

HUMIDITY CELL INVESTIGATION OF PARTICLE SIZE EFFECTS
ON WEATHER RATES OF MINE WASTE ROCK
FROM THE ANTAMINA MINE, PERU

by

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Abstract

A laboratory humidity cell experiment was performed on marble diopside waste rock from the Antamina Mine of Peru, one of the world's largest operating copper-zinc mines, in order to study the effects of particle size on weathering rates. There is currently little understanding of the geochemical characteristics of neutral drainage systems, and further knowledge is necessary to improve waste rock management techniques at mines hosted in rock with high neutralization capacity.

Grain sizes less than 0.053 to 9.50 mm were separated into individual cells and seven weeks of leachate were collected then analyzed by ICP-OES for elements of concern. Results suggest that the finer the particle size, the higher the alkalinity and release rates of calcium, sulphur, molybdenum, magnesium, and manganese. This trend was especially apparent in the results of magnesium and manganese, where, unlike all other samples, the release rates in the finest grained sample increased over time. Concentrations of copper, chromium, nickel, and iron were determined to be below the detection limit of this analysis. The saturation indices of calcite were found to be above the saturation level in two samples.

The continuation of this experiment will further characterize trends in particle size versus weathering rates. Additional parameters should be analyzed in the leachate to increase understanding of neutral drainage.

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1. INTRODUCTION

Acid rock drainage (ARD) is a well-studied area of mining due to its widespread environmental impacts and media coverage; however, there is relatively little understanding in the processes involved in neutral drainage systems. Ore at many mines in Canada and internationally are hosted in rock with high neutralization capacity, such as carbonates, but although neutral and alkaline drainage greatly limits the transport of copper, iron, and aluminum, other environmentally hazardous elements such as molybdenum, arsenic, chromium, selenium, and zinc are not strongly attenuated in these environments. The study of neutral drainage systems is needed to improve the management of waste rock and develop environmental mitigation techniques at these sites. An opportunity that is currently available to increase the knowledge in this area is the Antamina mine in Peru, as this location closely resembles Canadian mines with ore hosted in rock with high neutralization capacity.

UBC is currently involved in an extensive research project focussing on small and large scale field experiments, materials characterization, and integration of data using simulation modelling. Along with the theses conducted simultaneously by Diane Moug, Rajiv Joiya, and Nick Edgar, this thesis aims to supplement the project by providing data obtained through laboratory kinetic testing using humidity cell testing. It has been identified that the particle sizes of rocks have a significant effect on the drainage quality and reaction rates, thus focus is placed on the geochemical characterization of neutral drainage with respect to different grain sizes. Understanding of the relationship between grain

sizes and the geochemistry of drainage water will help to develop the waste rock management program at the Antamina mine, as well as provide insight about neutral drainage systems.

The drainage from Class B marble diopside waste rock was characterized geochemically by the ICP-OES instrument Varian 725-ES using a modified humidity cell experiment. Alkalinity was obtained using standard alkalinity titration methods, as outlined in the USGS manual of 2001. The results were input into Phreeqc Interactive 2. 15.0 to model other parameters of interest. The humidity cell testing was conducted for a total of seven weeks at a lab inside the main building of the Earth and Ocean Sciences department at the University of British Columbia under the supervision of Roger Beckie.

2. STUDY AREA

The Compañía Minera Antamina (Antamina) mine is located in Peru approximately 200km west of the city of Huaraz at an altitude of approximately 4,200 metres above sea level in the Peruvian Andes (see Figure 2-1). The average yearly precipitation is 1,100 to 1,300 mm and average temperature is 8°C, and experiences warmer winters and cooler summers than similar Canadian locations due to its tropical latitude and high elevation. In addition to processing about 70,000 to 100,000 tonnes of ore per day, 300,000 tonnes of waste rock are excavated daily that are used either as construction material or placed in one of several waste rock piles, depending on the waste rock classification. Owned by Teck-Cominco, Noranda, and others, this mine reached full production in the fall of 2001, and is one of the world's largest operating copper-zinc mines. Its mine life is currently anticipated to last until the year 2024. (Brown et al, 2006; Klein)

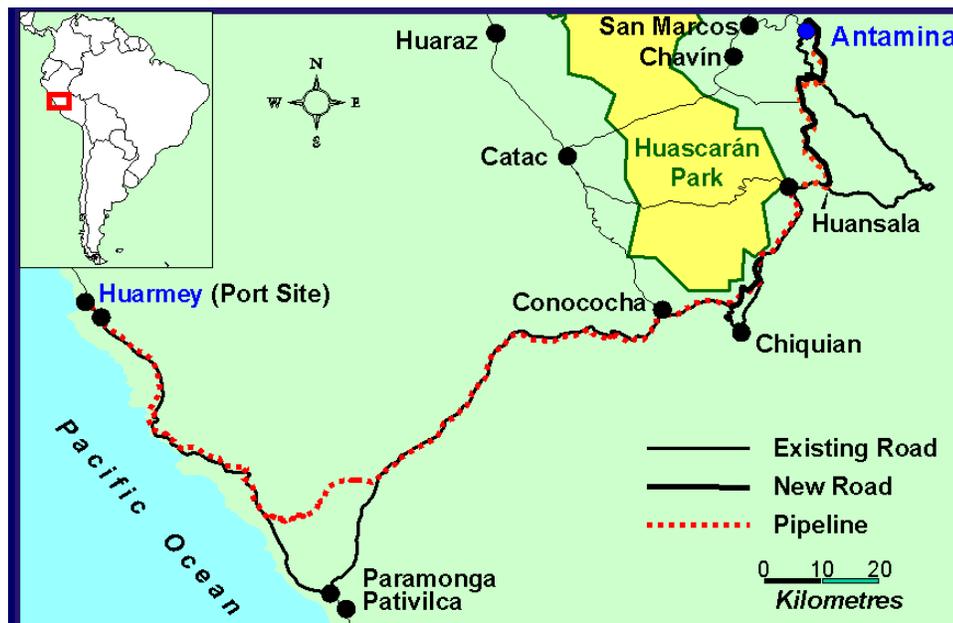


Figure 2-1: Antamina mine location map (Brown et al, 2006)

Deposit geology at the Antamina mine is a polymetallic skarn that consists of copper, zinc, molybdenum, lead, bismuth, and number of minor and trace elements of concern formed by the intrusion of quartz monzonite into limestone. Major rock types that have been identified at this mine include intrusives, endoskarn, exoskarn, hornfels, marble, and limestone. (Brown et al., 2006) In studying drainage from waste rocks, three principal groups of waste rock have been identified:

- Type A: “reactive” material – endoskarn, exoskarn, intrusive and hornfels, marble and limestone with greater than 1500 ppm zinc, greater than 400 ppm arsenic, greater than 3% sulfides and/or greater than 10% visual oxide staining;
- Type B: “slightly reactive” material – hornfels, marble and limestone with zinc levels between 1500 and 700 ppm, between 2 and 3% sulfides and visual oxide staining up to 10%;
- Type C: “nonreactive” material – hornfels, marble and limestone with less than 700 ppm zinc, less than 400 ppm arsenic and less than 3% sulfides and minimal oxide staining.

This study involves characterizing the drainage from the slightly reactive, neutral drainage type B material; specifically, a marble diopside, which can be closely characterized by the general composition of marble at Antamina, consisting predominantly of calcite with quartz, muscovite and plagioclase with minor amounts of mica and chlorite, pyrrhotite, diopside and traces of molybdenite (Brown et al, 2006). Other studies were conducted simultaneously on black

marble and gray hornfels. This humidity cell experiment was conducted as a part of a research program conducted by UBC on neutral drainage from waste rock using material from the Antamina mine. Other field experimentation includes experimental waste rock piles, barrel-sized field cells, and cover programs.
(Klein)

3. LITERATURE REVIEW

A wide variety of literature was consulted in order to assist in conducting this experiment. The following outlines literature that pertains to the areas of humidity cell methods, acid-base accounting, geochemical analysis using inductively coupled plasma – atomic emission spectrometry (ICP-AES), and geochemical characterization at the Antamina mine.

