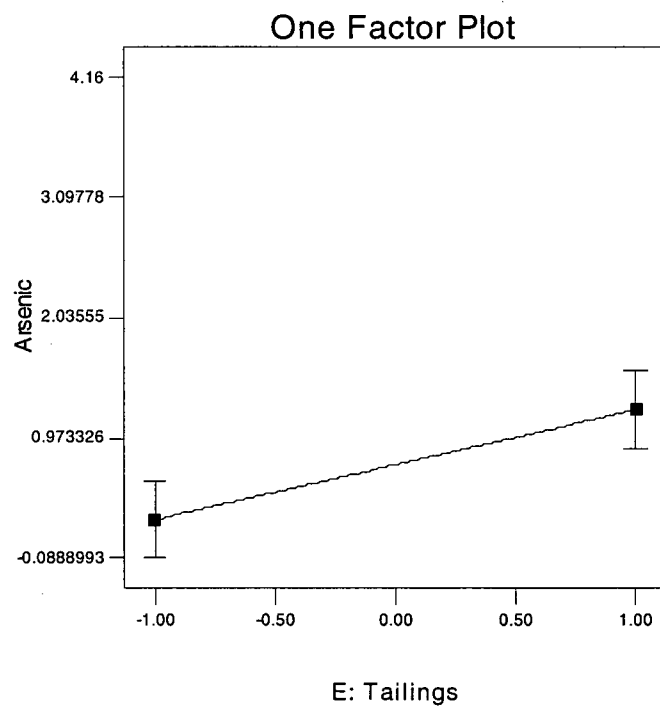
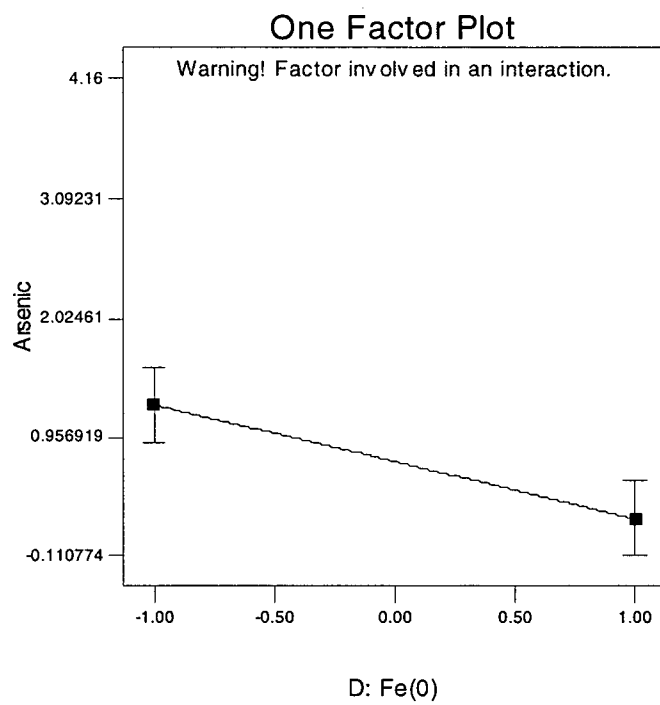
Appendix VII: Design Ease Results

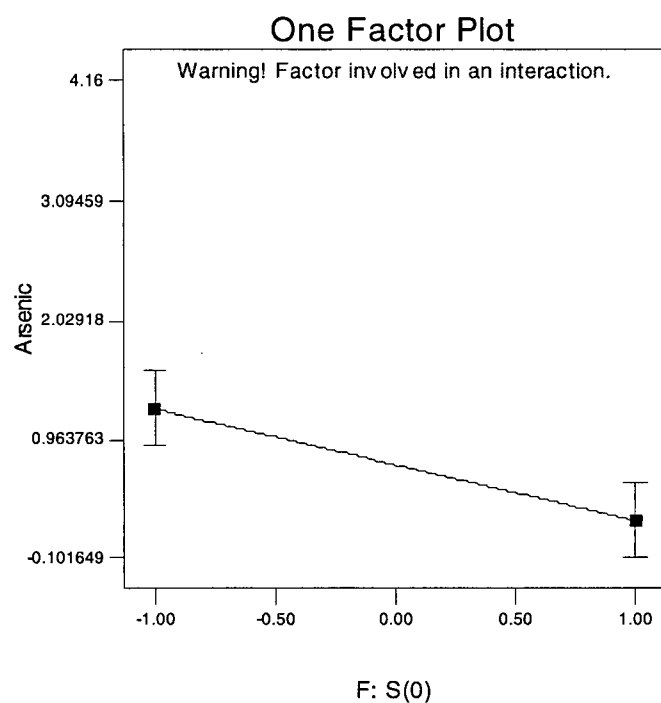
Set 1 – Day 40 Design Ease Graphs and ANOVA Table





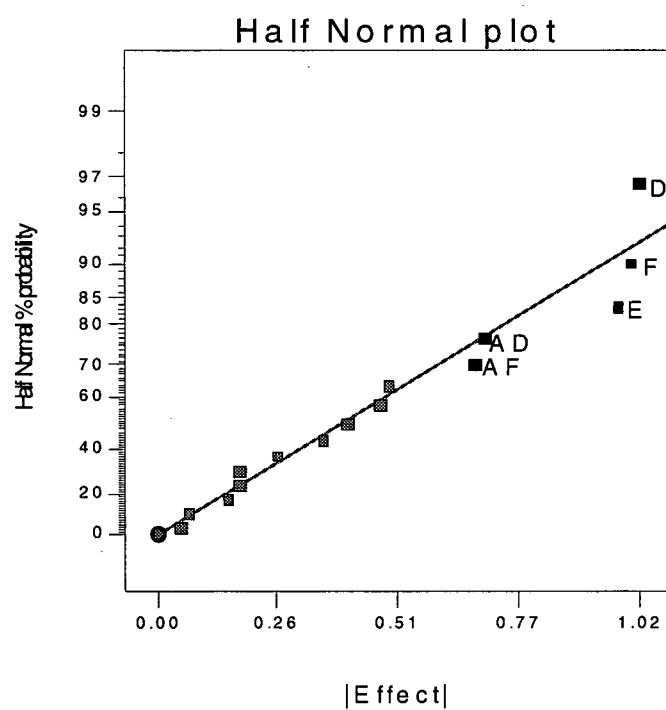






DESIGN-EXPERT Plot
Arsenic

A: DOC
B: SO₄
C: ATM
D: Fe(0)
E: Tailings
F: S(0)



Response: Arsenic

ANOVA for Selected Factorial Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob >F	
Model	15.84	5	3.17	8.69	0.0021	significant
D	4.19	1	4.19	11.49	0.0069	
E	3.84	1	3.84	10.53	0.0088	
F	4.04	1	4.04	11.08	0.0076	
AD	1.95	1	1.95	5.35	0.0433	
AF	1.83	1	1.83	5.02	0.0490	
Residual	3.64	10	0.36			
Cor Total	19.482	15				

The Model F-value of 8.69 implies the model is significant. There is only a 0.21% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.

In this case D, E, F, AD, AF are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant.

If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	0.6037	R-Squared	0.8129
Mean	0.7370	Adj R-Squared	0.7194
C.V.	81.9113	Pred R-Squared	0.5211
PRESS	9.3296	Adeq Precision	9.2025

The "Pred R-Squared" of 0.5211 is in reasonable agreement with the "Adj R-Squared" of 0.7194.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 9.203 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	0.737	1	0.1509	0.4007	1.0733	
D-Fe(0)	-0.512	1	0.1509	-0.8478	-0.1752	1
E-Tailings	0.490	1	0.1509	0.1534	0.8259	1
F-S(0)	-0.502	1	0.1509	-0.8386	-0.1661	1
AD	-0.349	1	0.1509	-0.6853	-0.0127	1
AF	-0.338	1	0.1509	-0.6744	-0.0019	1

Final Equation in Terms of Coded Factors:

$$\begin{aligned}\text{Arsenic} &= \\ &0.737 \\ &-0.5115 * D \\ &0.489625 * E \\ &-0.502375 * F \\ &-0.349 * A * D \\ &-0.338125 * A * F\end{aligned}$$

Diagnostics Case Statistics								
Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	0.712	1.553	-0.841	0.375	-1.7629	0.3108	-2.0146	11
2	0.36	0.267	0.093	0.375	0.1941	0.0038	0.1845	14
3	0.376	0.246	0.130	0.375	0.2732	0.0075	0.2601	13
4	4.16	2.928	1.232	0.375	2.5822	0.6668	4.244 *	15
5	0.098	0.246	-0.148	0.375	-0.3093	0.0096	-0.2949	12
6	2.66	2.928	-0.268	0.375	-0.5608	0.0314	-0.5405	8
7	1.43	1.553	-0.123	0.375	-0.2585	0.0067	-0.2461	6
8	0.192	0.267	-0.075	0.375	-0.1579	0.0025	-0.1500	2
9	0.275	0.249	0.026	0.375	0.0542	0.0003	0.0514	4
10	0	-0.474	0.474	0.375	0.9940	0.0988	0.9933	1
11	0.003	0.900	-0.897	0.375	-1.8792	0.3532	-2.2167	7
12	0.218	0.227	-0.009	0.375	-0.0196	0.0000	-0.0186	16
13	0.832	0.900	-0.068	0.375	-0.1422	0.0020	-0.1351	9
14	0.254	0.227	0.027	0.375	0.0558	0.0003	0.0529	10
15	0.206	0.249	-0.043	0.375	-0.0904	0.0008	-0.0858	3
16	0.016	-0.474	0.490	0.375	1.0275	0.1056	1.0307	5