3.1 Acid-Base Accounting

A tool for assessing the potential for acid generation, acid-base accounting (ABA) utilizes static tests to characterize ratio of the neutralization potential (NP) to the acid generation potential (AP). Though this method has been applied successfully in North American coalfields, it has had less success in predicting acid-rock drainage (ARD) problems in base-metal sulphide deposits, but is still used as a screening tool to assess where more extensive testing might be necessary. The NP/AP ratio is plotted against the weight percentage of the sulphide content to determine whether or not sample is likely to become acid generating. For application in British Columbia, samples usually have more than 0.3 wt% S_{sulphide} if it is potentially acid generating, and have an NP/AP ratio no greater than 4:1. (Scharer et al. 2000, Jambor et al. 2000) It has been suggested that acidification criteria should be established on a case-by-case basis, while others argue that the NP of carbonate provides the most realistic estimate of a sample's acid-generating potential, and that non-carbonate minerals help to attenuate acidity only to a modest degree.

Jambor et al. uses common test methods, the Sobek and Lawrence methods, to evaluate the NP/AP ratio. Both involve assessing the fizz rating to check the effervescence and grinding of the sample to pass a certain mesh size; however, both steps contribute to the inaccuracy of ABA. The fizz rating is classified as none, slight, moderate, and strong by adding a few drops of 25% HCl to a small split sample, and thus is highly subjective and can have a significant effect on the NP. Though sample sizes all pass a certain mesh size after grinding, this does not guarantee the reproducibility of the surface area, as it depends on the friability of the mineral, the duration of grinding, the amount of sample added to the mill, and the number of intermediate screening steps used. Jambor et al. minimizes the subjectivity of the fizz rating by only using silicate and aluminosilicate samples which have no gas evolution and thus result in a “no fizz” rating; however, it is noted that the use of higher acid concentrations resulted in higher NP values, thus demonstrating the importance of the subjective fizz ratings in the ABA. Along with the effect of surface area to chemical reaction rates, Jambor et al. notes that the accurate characterization of sulphide content is necessary to correctly classify a rock as acid generating or non-acid generating.

In determining the effect of grain size on the neutralization process, acidic drainage from pyrrhotite/pentlandite tailings from the Whistle mine in Ontario were added to various size fractions of limestone and examined under laboratory column tests and geochemical modelling by Scharer et al. The composition of the filtered drainage water consisted of sulphate, dissolved iron, and dissolved calcium, which promoted the precipitation of presumably ferric hydroxide and

gypsum that limited mass transport processes, especially on larger size particles as the precipitates decreased the buffering ability of larger grain sizes of limestone. Furthermore, it was observed that particles of less than 1mm size showed no obvious evidence of mass transport limitations, and that neutral conditions were reached relatively quickly. Modelling of long-term simulations that even at NP/AP ratios considered non-acid producing, a certain amount of carbonate material needs to be present in the fines fraction in order to maintain a neutral seepage for a minimum of 200 years. Thus, even if the total amount of buffering minerals present in a waste rock pile may be high in comparison to sulphide minerals, the pile may produce acidic drainage if the carbonate material in the fines is too low.

Since waste rock from mines are not necessarily acid generating, acid base accounting may suggest that these mines are not of concern; however, there are important ramifications of dissolved metals in drainage water, even if the water is neutral. Furthermore, Jambor et al. highlights the inaccuracies of ABA, while Scharer et al. demonstrates the affect of grain size on reactivity and mass transport. Thus, the humidity cell experiment was a better alternative to static tests, and an emphasis was placed on analysing the variation of drainage properties due to the grain sizes of waste rock.

3.2 Humidity Cell

The humidity cell style weathering test is a type of kinetic testing used to characterize the drainage from waste rock and is an important tool in assisting the

development of mitigation techniques. Although a standard method has been developed by the ASTM, the standard is often very tedious and simplified methods have been tested successfully. The standard method calls for 1000 g solid material samples in a cylindrical cell to be circulated with dry and wet pumped air in order to accelerate weathering and oxidation (ASTM 1998). The repeatability and reproducibility of the ASTM standard was questioned, and Lappako et al. developed simplified methods. In the simplified method, samples were subjected to humid and dry air pumping with a drip-trickle rinse method, and duplicate samples were stored in a controlled temperature and humidity room and flood rinsed; results were comparable between the two methods (Lappako et al. 2000). Thus, actively circulating air does not show an appreciable effect on weathering rates, as was the original purpose of this step.

The effect of particle size on drainage quality in the humidity cell test is a topic that has been studied thoroughly. Particle size variation can alter the magnitude of exposed mineral surface area available for reaction. Firstly, mineral contents can be affected through particle size reduction as the hardness of a mineral relative to other minerals can preferentially concentrate it to a certain size fraction. Secondly, the specific surface area increases as particle size decreases. Individual minerals also tend to be released from the rock matrix as particle size decreases, a phenomenon known as mineral liberation, allowing all surfaces of a mineral grain to be exposed for reaction. (Lappako et al. 2006) The effects of particle size on drainage quality were observed by Lappako et al. from three different lithologies by subjecting five to six particle size fractions to humidity

cell tests. Reaction rates were generally proportional to the mineral surface area exposed to gaseous and aqueous phase reactants, which makes the mineral available for reaction. (Lappako et al. 2006) The effect of particle size and surface area was also noted by Bowell et al. It was also observed in their experiments that the amount of water retention affected the reaction rates, especially for pyrite rich samples, as sulphide oxidation is limited by the rate of oxygen supply. In finer, water-saturated particle size fractions, the rate of oxygen supply decreases and may suppress oxidation rates, as shown in Figure 3-1 below:

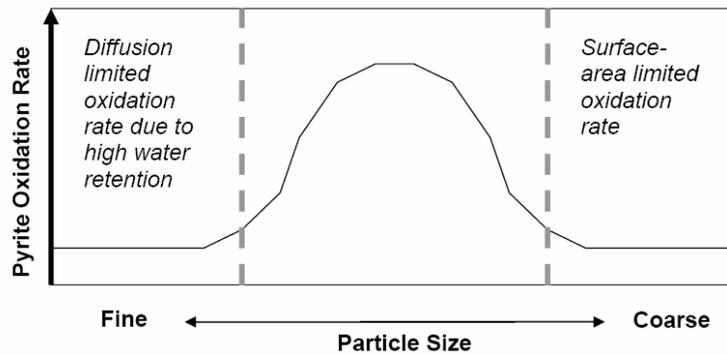


Figure 3-1: Possible influence of particle size on pyrite oxidation rate (Bowell et al., 2006)

The humidity cell experiment was chosen to characterize the waste rock as it is a common method and is also able to show the effects of particle grain size on reaction rates, which is of great interest in this experiment. The methodology of this humidity cell experiment was simplified from the standard procedure outlined by the ASTM and some of Lappako et al.'s methodology was incorporated, such as passive humidity and non-aeration of the cells. This experiment will aid in the development of a mitigation program.

3.3 Inductively Coupled Plasma (ICP)

Inductively coupled plasma – atomic emission spectrometry (ICP-AES) is an emission spectrophotometric technique used for geochemical analysis, and requires samples to be in solution. This analysis technique utilizes the fact that excited electrons emit energy at a given wavelength as they return to ground state, and that each element emits energy at specific wavelengths. Each element emits energy at multiple wavelengths, but specific wavelengths can be selected for analysis of each element. By creating standards of known elemental concentrations, the intensity of the energy emitted at the chosen wavelength can be correlated with the concentration of that element in the sample. Thus, by determining the wavelengths emitted by a sample and their intensities, the amount of an element in solution can be quantified. (Murray et al. 2000)

In order to utilize the ICP-AES method, samples must be prepared properly, as outlined by Murray et al. To keep maintenance simple, solutions must be filtered, such as through Acrodisc filters that fit over a syringe, which helps prevent the instrument from being clogged. The matrix of all standards and samples must match in terms of composition, total dissolved solids, and acid concentration. Great care and diligence must also be exercised in keeping all sample bottles, glassware, and instrumentation clean and uncontaminated by foreign substances in order to obtain accurate results.

Although the instrument available was the ICP-OES, the methods and operation of the AES are very similar, and thus Murray et al's technical note was

consulted in producing a procedure for the analysis of the drainage waters from the humidity cell experiment.

3.4 Geochemical Characterization of Drainage Water at the Antamina Mine

A geochemical characterization program is currently in place at the Antamina Mine as well as collaboration with UBC. The programs have the objective of understanding potential environmental impacts during operation and closure of the mine, to aid in the development of mitigation programs, and to refine the current waste rock management program (Brown et al. 2006). Detailed geochemical testing has been performed by Golder Associates Ltd. (2004), which included acid base accounting, humidity cell testing, field cell testing, and ICP analysis of ore, waste rock, and lake sediment samples. However, samples tested were not separated by particle size, but instead, were all crushed to be within similar grain size distributions. Results indicated that elevated concentrations of elements of concern appeared mostly in ore and Class A waste rock; furthermore, elevated concentrations were also seen for a few elements in Class B waste rock.

With the geochemical testing performed by Golder (2004), it can be seen that information needs to be obtained concerning the effect of particle size, especially on Class B material which showed signs of leaching elements of concern at noteworthy concentrations. By performing humidity tests on particular grain sizes, important information can be obtained to aid in developing appropriate waste rock management techniques.

4. METHODS

In order to characterize the drainage of the marble diopside waste rock, several different stages were necessary, mainly consisting of the humidity cell experiment, the alkalinity titrations, and the ICP analyses. This section outlines the methods used in each stage of the experiment.

4.1 Humidity Cell Experiment

Due to monetary constraints, the humidity cell experiment constructed is highly simplified compared to the standard set out by the ASTM and other simplified methods; however, these simplifications were made under recommendations by literature and the thesis supervisor, and were determined to not have a large effect on the accuracy of the experiment.

4.1.1 Construction of the Apparatus

A solid, flat base was created with Styrofoam and corrugated plastic boards cut to size to fit a large Rubbermaid container. Ten small diameter PVC pipes were secured onto the board with zap-straps and housed the small, 400 mL Nalgene bottles used for collecting the sample. Two wires were secured across the inside of each of the ten large PVC pipes in order to house the large Nalgene bottles that the soil samples would be placed. Rubber stops were fitted with small HDPE tubing, which were slit wrapped with filter paper. The bottom of the large Nalgene bottles were cut off and the mouth was fitted with the modified rubber stopper, and large LDPE tubing was placed over the smaller tubing. The entire

apparatus was placed inside the large Rubbermaid container with a lid, which created a closed environment for the experiment. Photos of the apparatus can be found in the Appendices.

4.1.2 Preparation of the Waste Rock

The rock samples of marble diopside waste rock were already separated into size fractions when received at UBC and were labelled by a separate naming scheme. Size fractions and the masses of each sample were selected according to the samples list available in the Appendix B, and are listed in Table 4-1.

Sample #	Soil	Sieve Size	Particle Size (mm)	Mass (kg)	Total mass (kg)
1	FC3-H	3/8"	9.50	0.800	0.800
2	FC3-I	1/4"	6.30	0.800	0.800
3	FC3-J	#4	4.75	0.433	0.800
	FC3-K	#6	3.35	0.367	
4	FC3-L	#8	2.36	0.332	0.800
	FC-M	#16	1.18	0.468	
5	FC3-N	#30	0.600	0.528	0.792
	FC3-O	#50	0.300	0.264	
6	FC3-P	#100	0.150	0.492	0.800
	FC3-Q	#140	0.106	0.308	
7	FC3-R	#200	0.075	0.444	0.800
	FC3-S	#270	0.053	0.356	
8	FC3-T	-#270	-0.053	0.801	0.801
9	FC3-P	#100	0.150	0.400	0.652
	FC3-Q	#140	0.106	0.252	
10	FC3-T	-#270	-0.053	0.226	0.226

Table 4-1: Size fraction and mass of soil samples

Although the samples for column testing had been specified by mass, there was not enough soil received to meet the requirements outlined; therefore, size fractions were combined by modifying the masses specified to the same percentage by mass to weigh a total of 0.800 kg. Size fractions of interest were duplicated to make samples 9 and 10.

The bottom of the Rubbermaid container was flooded with approximately 2 L of distilled water to create a humidified environment. After placing the samples back into the contraption, 500 mL of distilled water was poured into each rock sample to flush out any unwanted substances. The water was leached and sampled after an hour.

Weekly leaches used a 1:2 water to rock ratio as the flood volume. Most samples required 400 mL, but for sample 9 and 10, less water was required as the rock sample available was smaller. For samples 1 to 8, distilled water was measured in a graduated cylinder and then slowly poured into the top of the rock samples. For sample 9 and 10, the leached water from the previous week was measured in a graduated cylinder, and the remaining amount of water needed for the 1:2 water to rock ratio was made up using distilled water; however, this procedure was not implemented until the third week of the experiment after some clarification of the procedure. The samples were allowed to sit for an hour in a closed environment before being leached for one week by opening the bottom tubing to allow water to drain into the small Nalgene bottle.

4.1.3 Sampling

Sampling was performed after one week of leaching, except in the case of the flush sample. Samples 9 and 10 were sampled for the flush and first two weeks of leaching, after which the procedure was modified. They were also sampled during week 7, the last week of the experimentation. First each small Nalgene bottle containing the leached water sample and each large Nalgene bottle containing the saturated rock sample were weighed, except for samples 9 and 10. Samples were collected weekly with 60 mL Norm-Ject syringes rinsed first with a small amount of sample, then filter sampled into two collection bottles through 0.45 μm Acrodisc syringe filters. A separate filter was used for each rock sample. One collected sample was stored with two drops of 50% HNO_3 while the other was collected for titration purposes. After a sample was collected, initial pH was measured with an Orion 250A meter.

After all samples had been collected, the water level of the Rubbermaid container was checked to make sure that humidity was still present, and next week's experiment would begin with the flooding of the samples.

4.2 Alkalinity Titration

For samples 1 to 8 collected except for the flush, alkalinity titrations were performed. The acid used was 0.2N H_2SO_4 except for week 2 when 0.02N H_2SO_4 was used, and the pH meter used was the Orion 250A, except for week 5 when the Hanna HI9025 was used. Calibration of pH meters was performed using pH 4

and pH 7 standards. Duplicate samples were taken so that titrations could be performed on a different day due to equipment constraints.

Samples were poured into a 50 mL beaker and weighed to determine its volume. Typically, a volume ranging from 20 to 8 mL was used, depending on the sample being analyzed. The pH was allowed to stabilize on the pH meter before using a 2 mL buret to dispense a volume of acid, typically between 0.01 to 0.04 mL at a time. Each time acid was dispensed, the pH probe was used to mix the sample and pH was allowed to stabilize. Titrations were performed until the pH reached a value between 2.9 and 2.8. The alkalinity was determined using the Gran Function plot method by plotting the following Gran function against the volume of acid titrant added in total:

$$(V_o + V_t) 10^{-pH} / \gamma$$

where V_o is initial volume of the sample (in mL), V_t is volume of acid titrant added (in mL), and γ is the activity coefficient of H^+ , which was set to 1. The alkalinity was then calculated using the formula

$$Alk (eq/L) = (B)(Ca)(CF) / V_s$$

where Alk is alkalinity of the sample, B is volume of acid titrant added from the initial pH to the bicarbonate equivalence point (in mL), Ca is concentration of acid titrant (in N), CF is correction factor, which is set to 1, and V_s is volume of the sample (in mL). (USGS 2001)

4.3 ICP-OES Analysis

The analyst Maureen Soon assisted in performing the ICP-OES analysis and Olga Singurindy assisted in creating the standards and blanks used to calibrate the instrument. The instrument used was the ICP-OES Varian 725-ES and the computer program used was the ICP Expert II.