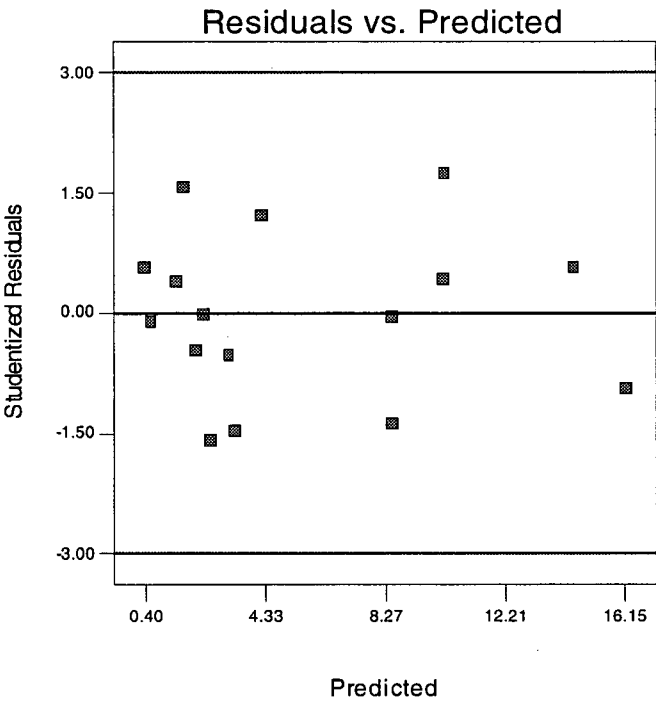
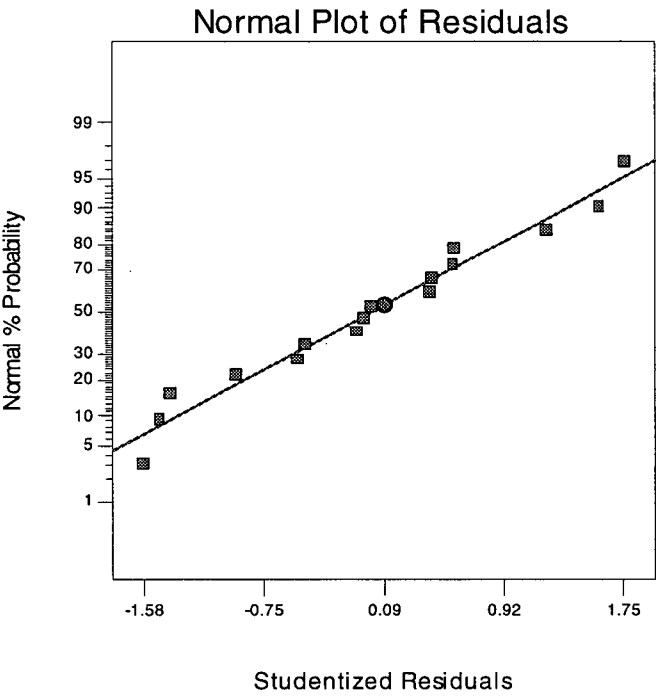
* Case(s) with |Outlier T| > 3.50

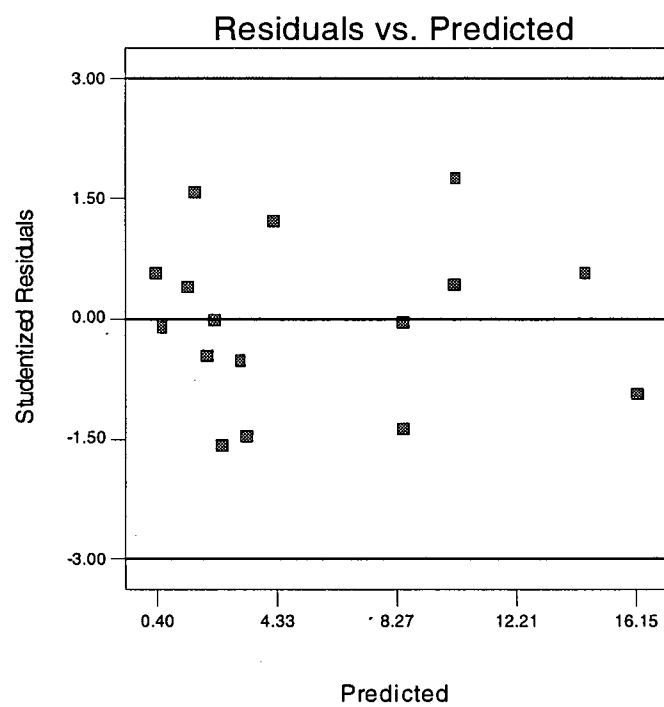
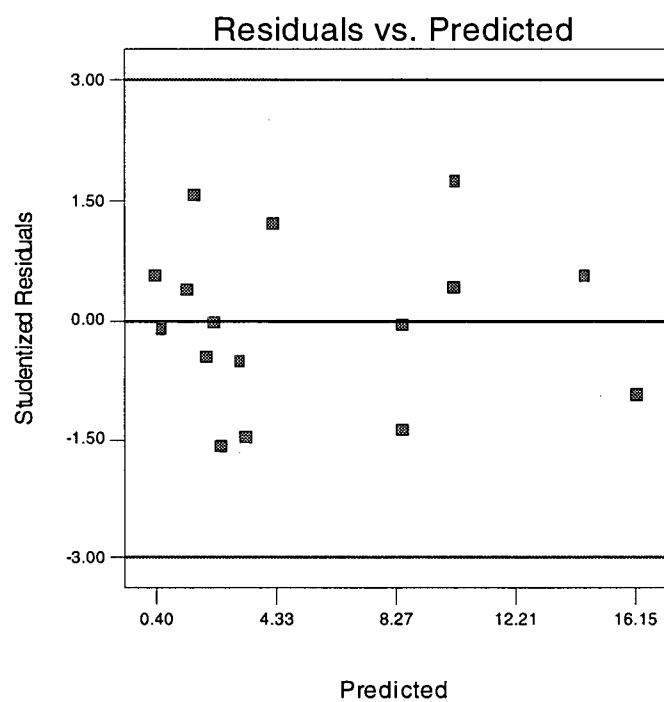
Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:

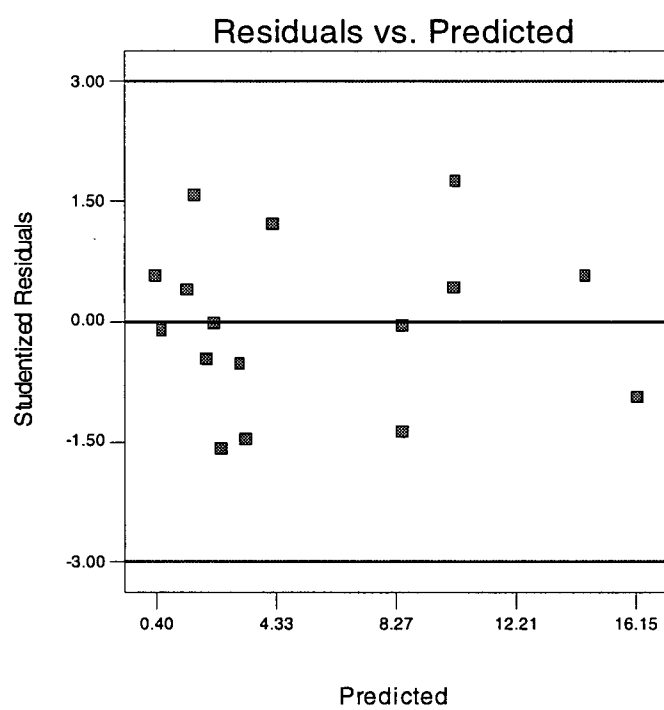
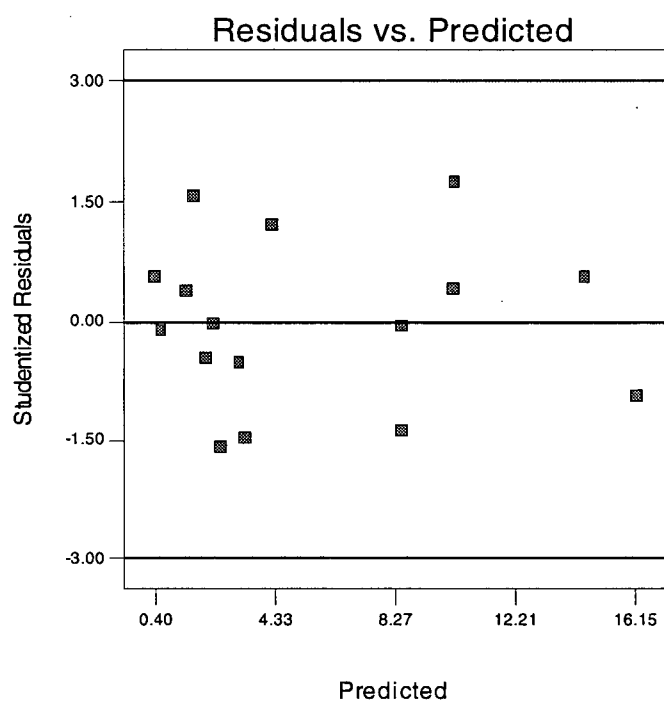
- 1) Normal probability plot of the studentized residuals to check for normality of residuals.
- 2) Studentized residuals versus predicted values to check for constant error.
- 3) Outlier t versus run order to look for outliers, i.e., influential values.
- 4) Box-Cox plot for power transformations.

If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.