4.3.1 Sample Preparation

Test tubes specified for the use of the ICP-OES analysis were acid washed by immersing fully in an acid bath for one day, then immersed in a DI water bath for one day, and then air dried before being labelled for each sample and standard used. A total of 72 samples were collected from the humidity cell experiment and analysed, while 10 standards and one blank was used. Standards and blanks were created by mixing 50% HNO₃ with a specified amount of standard solution and DI water, respectively. Table 4-2 lists the standards used to calibrate the instrument:

Standard name	Concentration (mg/L)	Elements Analyzed
ME 0.1	0.1	S, Ca, Mo, Zn, As, Se, Mg, Mn, Cu, Cr, Ni, Fe, K, Na, Si
ME 1	1	
ME 5	5	
ME 20	20	
Ca 50	50	Ca, Mg, Na, Si, K
S 10	10	S
S 50	50	
S 100	100	
S 250	250	
S 500	500	

Table 4-2: Standards used for the ICP-OES calibration

Approximately half of each test tube was carefully filled with its designated blank or standard and placed on the smaller test tube rack. Samples were stored with two drops of 50% HNO₃ at the time of sampling. Approximately half of each test tube was carefully filled with its designated sample and placed on the instrument's test tube rack. Samples were not diluted. Standard, blank, and sample names were entered into the computer program in order of placement in the racks. Compositions of the standards and blank were also entered into the program and analytical wavelengths were selected (see Appendices).

4.3.2 Analytical Run

The instrument was subjected to a warm-up period of greater than 30 minutes and set up by Maureen Soon. The analysis began with calibration using the blanks then the standards, after which thirty-seven samples were analyzed before another calibration was performed. Samples were analyzed in the order they were sampled, starting with EY 0-1 to 0-10 and ending with EY 7-10. Rinsing of the sample uptake tube was performed between each uptake and scheduled to be a maximum of 3 minutes. The analysis was completed in approximately three hours.

4.3.3 Data Reduction

The calibration feature of the computer program was utilized and any data point that had an error greater than 85% was not used in calibrating the instrument. Full calibration curves were later created using Microsoft Excel and are available

in the appendices, as well as details on the points that were discarded. Notably, the lowest concentration calibration point was not used for a few elements analyzed, thus giving values that were out of range for the instrument and unusable for the analysis. However, the instrument also returned some values that were less than the calibration limit without any errors. For the purposes of the analyses, all values returned without errors were used.

Release rates were determined by multiplying the concentration and the total volume of water leached of a sample each week, then dividing the value by the total rock mass of each sample. Rates were not calculated for samples obtained during the flush period (i.e. week 0) as they were not obtained under the same conditions as the other samples and would not be representative of the overall experiment.

5. RESULTS

The following sections present data resulting from the analysis of water samples obtained from the humidity cell experiment. Data are presented in the form of graphs with data points connected by smoothed lines to better illustrate the trends that appear to be forming; however, lines connecting data points are not to be interpreted as accurate interpolations.

5.1 pH

The pH of the leachate is plotted in Figure 5-1 against the sample number which corresponds to grain size. Readings ranged from 7.30 to 8.68, with the lowest pH reading occurring in week 1, and the highest in week 3. Sample 2 consistently showed the highest pH throughout the experiment with the exception of week 1, where sample 3 and 4 showed higher readings. The pH readings of sample 3 and 4 were also the narrowest, with values ranging from 7.91 to 8.37 and 7.76 to 8.23, respectively, while the pH of sample 2 ranged from 7.73 to 8.68.

Figure 5-2 shows pH readings versus time in weeks. Generally, pH was elevated, seen in samples 2, 5, 6, 7, and 8, or remained similar, as observed in samples 1, 3, and 4, compared to the beginning of the experiment. All readings increased by the second week, and some continued to increase until week 4 or 5, after which all readings showed a decreasing trend. Though sample 1 did not begin with the lowest pH reading, by the end of the experiment its pH was significantly lower than all other samples. Sample 2 has the highest pH reading

by the end of the experiment, while finer grained samples also show a significant increase in pH.

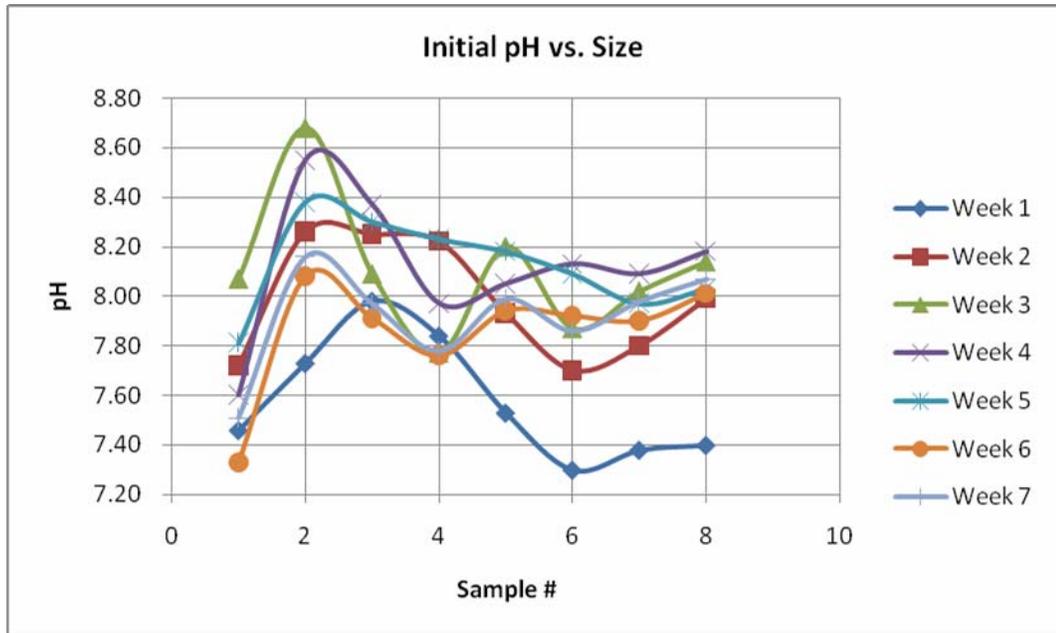


Figure 5-1: pH vs. Sample Number, corresponding to grain size

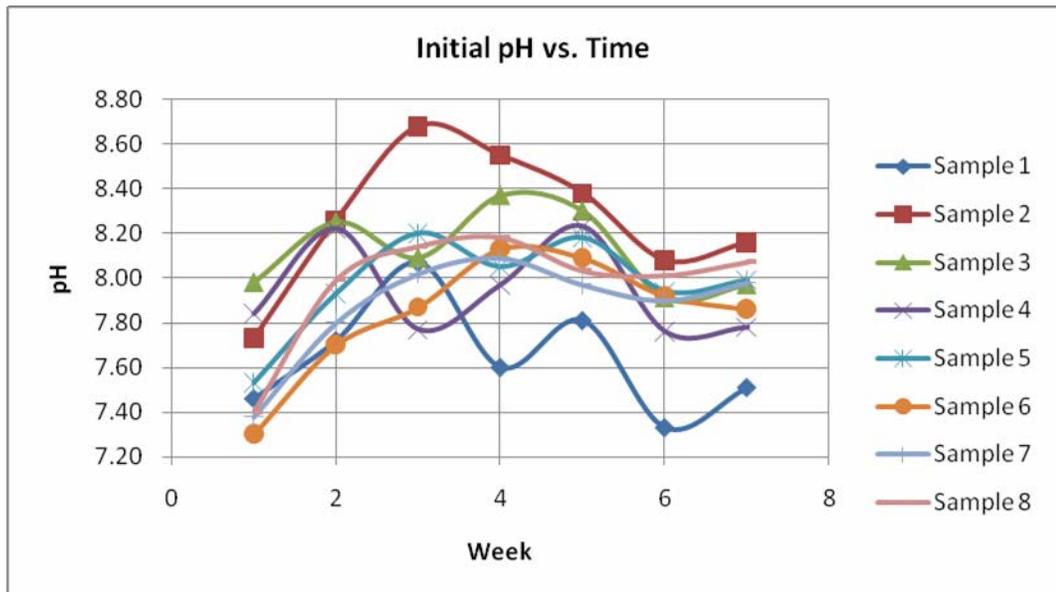


Figure 5-2: pH vs. time

5.2 Alkalinity

The results of the alkalinity titrations were plotted for each sample throughout the experiments, as was the weekly trend of all the sample sizes. The alkalinity of the samples ranged from $2.33\text{E-}4$ to $1.75\text{E-}3$ eq/L, appearing in sample 1 and sample 8 respectively. The lowest average alkalinity is seen in sample 3 at $3.18\text{E-}4$ eq/L, with sample 1 and 2 having comparable average values of $3.45\text{E-}4$ and $3.40\text{E-}4$ eq/L, respectively. The highest average value is seen in sample 8 at $1.40\text{E-}3$ eq/L, with sample 7 having a comparable average value of $1.09\text{E-}3$ eq/L.

Figure 5-3 graphs alkalinity against the sample number, showing trends of increasing alkalinity with decreasing grain size. The alkalinity stays rather stable from samples 1 through 4, after which there appears to be an increasing trend, showing the significance of grain size in alkalinity determination. These trends may be due to the type of minerals present in the smaller size fractions, as softer particles tend to accumulate in finer grain sizes. Also, the surface area available for reaction increases significantly as grain size decreases. Furthermore, the range of samples 7 and 8 are significantly larger than the other samples.

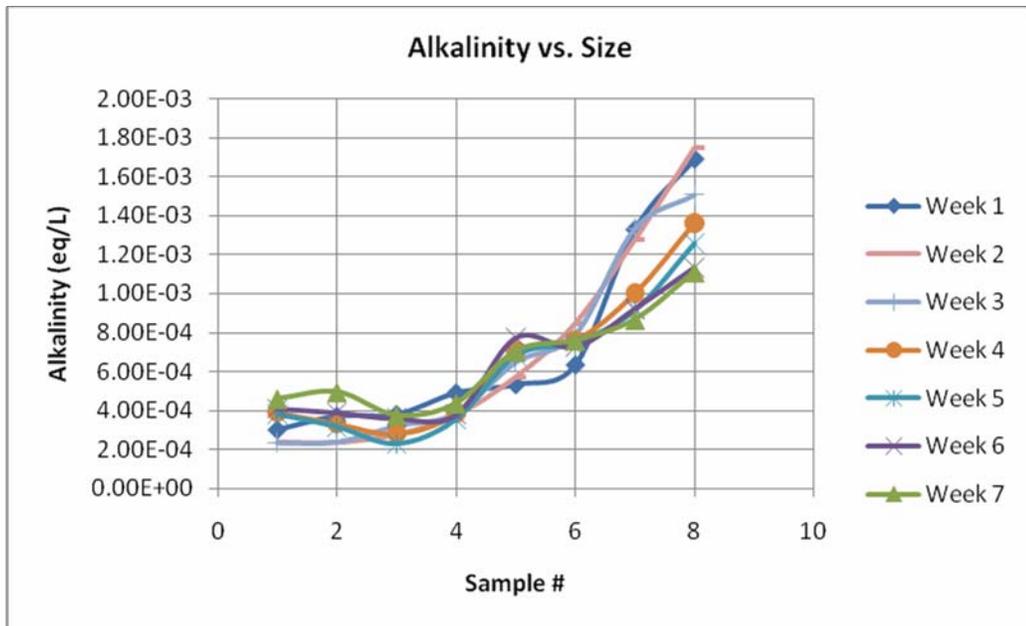


Figure 5-3: Alkalinity vs. Sample Number, corresponding to grain size

In Figure 5-4, alkalinity is graphed against time in weeks, showing the trends of alkalinity in each sample throughout the experiment. Samples 1 to 4 show flat trends, suggesting little variation in alkalinity from the beginning of the experiment to week 7. A slight increasing trend appears in samples 5 and 6, and show alkalinities distinctively higher than samples 1 to 4. In samples 7 and 8, alkalinity appears to decrease from high values observed in weeks 1 to 3. Furthermore, the two smallest grain sizes show significantly higher alkalinities than larger grain sizes. While sample 7 looks to be decreasing towards alkalinities in the range of samples 5 and 6, the alkalinity in sample 8 is still significantly higher than all samples by week 7 of the experiment.

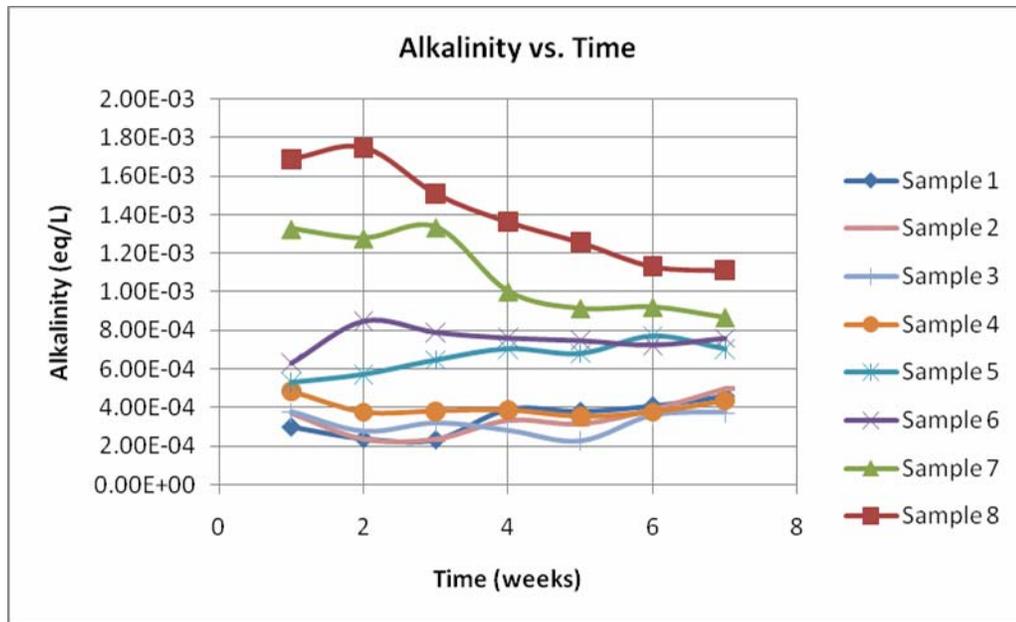


Figure 5-4: Alkalinity vs. Time

The results of the alkalinity titration reveal the significance of grain size in predicting alkalinity. At small grain sizes, high alkalinities are observed initially and decrease over time; however, these alkalinities are still higher than larger grain sizes at the end of the experiment.