Set 1 – Day 7 Design Ease Graphs and ANOVA Table







One Factor Plot

DESIGN-EXPERT Plot

Arsenic

X = C: ATM

Actual Factors

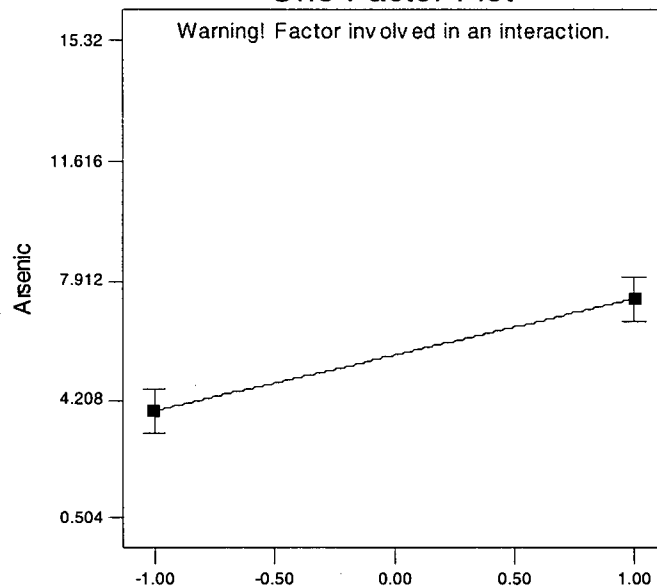
A: DOC = 0.00

B: SO₄ = 0.00

D: Fe(0) = 0.00

E: Tailings = 0.00

F: S(0) = 0.00



C: ATM

Interaction Graph

E: Tailings

DESIGN-EXPERT Plot

Arsenic

X = C: ATM

Y = E: Tailings

■ E- -1.000

▲ E+ 1.000

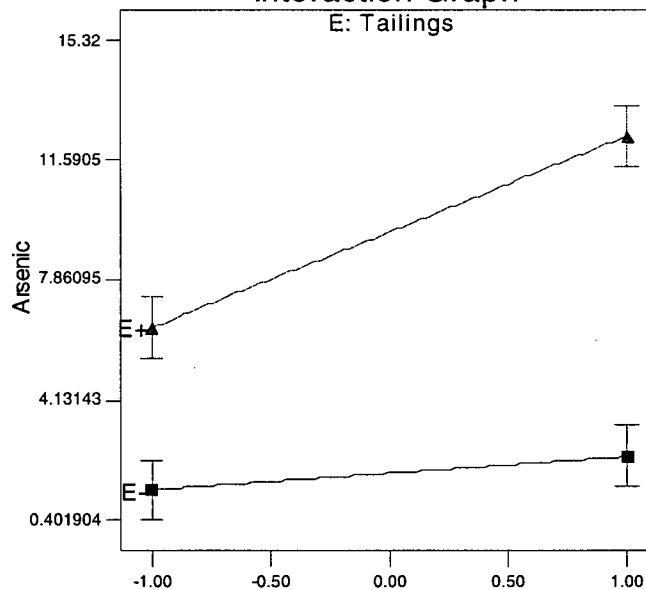
Actual Factors

A: DOC = 0.00

B: SO₄ = 0.00

D: Fe(0) = 0.00

F: S(0) = 0.00



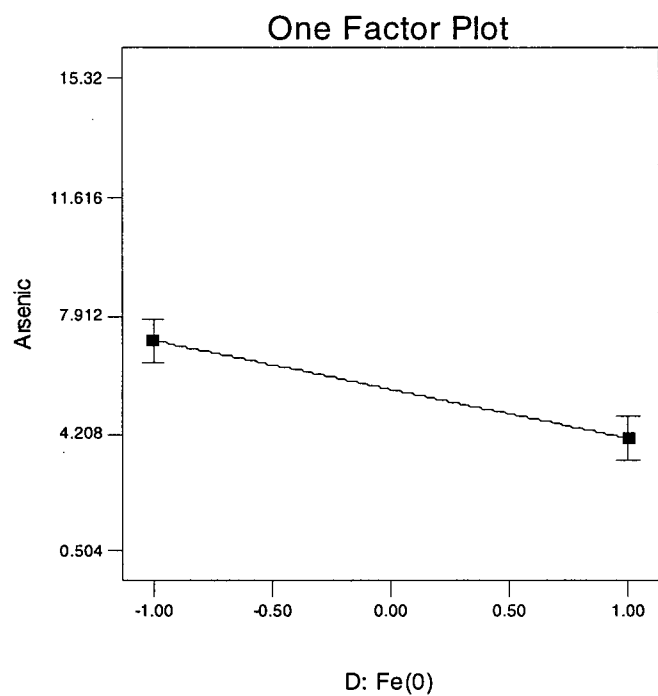
C: ATM

DESIGN-EXPERT Plot

Arsenic

X = D: Fe(0)

Actual Factors
A: DOC = 0.00
B: SO₄ = 0.00
C: ATM = 0.00
E: Tailings = 0.00
F: S(0) = 0.00

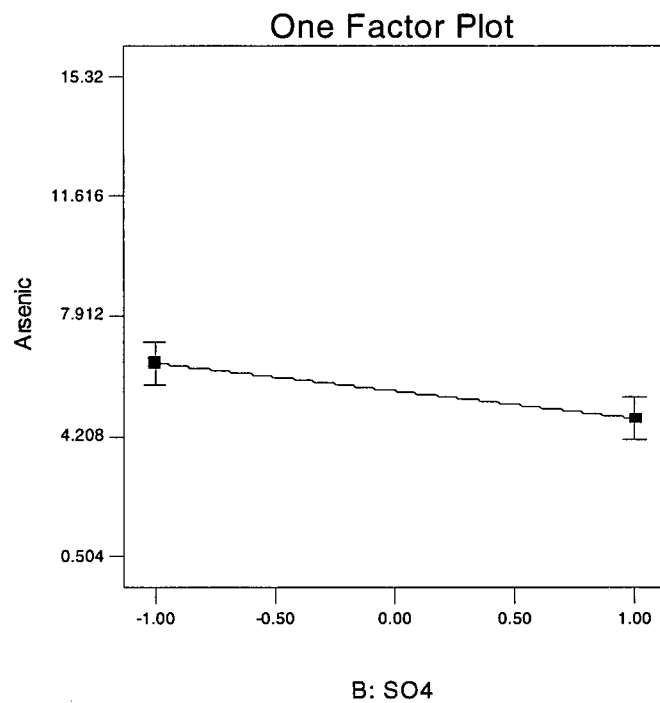


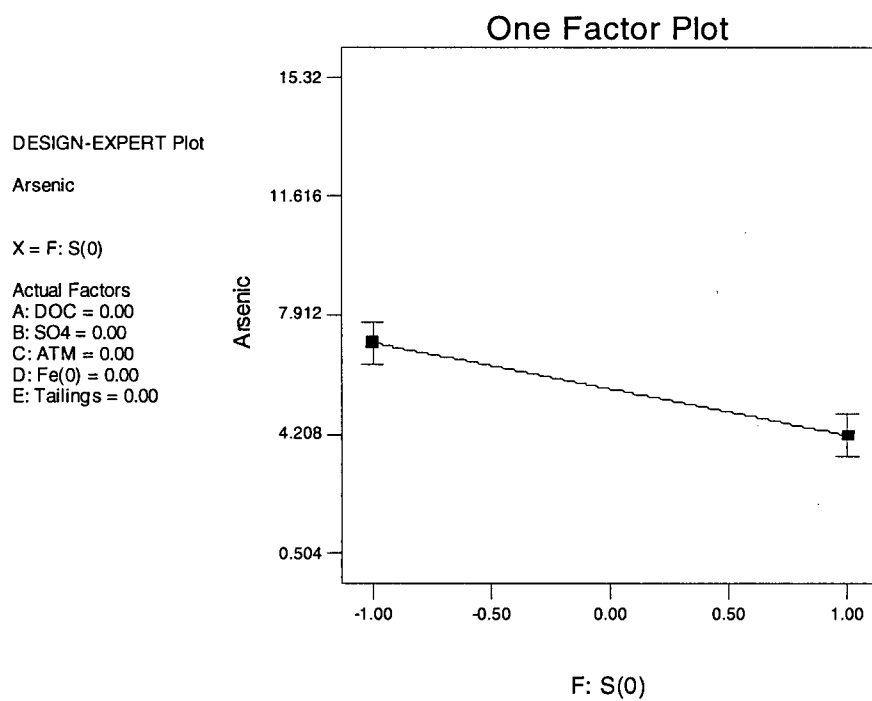
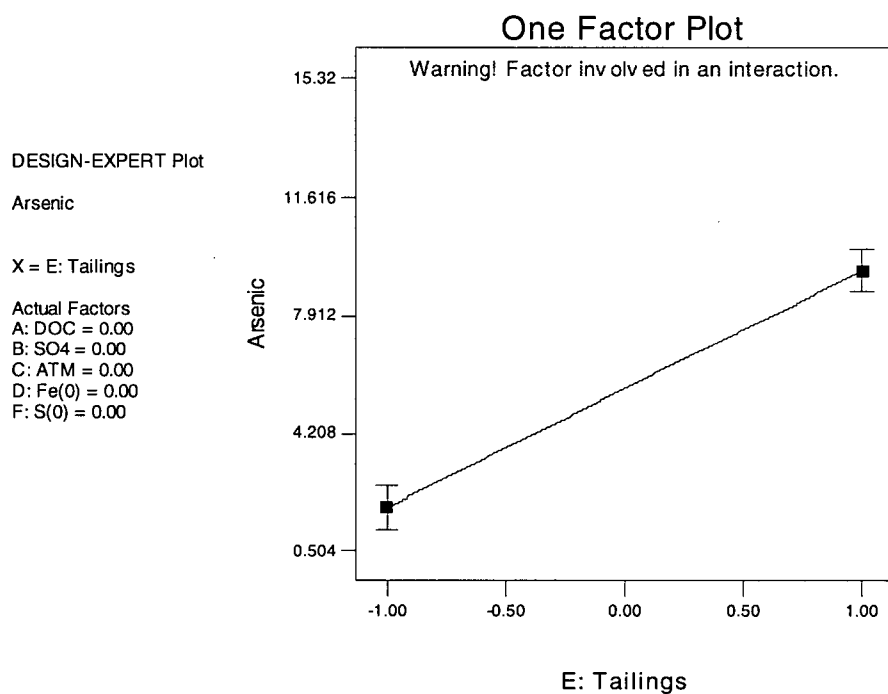
DESIGN-EXPERT Plot

Arsenic

X = B: SO₄

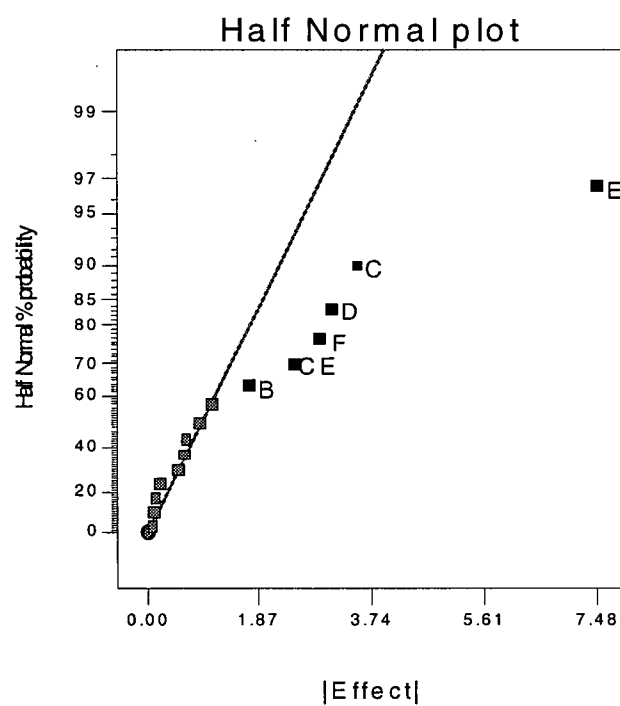
Actual Factors
A: DOC = 0.00
C: ATM = 0.00
D: Fe(0) = 0.00
E: Tailings = 0.00
F: S(0) = 0.00





DESIGN-EXPERT Plot
Arsenic

A: DOC
B: SO₄
C: ATM
D: Fe(0)
E: Tailings
F: S(0)



Response: Arsenic

ANOVA for Selected Factorial Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob >F	
Model	379.37	6	63.23	45.47	< 0.0001	significant
B	11.56	1	11.56	8.31	0.0181	
C	49.14	1	49.14	35.34	0.0002	
D	37.72	1	37.72	27.13	0.0006	
E	223.80	1	223.80	160.96	< 0.0001	
F	32.98	1	32.98	23.72	0.0009	
CE	24.16	1	24.16	17.37	0.0024	
Residual	12.51	9	1.39			
Cor Total	391.88	15				

The Model F-value of 45.47 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.

In this case B, C, D, E, F, CE are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant.