5.3 ICP Analysis

Concentrations of analyzed elements in the samples are presented in the appendices, as determined by the ICP-OES instrument. Due to high error in the calibration curves determined from the standards, the lowest point of calibration was not used in the analysis of some elements to avoid inaccurate representations (see Appendix D). Concentrations of copper, chromium, nickel, and iron were determined to be below the detection limit of 0.1 mg/L. Although concentrations

for potassium, sodium, and silicon were also returned by the instrument, only a 50 mg/L standard was used in creating the calibration curve, and the results obtained may not be representative of the true concentrations; thus, they were not analysed. Plots of concentration versus time and sample number are available in Appendix E.

5.3.1 Sulphur

The highest sulphur concentrations are seen during the flush, with a maximum value observed in sample 7 at 591.52 mg/L, and the minimum value of 10.95 mg/L occurs in sample 2. Spikes in concentration diminish throughout time, and a more linear trend is observed by week 7, where the concentration ranges from 1.27 mg/L to 7.91 mg/L in samples 1 and 8, respectively. Sulphur concentrations in all samples are below 9 mg/L by week 4. An extrapolation of the concentrations in samples 1, 2, and 3 appear to be decreasing after week 4, while the concentrations in all other samples appear to be increasing. A trend can most clearly be seen in sample 8, where concentrations are increasing steadily from week 3 after a steep decline from week 0 to 2.

In general sulphur is released at high concentrations initially which lowers to a more constant rate after three to four weeks. Sample 6 shows the highest release rates until week 5, where its release rate begins to match that of sample 7. The release rates of all samples begin to match closely by week 4, ranging from a rate of 1.64 mg/kg in sample 1 to 3.94 mg/kg in sample 6. Release rates are plotted against time in figure 5-5 below:

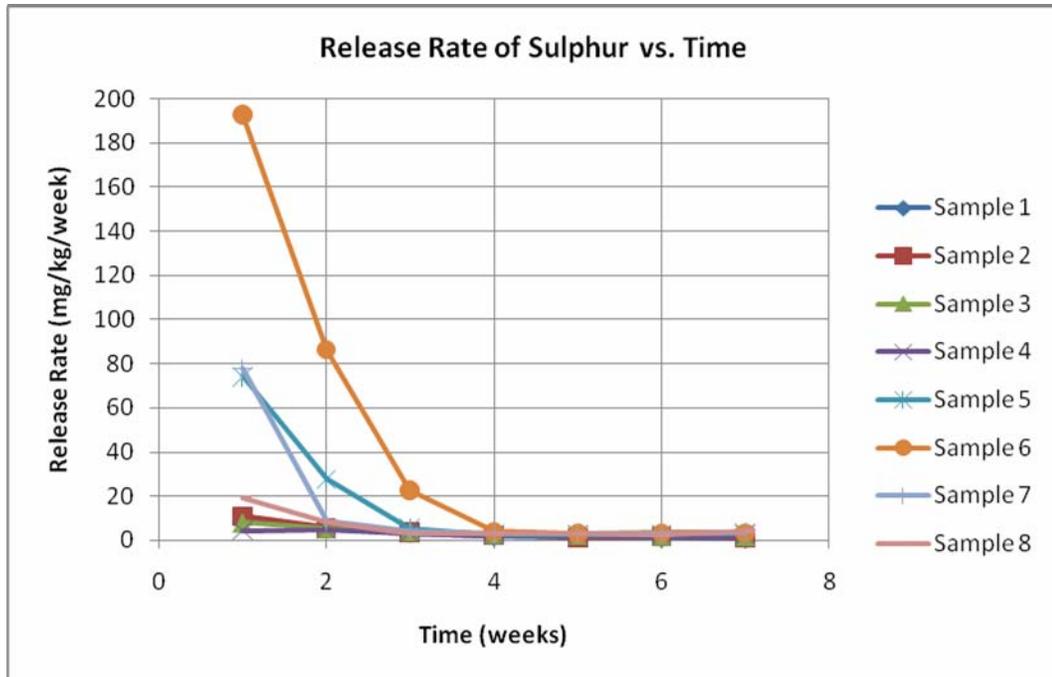


Figure 5-5: Sulphur Release Rate vs. Time

5.3.2 Calcium

High calcium concentrations in weeks 0 to 3 exceeded the range of the calibration curve of 50 mg/L; thus, some values above this concentration could not be determined, and can only be interpreted as having a concentration above 50 mg/L.

Although large values could not be precisely determined, it can be seen that very high concentrations of calcium are present initially. The highest concentration detected was in sample 3 during week 0 with a concentration of 98.15 mg/L; however, this point does not agree with the general trends of the results, and may be an anomalous point. Significantly higher concentrations can be recognized in samples 5 to 8, as their concentrations are much higher than the

detectable limit of the calibrated curve in the first few weeks. The minimum concentration observed was in sample 1 during week 7 at 8.66 mg/L. The concentrations of all samples appear to be stabilizing at the end of this experiment, and range from 8.66 mg/L in sample 1 and 34.39 mg/L in sample 8.

The highest calculated release rate occurred in sample 8 during week 2 at 27.20 mg/kg, while the lowest rate occurred in sample 2 during week 5 at 3.60 mg/kg; however, sample 1 consistently showed the lowest release rates throughout the experiment, and the observed low point in sample 2 appears to be an anomalous point as it does not agree with the overall trend. Sample 8 showed the highest release rates overall. A good correlation can be made between grain size and calcium release rates from these results, as the smaller the grain size, the higher the calcium release rate is. The release rate for calcium is presented in figure 5-6 below:

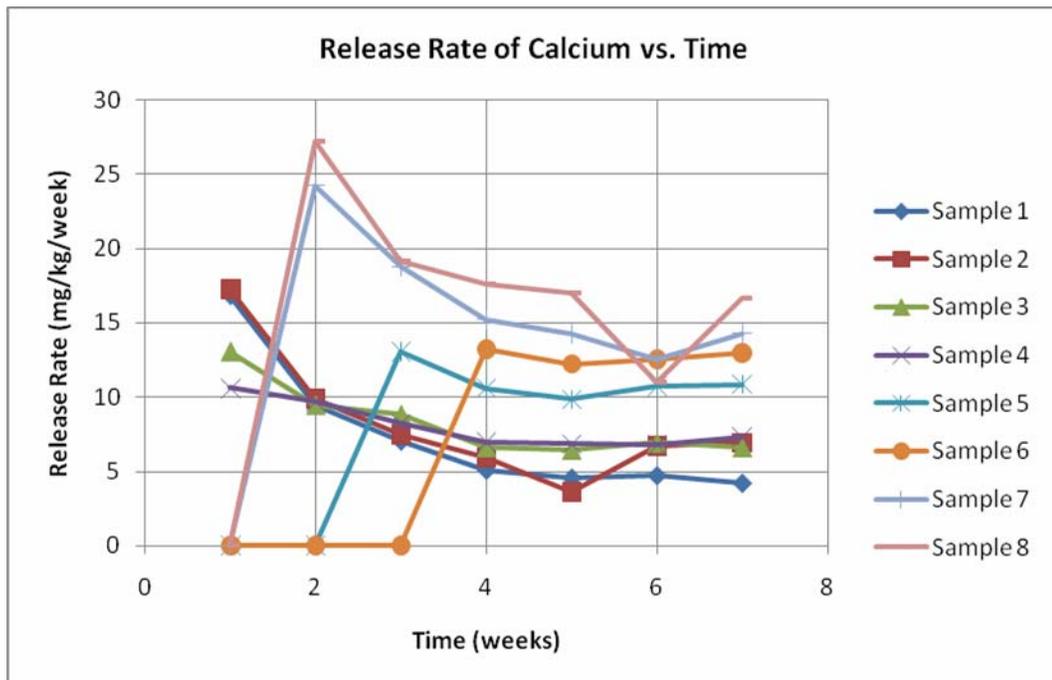


Figure 5-6: Calcium Release Rate vs. Time

5.3.3 Molybdenum

All concentrations could not be determined by the instrument for samples 1 to 4 as they were well below the calibration limit of 0.1 mg/L, as were the concentrations up to week 3 of sample 5. It is interpreted that these concentrations are below 0.1 mg/L.