If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	1.1792	R-Squared	0.9681
Mean	5.6088	Adj R-Squared	0.9468
C.V.	21.0238	Pred R-Squared	0.8991
PRESS	39.5506	Adeq Precision	20.2013

The "Pred R-Squared" of 0.8991 is in reasonable agreement with the "Adj R-Squared" of 0.9468.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 20.201 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	5.609	1	0.2948	4.9419	6.2756	
B-SO4	-0.850	1	0.2948	-1.5169	-0.1831	1
C-ATM	1.753	1	0.2948	1.0856	2.4194	1
D-Fe(0)	-1.536	1	0.2948	-2.2024	-0.8686	1
E-Tailings	3.740	1	0.2948	3.0731	4.4069	1
F-S(0)	-1.436	1	0.2948	-2.1026	-0.7689	1
CE	1.229	1	0.2948	0.5619	1.8956	1

Final Equation in Terms of Coded Factors:

$$\begin{aligned} \text{Arsenic} = & 5.60875 \\ & -0.85 * B \\ & 1.7525 * C \\ & -1.5355 * D \\ & 3.74 * E \\ & -1.43575 * F \\ & 1.22875 * C * E \end{aligned}$$

Final Equation in Terms of Actual Factors:

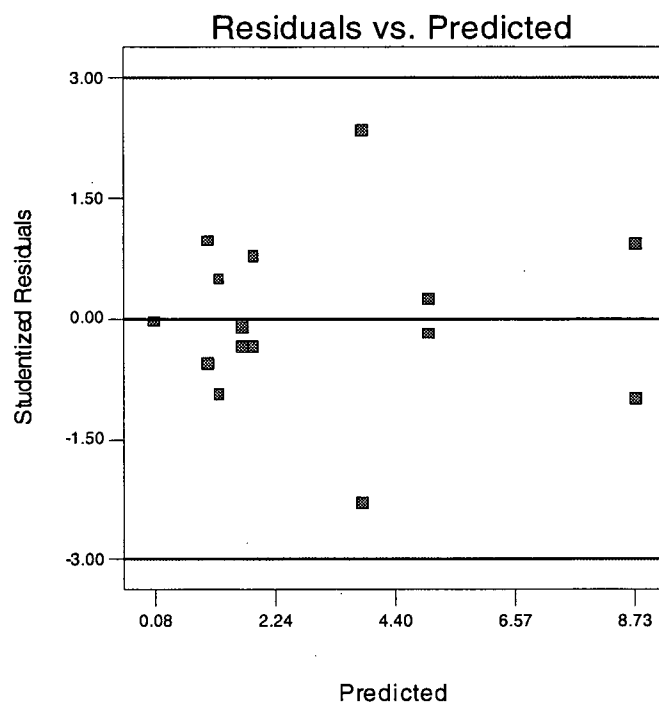
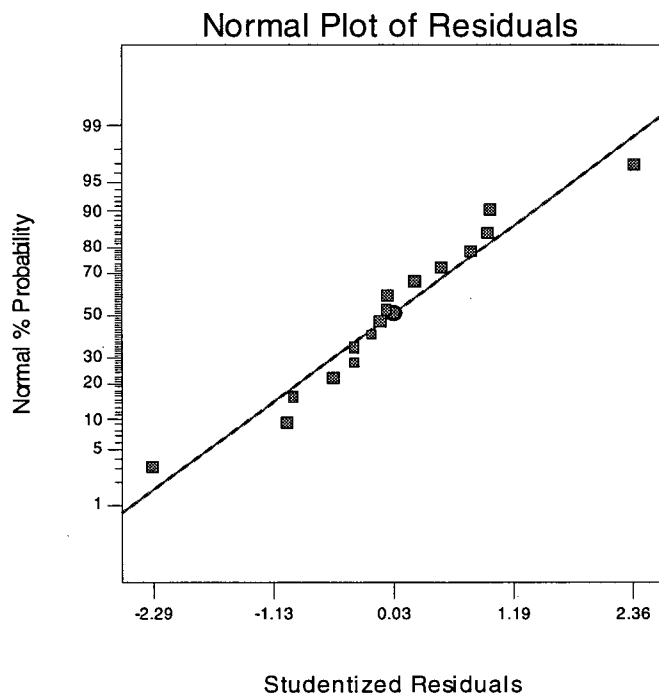
$$\begin{aligned} \text{Arsenic} = & 5.60875 \\ & -0.85 * \text{SO}_4 \\ & 1.7525 * \text{ATM} \\ & -1.5355 * \text{Fe(0)} \\ & 3.74 * \text{Tailings} \\ & -1.43575 * \text{S(0)} \\ & 1.22875 * \text{ATM} * \text{Tailings} \end{aligned}$$

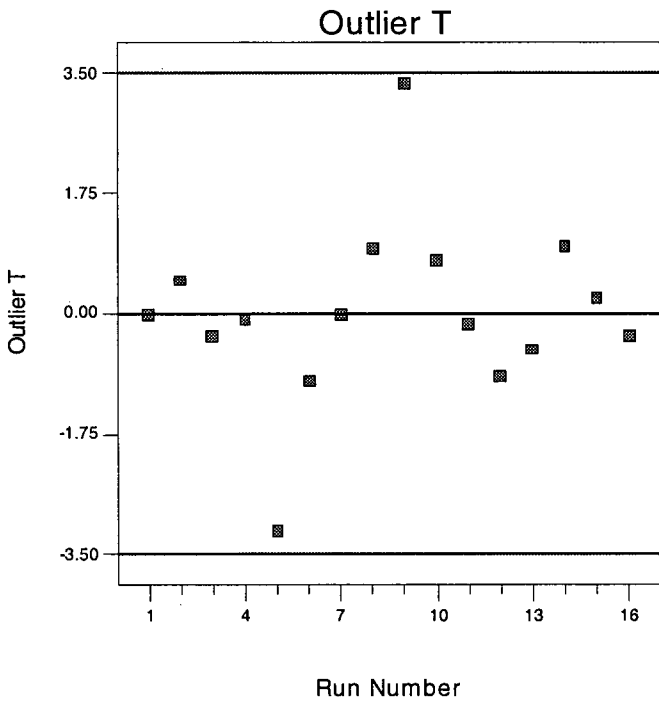
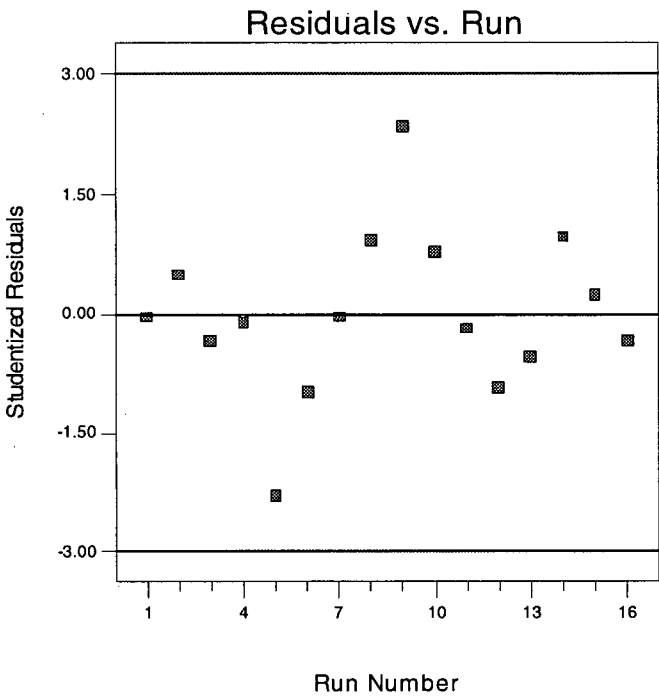
Diagnostics Case Statistics								
Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	10.56	10.189	0.371	0.4375	0.4198	0.0196	0.3997	11
2	2.29	2.295	-0.005	0.4375	-0.0054	0.0000	-0.0051	14
3	0.504	0.595	-0.091	0.4375	-0.1026	0.0012	-0.0968	13
4	8.44	8.489	-0.049	0.4375	-0.0551	0.0003	-0.0520	15
5	2.04	3.342	-1.302	0.4375	-1.4725	0.2409	-1.5934	12
6	15.32	16.151	-0.831	0.4375	-0.9399	0.0982	-0.9332	8
7	14.96	14.451	0.509	0.4375	0.5753	0.0368	0.5526	6
8	3.04	1.642	1.398	0.4375	1.5805	0.2775	1.7531	2
9	1.69	2.095	-0.405	0.4375	-0.4582	0.0233	-0.4372	4
10	5.32	4.246	1.074	0.4375	1.2141	0.1638	1.2518	1
11	1.15	2.546	-1.396	0.4375	-1.5788	0.2770	-1.7505	7
12	0.896	0.395	0.501	0.4375	0.5662	0.0356	0.5436	16
13	11.76	10.209	1.551	0.4375	1.7541	0.3419	2.0385	9
14	2.69	3.143	-0.453	0.4375	-0.5119	0.0291	-0.4898	10
15	1.8	1.443	0.357	0.4375	0.4040	0.0181	0.3844	3
16	7.28	8.509	-1.229	0.4375	-1.3894	0.2145	-1.4780	5

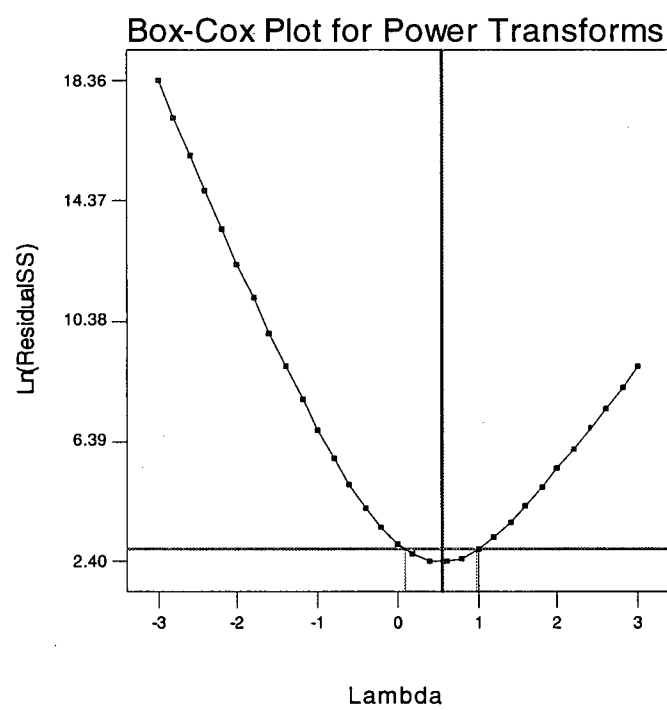
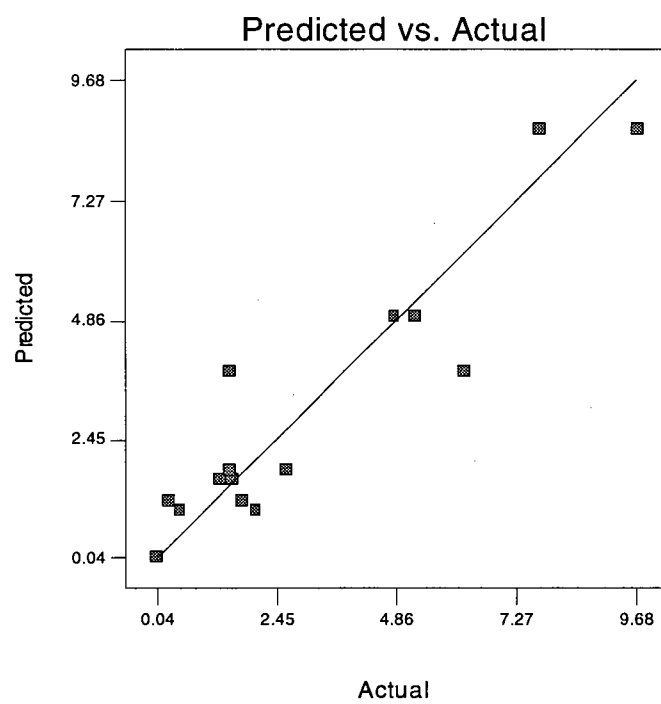
Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:

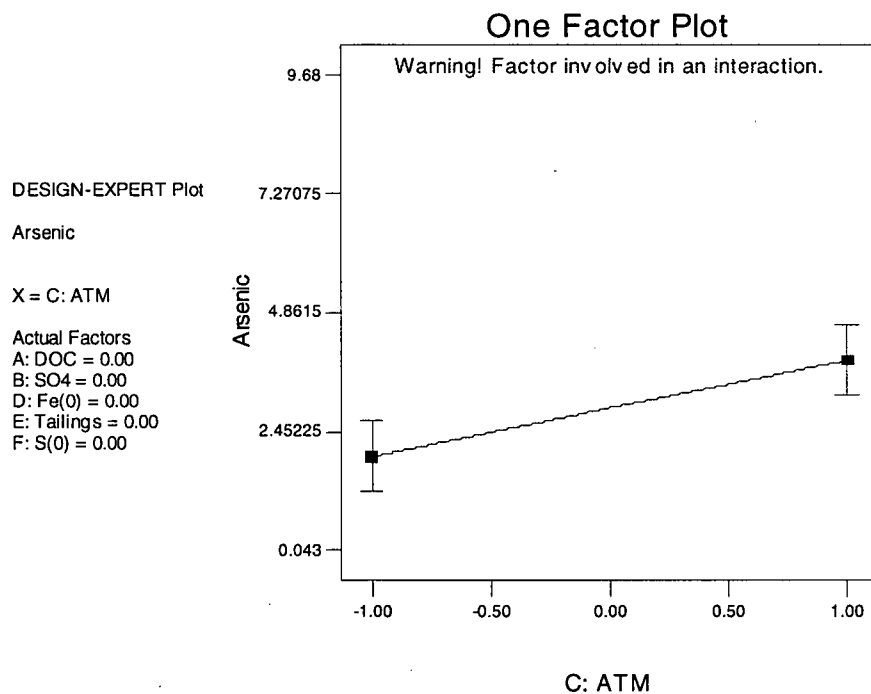
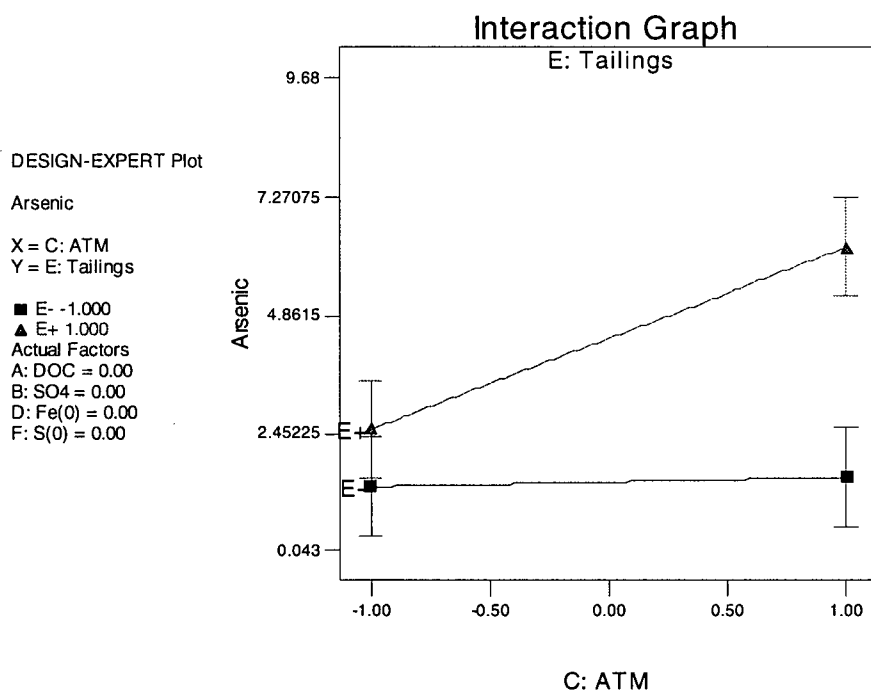
- 1) Normal probability plot of the studentized residuals to check for normality of residuals.
- 2) Studentized residuals versus predicted values to check for constant error.
- 3) Outlier t versus run order to look for outliers, i.e., influential values.
- 4) Box-Cox plot for power transformations.

If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.

Set 1 – Day 14 Design Ease Graphs and ANOVA Table





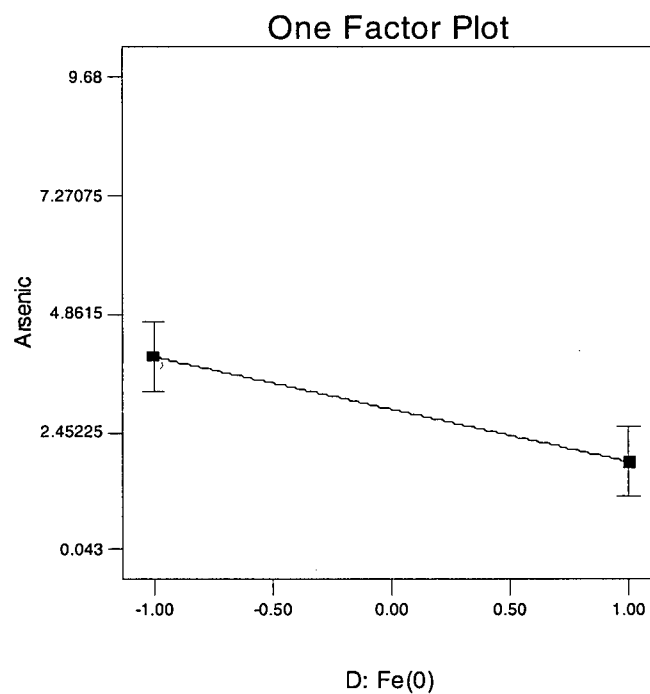


DESIGN-EXPERT Plot

Arsenic

X = D: Fe(0)

Actual Factors
A: DOC = 0.00
B: SO₄ = 0.00
C: ATM = 0.00
E: Tailings = 0.00
F: S(0) = 0.00

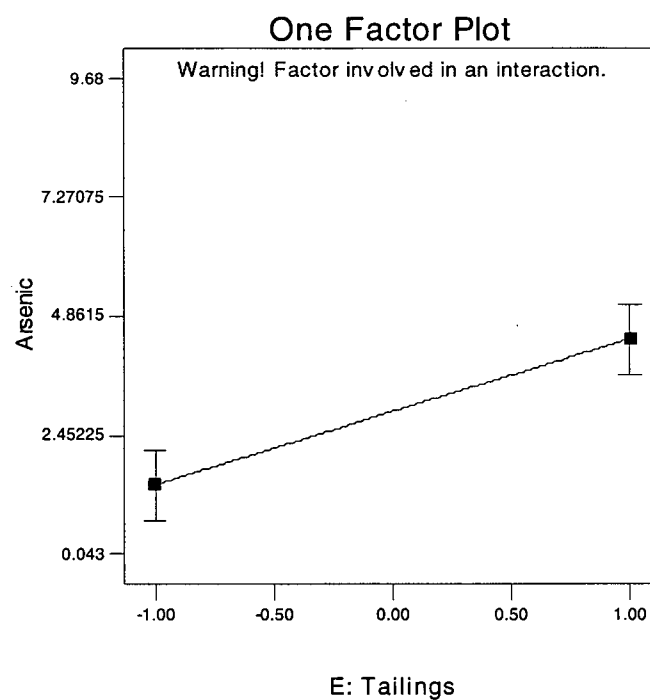


DESIGN-EXPERT Plot

Arsenic

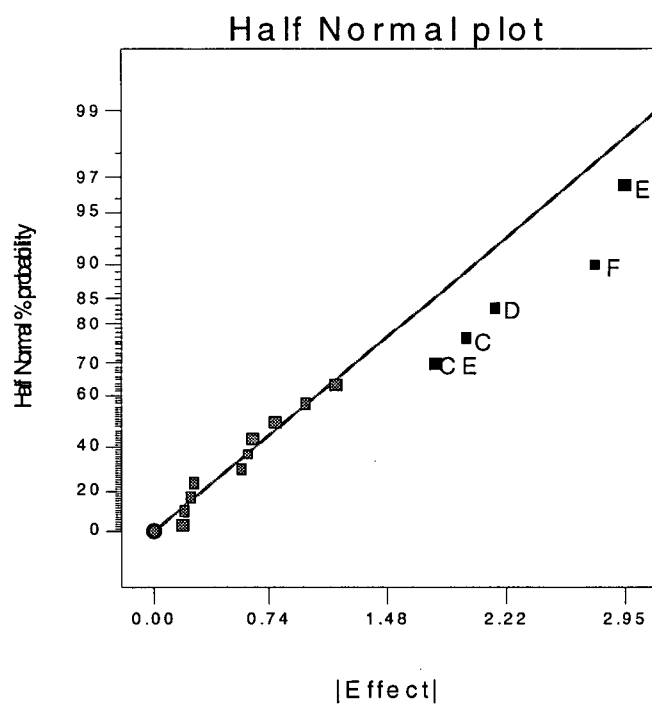
X = E: Tailings

Actual Factors
A: DOC = 0.00
B: SO₄ = 0.00
C: ATM = 0.00
D: Fe(0) = 0.00
F: S(0) = 0.00



DESIGN-EXPERT Plot
Arsenic

A: DOC
B: SO₄
C: ATM
D: Fe(0)
E: Tailings
F: S(0)



Response: Arsenic

ANOVA for Selected Factorial Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob >F	
Model	112.07	5	22.41	13.71	0.0003	significant
C	15.45	1	15.45	9.45	0.0117	
D	18.45	1	18.45	11.29	0.0072	
E	34.92	1	34.92	21.37	0.0009	
F	30.64	1	30.64	18.75	0.0015	
CE	12.60	1	12.60	7.71	0.0195	
Residual	16.34	10	1.63			
Cor Total	128.410	15				

The Model F-value of 13.71 implies the model is significant. There is only a 0.03% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.

In this case C, D, E, F, CE are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant.