Concentrations of molybdenum detected ranged from 0.0071 mg/L in sample 6 in week 2 to 0.078 mg/L in sample 8 during week 4. Concentrations in sample 5 appear to be increasing from a minimum of 0.0086 mg/L detected in week 4 to 0.014 in week 7. The trend in sample 6 concentrations also appears to be increasing, with a range of 0.0071 to 0.028 mg/L. No trend is apparent in samples 7 and 8; however, concentrations in sample 8 increase dramatically from week 1 to 2, nearly doubling its value from 0.024 to 0.055 mg/L. At the end of the experiment, detected concentrations range from 0.014 to 0.052 mg/L.

The maximum release rate was observed in sample 8 during week 4 at 0.038 mg/kg, while the lowest release rate was observed in sample 5 in week 5 at 0.0038 mg/kg. An increasing trend appears in sample 5 and 6, but no distinguishable trend was observed in samples 7 and 8. Sample 8 clearly shows the highest release rates overall, while the lowest appear in sample 5. Release rates could not be calculated for samples 1 to 4. Molybdenum release rates are presented in figure 5-7 below:

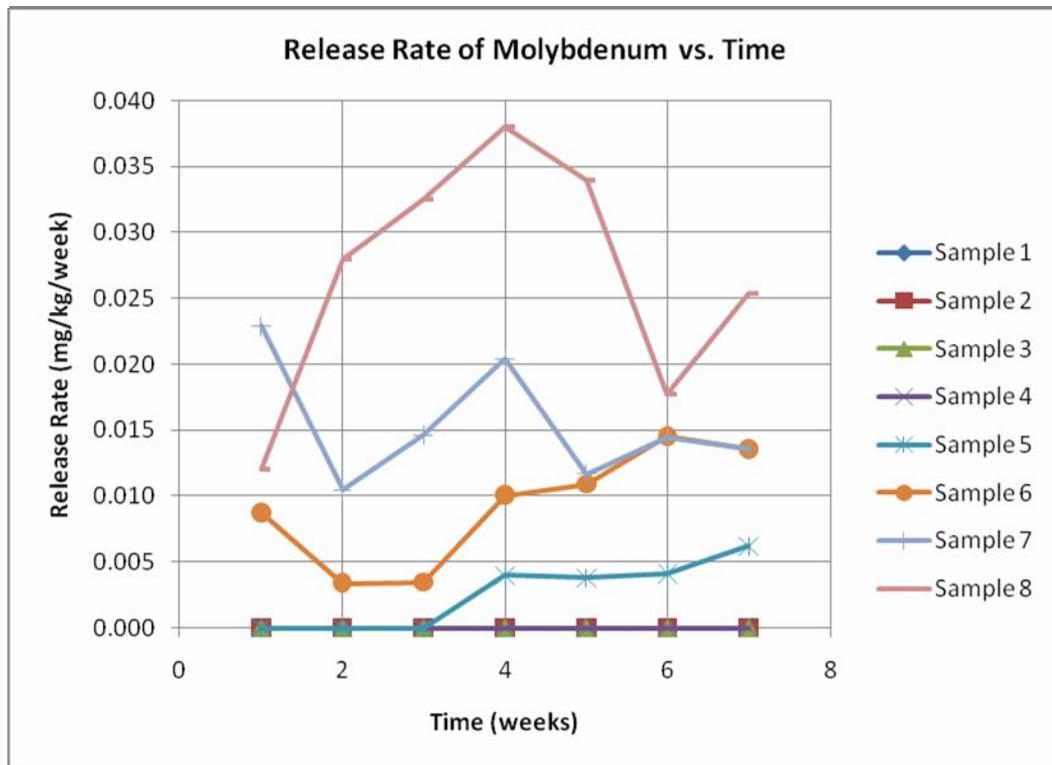


Figure 5-7: Molybdenum Release Rate vs. Time

5.3.4 Zinc

Due to the high error encountered when creating the calibration curve, the lowest standard concentration of 0.1 mg/L was rejected and not used for calibrating. However, the instrument was still able to determine certain points below the calibration limit of 1 mg/L without encountering further errors, which were used in results analyses. For concentrations that were returned without a value, it is interpreted that they have concentrations below 1 mg/L.

Although many concentrations could not be determined, it can be seen that almost all concentrations in the samples were below 0.3 mg/L, except for three points. The highest concentration found was in sample 7 during week 0 of 0.85

mg/L and the lowest concentration of 0.0037 mg/L was seen in sample 5 in week 0. For samples collected in week 7, only sample 6 had a measurable concentration of 0.20 mg/L while concentrations from all other samples could not be determined. No trends were discernable due to limited results available.

The maximum calculated release rate was seen in sample 7 during week 1 at 0.24 mg/kg and the minimum rate was 0.0046 mg/kg in sample 6 in week 4. No trends could be observed due to the limited data available. Zinc release rates are plotted against time in figure 5-8 below:

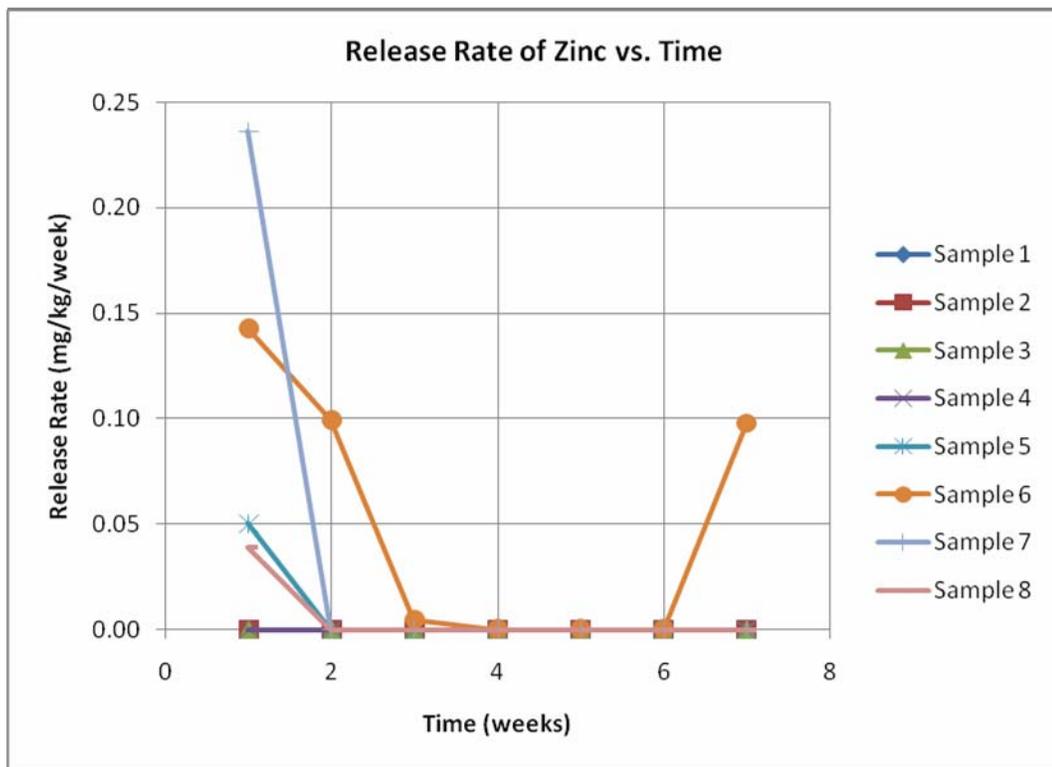


Figure 5-8: Zinc Release Rate vs. Time

5.3.5 Arsenic

Some concentrations of arsenic could not be determined as the instrument found them well under the calibration limit of 0.1 mg/L. Furthermore, the second calibration run found the standard concentration of 0.1 mg/L erroneous for one of the wavelengths, and thus was not used in creating its calibration curve, making the concentrations for this wavelength out of range after the second calibration. All concentrations returned without a value was interpreted to be less than 0.1 mg/L.