If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	1.2784	R-Squared	0.8727
Mean	2.9274	Adj R-Squared	0.8091
C.V.	43.6702	Pred R-Squared	0.6742
PRESS	41.8395	Adeq Precision	11.0568

The "Pred R-Squared" of 0.6742 is in reasonable agreement with the "Adj R-Squared" of 0.8091.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 11.057 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	2.927	1	0.3196	2.2153	3.6396	
C-ATM	0.983	1	0.3196	0.2706	1.6948	1
D-Fe(0)	-1.074	1	0.3196	-1.7861	-0.3618	1
E-Tailings	1.477	1	0.3196	0.7652	2.1894	1
F-S(0)	-1.384	1	0.3196	-2.0959	-0.6717	1
CE	0.888	1	0.3196	0.1754	1.5997	1
CE	1.229	1	0.2948	0.5619	1.8956	1

Final Equation in Terms of Coded Factors:

$$\begin{aligned} \text{Arsenic} = & 2.9274375 \\ & 0.9826875 * C \\ & -1.073938 * D \\ & 1.4773125 * E \\ & -1.383813 * F \\ & 0.8875625 * C * E \end{aligned}$$

Final Equation in Terms of Actual Factors:

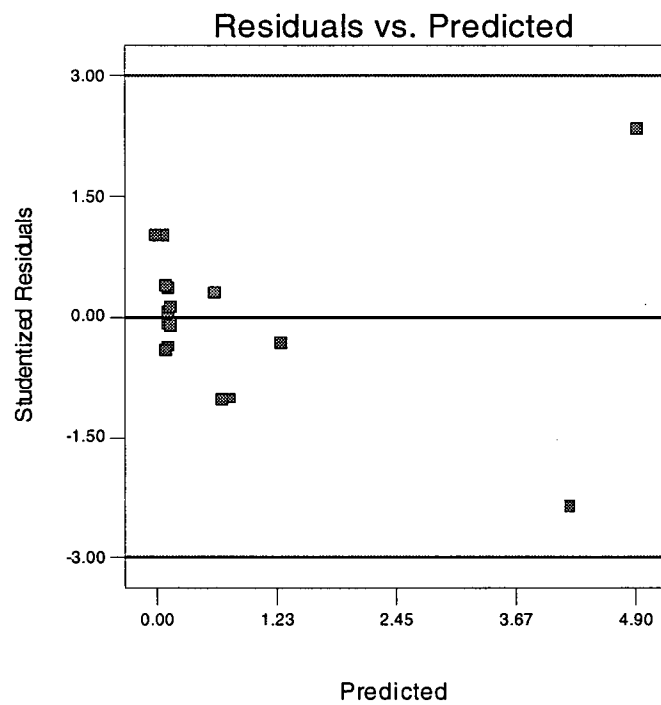
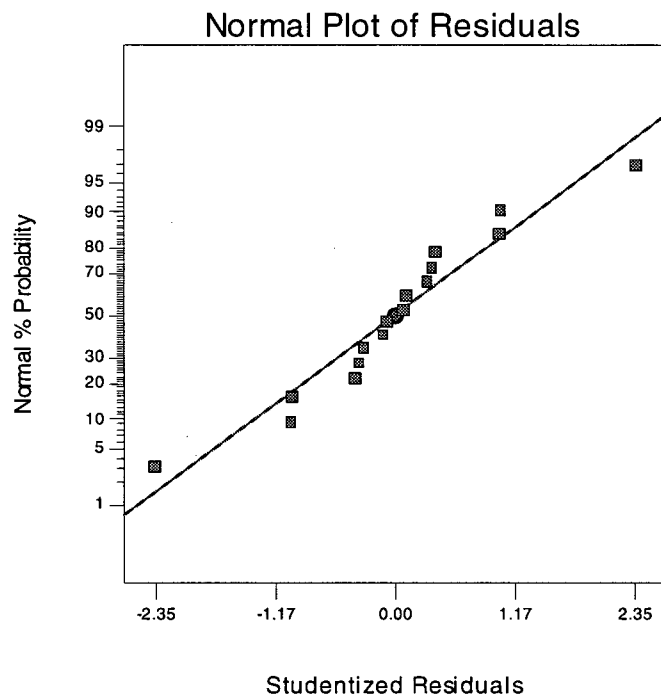
$$\begin{aligned} \text{Arsenic} = & 2.9274375 \\ & 0.9826875 * \text{ATM} \\ & -1.073938 * \text{Fe}(0) \\ & 1.4773125 * \text{Tailings} \\ & -1.383813 * \text{S}(0) \\ & 0.8875625 * \text{ATM} * \text{Tailings} \end{aligned}$$

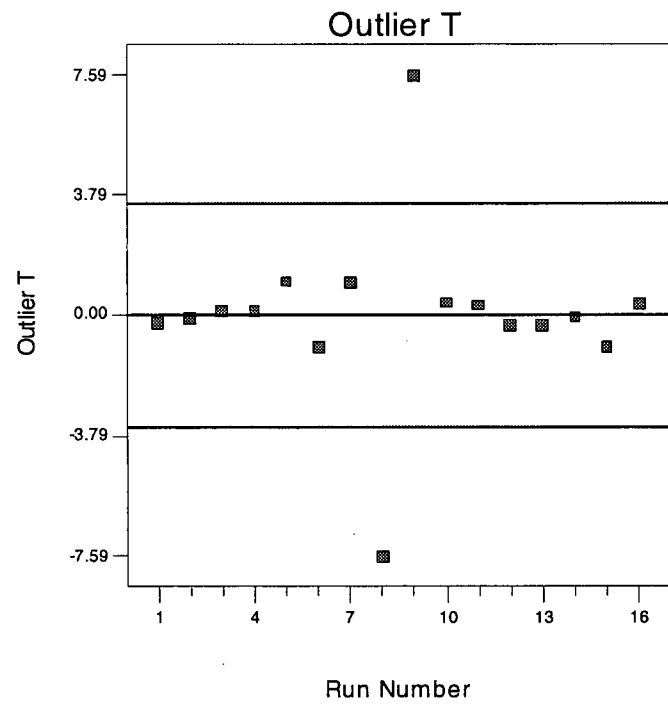
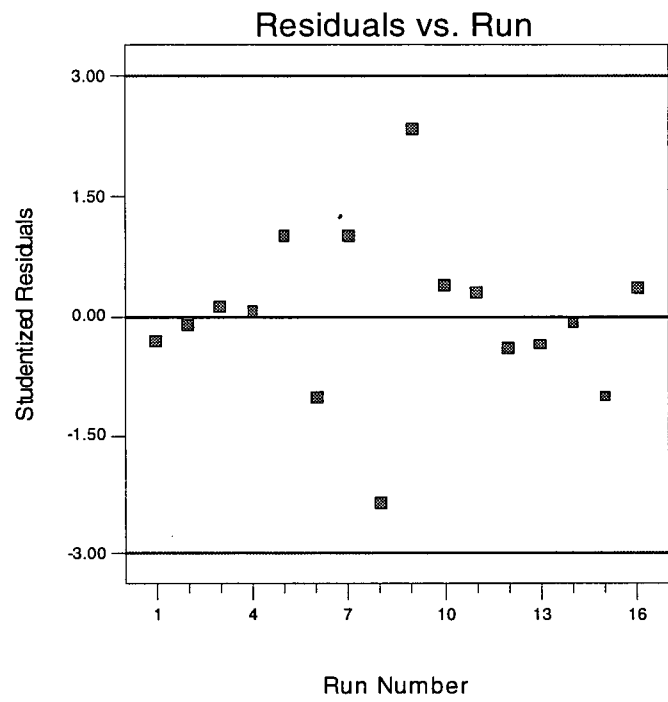
Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	4.81	4.992	-0.182	0.375	-0.1803	0.0033	-0.1713	11
2	2.03	1.045	0.985	0.375	0.9745	0.0950	0.9718	14
3	0.5	1.045	-0.545	0.375	-0.5394	0.0291	-0.5193	13
4	5.24	4.992	0.248	0.375	0.2451	0.0060	0.2333	15
5	0.291	1.235	-0.944	0.375	-0.9344	0.0873	-0.9279	12
6	9.68	8.733	0.947	0.375	0.9372	0.0878	0.9310	8
7	7.72	8.733	-1.013	0.375	-1.0020	0.1004	-1.0023	6
8	1.74	1.235	0.505	0.375	0.4993	0.0249	0.4797	2
9	1.57	1.665	-0.095	0.375	-0.0939	0.0009	-0.0891	4
10	0.045	0.077	-0.032	0.375	-0.0314	0.0001	-0.0298	1
11	0.043	0.077	-0.034	0.375	-0.0334	0.0001	-0.0317	7
12	1.32	1.665	-0.345	0.375	-0.3412	0.0116	-0.3256	16
13	6.2	3.817	2.383	0.375	2.3576	0.5558	3.3559	9
14	2.64	1.855	0.785	0.375	0.7766	0.0603	0.7600	10
15	1.51	1.855	-0.345	0.375	-0.3415	0.0117	-0.3259	3
16	1.5	3.817	-2.317	0.375	-2.2928	0.5257	-3.1582	5

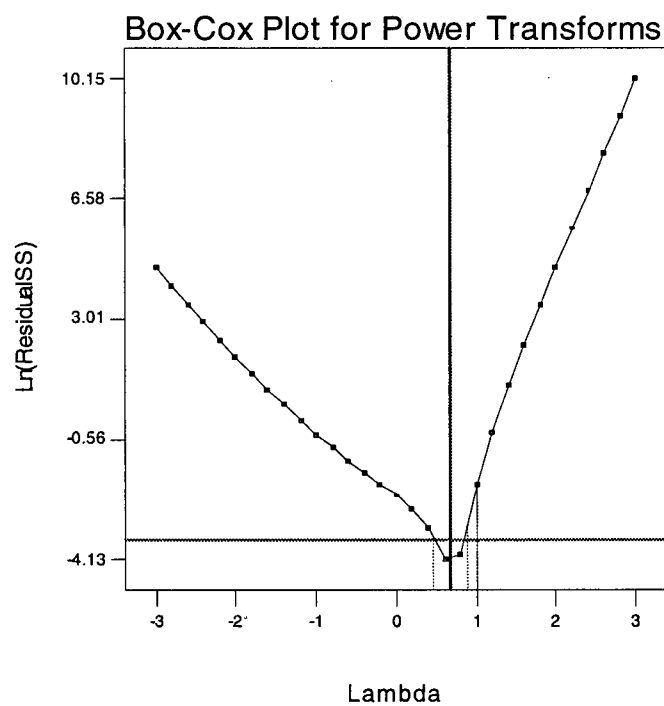
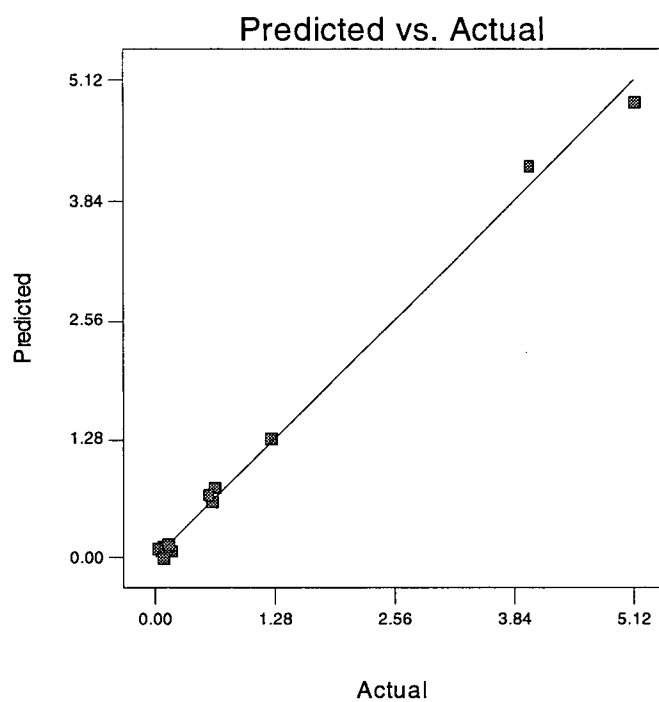
Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:

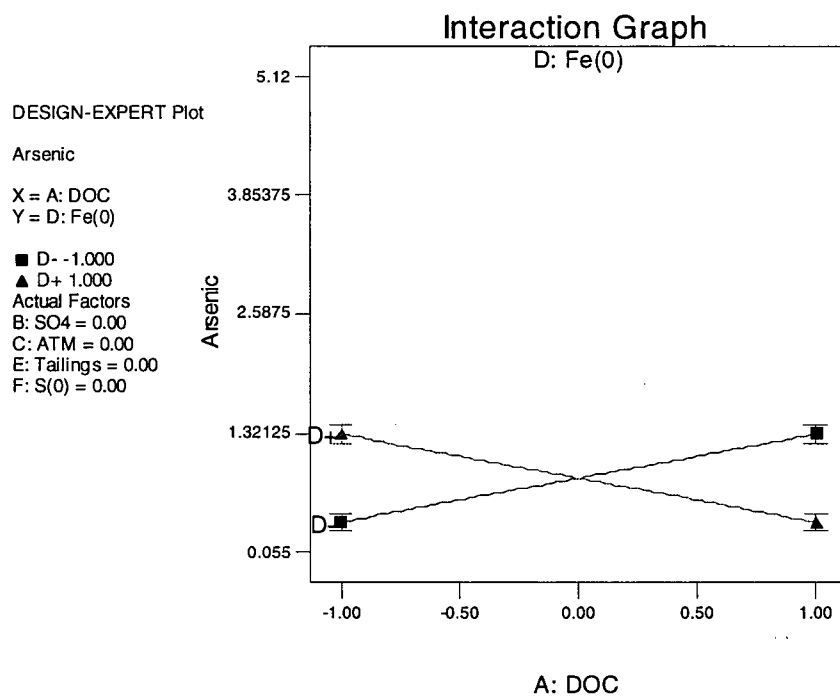
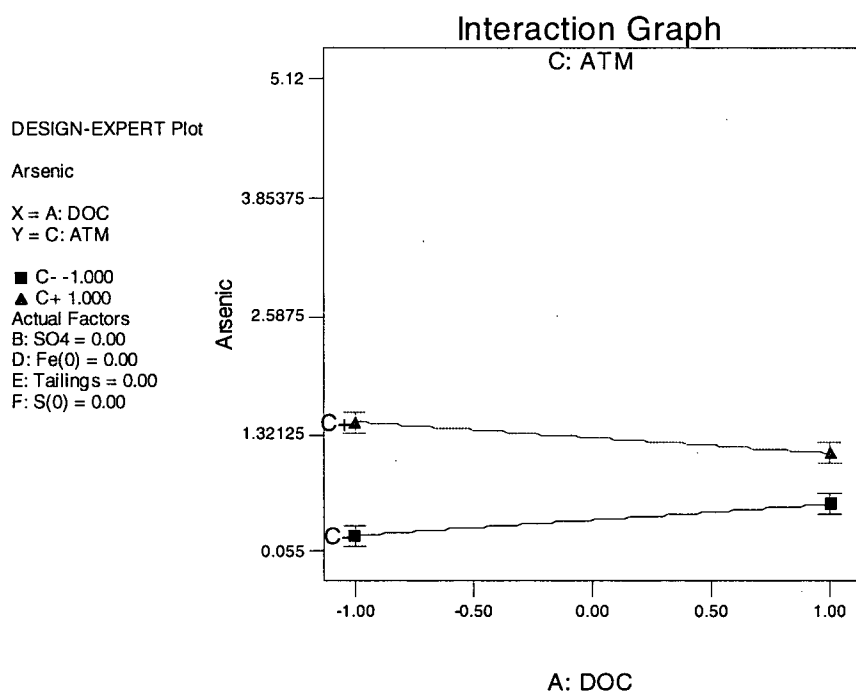
- 1) Normal probability plot of the studentized residuals to check for normality of residuals.
- 2) Studentized residuals versus predicted values to check for constant error.
- 3) Outlier t versus run order to look for outliers, i.e., influential values.
- 4) Box-Cox plot for power transformations.

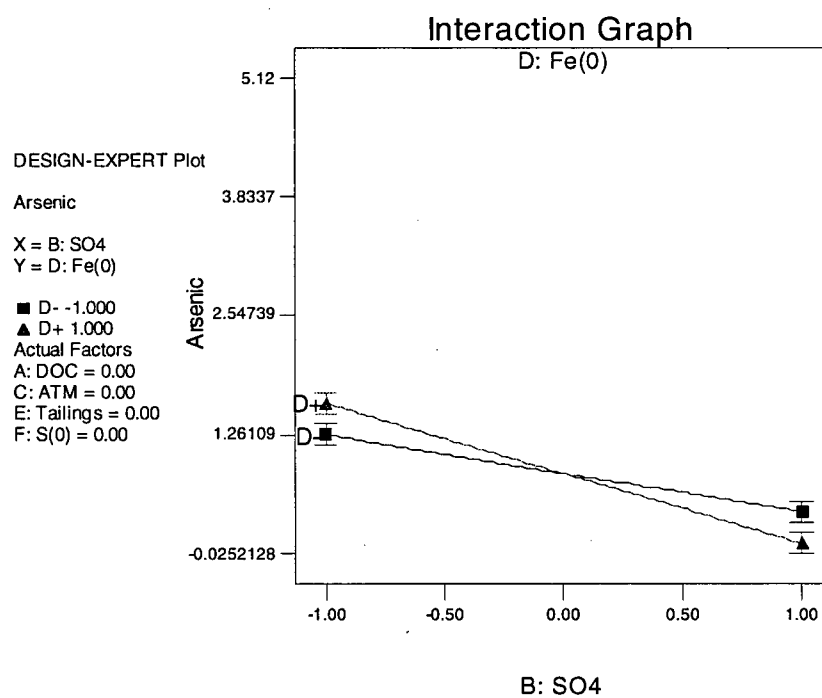
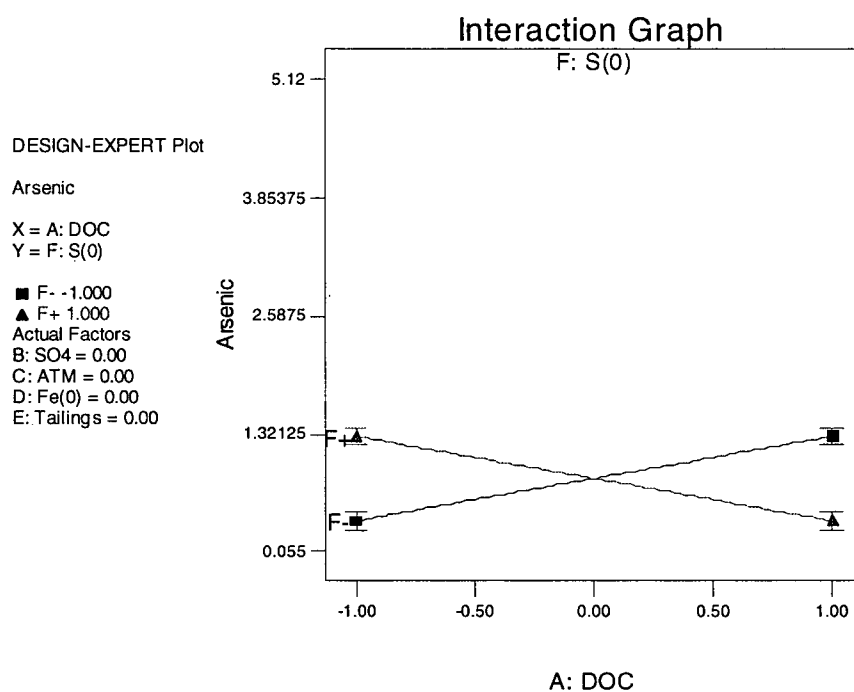
If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.

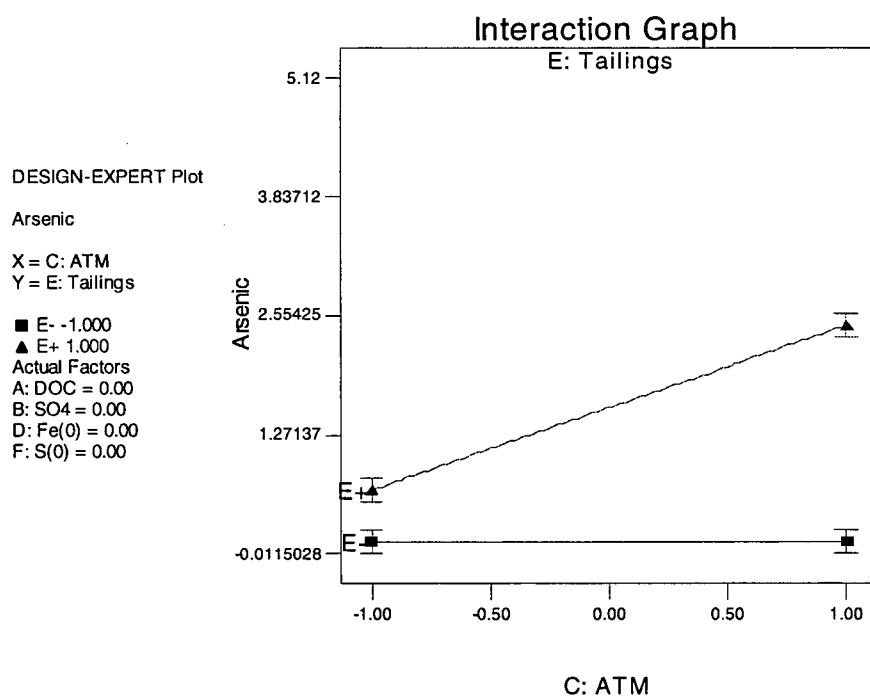
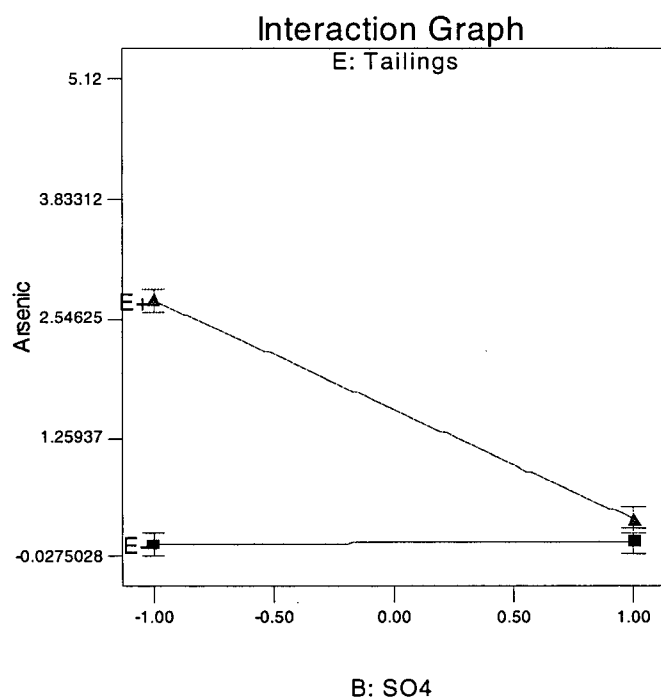
Set 2 – Day 40 Design Ease Graphs and ANOVA Table

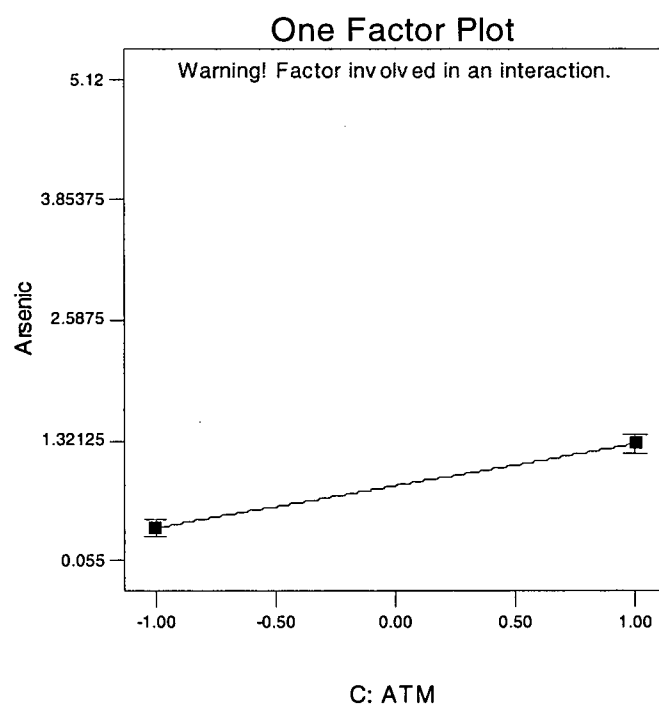
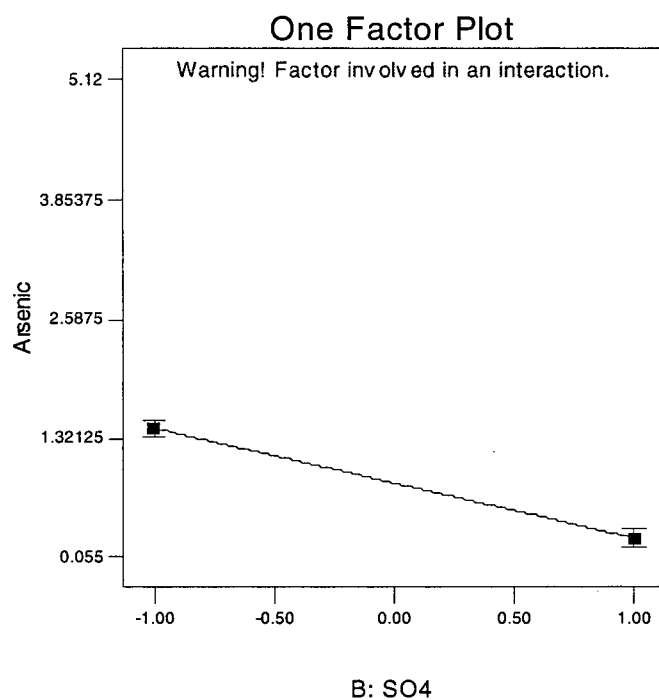


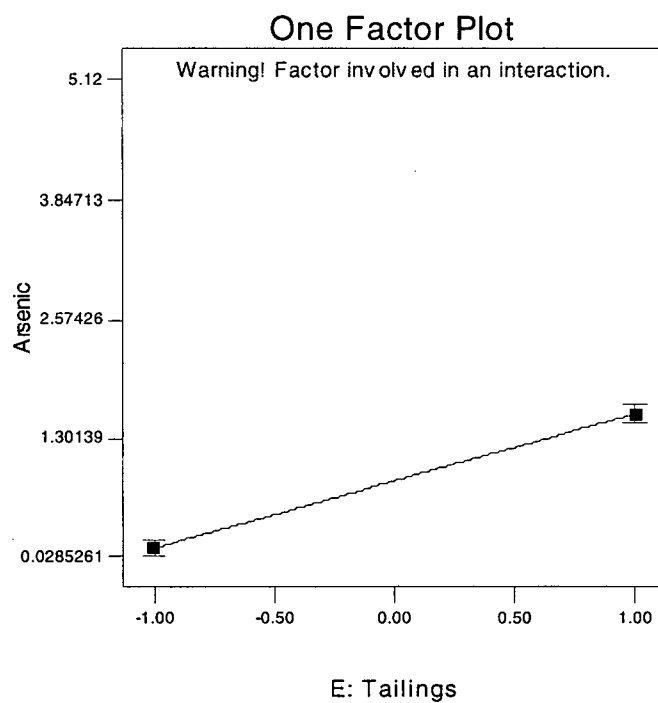






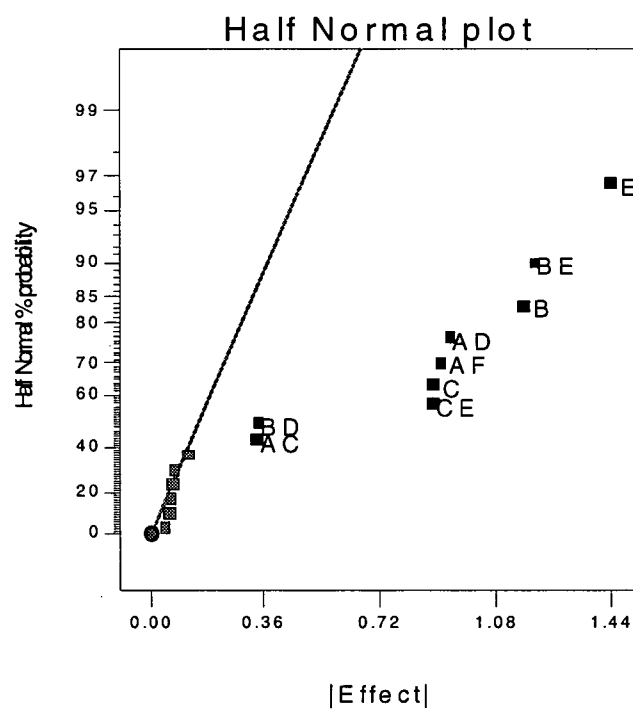






DESIGN-EXPERT Plot
Arsenic

A: DOC
B: SO₄
C: ATM
D: Fe(0)
E: Tailings
F: S(0)



Response: Arsenic

ANOVA for Selected Factorial Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob >F	
Model	33.59	9	3.73	157.29	< 0.0001	significant
B	5.46	1	5.46	230.15	< 0.0001	
C	3.15	1	3.15	132.69	< 0.0001	
E	8.32	1	8.32	350.76	< 0.0001	
AC	0.46	1	0.46	19.22	0.0046	
AD	3.51	1	3.51	148.06	< 0.0001	
AF	3.31	1	3.31	139.50	< 0.0001	
BD	0.460	1	0.46	19.39	0.0046	
BE	5.783	1	5.78	243.74	< 0.0001	
CE	3.134	1	3.13	132.09	< 0.0001	
Residual	0.142	6	0.02			
Cor Total	33.728	15				

The Model F-value of 157.29 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.

In this case B, C, E, AC, AD, AF, BD, BE, CE are significant model terms.

Values greater than 0.1000 indicate the model terms are not significant.

If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Std. Dev.	0.1540	R-Squared	0.9958
Mean	0.8439	Adj R-Squared	0.9894
C.V.	18.2513	Pred R-Squared	0.9700
PRESS	1.0123	Adeq Precision	40.1923

The "Pred R-Squared" of 0.9700 is in reasonable agreement with the "Adj R-Squared" of 0.9894.

"Adeq Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 40.192 indicates an adequate signal. This model can be used to navigate the design space.

Factor	Coefficient Estimate	DF	Standard Error	95% CI Low	95% CI High	VIF
Intercept	0.844	1	0.0385	0.7497	0.9382	
B-SO4	-0.584	1	0.0385	-0.6784	-0.4900	1
C-ATM	0.444	1	0.0385	0.3493	0.5378	1
E-Tailings	0.721	1	0.0385	0.6270	0.8154	1
AC	-0.169	1	0.0385	-0.2630	-0.0746	1
AD	-0.469	1	0.0385	-0.5628	-0.3743	1
AF	-0.455	1	0.0385	-0.5490	-0.3606	1
BD	-0.170	1	0.0385	-0.2638	-0.0753	1
BE	-0.601	1	0.0385	-0.6954	-0.5070	1
CE	0.443	1	0.0385	0.3483	0.5368	1

Final Equation in Terms of Coded Factors:

$$\begin{aligned}
 \text{Arsenic} = & 0.8439375 \\
 & -0.584188 * B \\
 & 0.4435625 * C \\
 & 0.7211875 * E \\
 & -0.168813 * A * C \\
 & -0.468563 * A * D \\
 & -0.454813 * A * F \\
 & -0.169563 * B * D \\
 & -0.601188 * B * E \\
 & 0.4425625 * C * E
 \end{aligned}$$

Diagnostics Case Statistics								
Standard Order	Actual Value	Predicted Value	Residual	Leverage	Student Residual	Cook's Distance	Outlier t	Run Order
1	0.632	0.603	0.029	0.625	0.3114	0.0162	0.2866	11
2	0.11	0.118	-0.008	0.625	-0.0822	0.0011	-0.0750	14
3	0.092	0.126	-0.034	0.625	-0.3578	0.0213	-0.3302	13
4	0.66	0.755	-0.095	0.625	-1.0112	0.1704	-1.0134	15
5	0.055	0.092	-0.037	0.625	-0.3949	0.0260	-0.3653	12
6	4	4.222	-0.222	0.625	-2.3496	0.9201	-7.590 *	8
7	0.584	0.681	-0.097	0.625	-1.0271	0.1758	-1.0327	6
8	0.144	0.155	-0.011	0.625	-0.1193	0.0024	-0.1090	2
9	0.127	0.119	0.008	0.625	0.0822	0.0011	0.0750	4
10	1.25	1.279	-0.029	0.625	-0.3114	0.0162	-0.2866	1
11	0.174	0.079	0.095	0.625	1.0112	0.1704	1.0134	7
12	0.158	0.124	0.034	0.625	0.3578	0.0213	0.3302	16
13	5.12	4.898	0.222	0.625	2.3496	0.9201	7.590 *	9
14	0.131	0.094	0.037	0.625	0.3949	0.0260	0.3653	10
15	0.165	0.154	0.011	0.625	0.1193	0.0024	0.1090	3
16	0.101	0.004	0.097	0.625	1.0271	0.1758	1.0327	5

* Case(s) with |Outlier T| > 3.50

Proceed to Diagnostic Plots (the next icon in progression). Be sure to look at the:

- 1) Normal probability plot of the studentized residuals to check for normality of residuals.
- 2) Studentized residuals versus predicted values to check for constant error.
- 3) Outlier t versus run order to look for outliers, i.e., influential values.
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If all the model statistics and diagnostic plots are OK, finish up with the Model Graphs icon.