Generally, arsenic concentrations are below 0.1 mg/L except for three points. Concentrations ranges from a maximum of 0.11 mg/L, seen in sample 5 in week 3, to a minimum of 0.0067 mg/L, seen in sample 6 of week 7. For all samples, concentrations appear to be decreasing over time, as the detected concentrations range from 0.033 to 0.10 mg/L in week 0 to 0.0067 to 0.012 mg/L in week 7; furthermore, many points were below the calibration range by week 7.

The maximum release rate calculated was 0.053 mg/kg seen in sample 7 of week 2, while the lowest release rate was 0.0033 mg/kg in sample 6 of week 7. Generally, release rates appear to be decreasing over time, as the range of release rates progress from 0.037 to 0.051 mg/kg in week 1 to 0.0033 to 0.0056 mg/kg in week 7. Arsenic release rates are plotted against time, presented in figure 5-9 below:

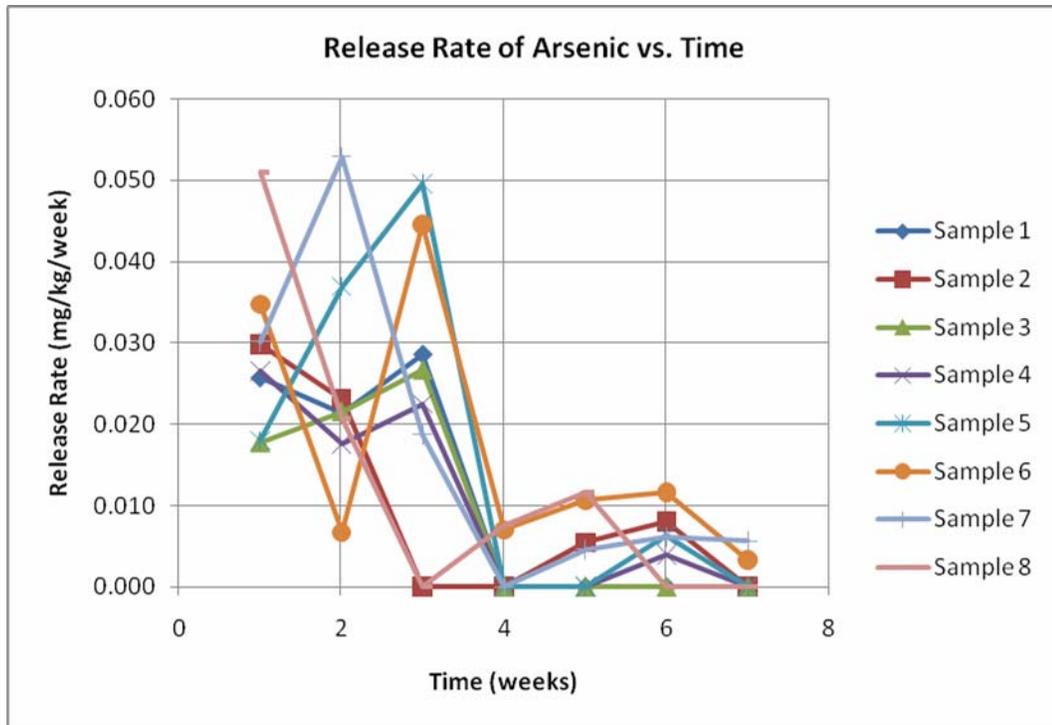


Figure 5-9: Arsenic Release Rate vs. Time

5.3.6 Selenium

For the first calibration run, the calibration point of 0.1 mg/L for one wavelength of selenium was considered erroneous by the instrument, and therefore was not used in creating the calibration curve for this wavelength. Furthermore, there were points that the instrument could not determine a value for; these concentrations were interpreted to be less than 0.1 mg/L.

Detected concentrations ranged from 0.011 mg/L in sample 1 of week 2 to 6.1 mg/L in sample 6 of week 1. In weeks 6 and 7, only concentrations from sample 2 and sample 8, respectively, could be detected. Furthermore, points detected at relatively high concentrations (i.e. greater than 1 mg/L) one week

returned no value the next week. Detected points appear to be sporadic, and no clear trend could be interpreted.

The highest release rate calculated was in sample 6 in week 1 with a value of 2.86 mg/kg, while the lowest release rate appeared in sample 1 in week 3 with a value of 0.29 mg/kg. Since many release rates could not be calculated, points appear sporadic on the graph (see Figure 5-10) and a clear trend could not be interpreted.

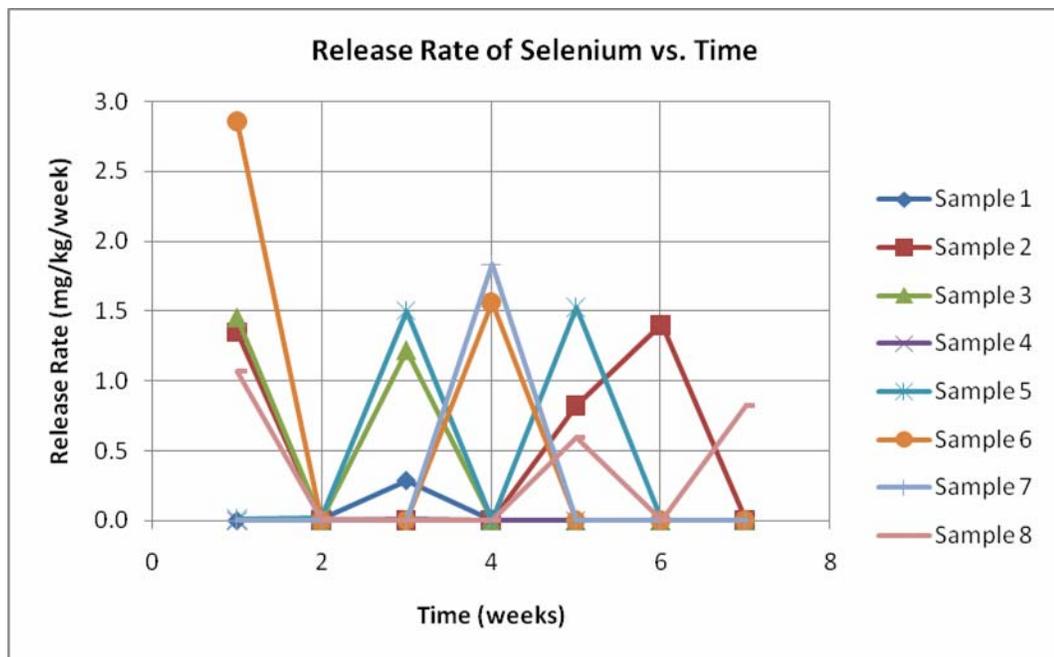


Figure 5-10: Selenium Release Rate vs. Time

5.3.7 Magnesium

The standard calibration concentration of 0.1 mg/L showed high errors, and was not used in the creation of the calibration curve; thus, any points that the instrument could not determine a value for was interpreted to be less than 1 mg/L.

However, any values returned that were less than 1 mg/L were still used in the analyses.

Most concentrations of magnesium are below 5 mg/L except for an anomalous value of 27 mg/L appearing in sample 7 during week 0. Aside from this value, the maximum concentration during week 0 appears in sample 8 at 4.8 mg/L, while the minimum value is seen in sample 2 at 0.057 mg/L. The minimum concentration detected is 0.005 mg/L in sample 2 during week 7. In general, the concentrations appear to be decreasing; however, sample 8 seems to be decreasing at a much slower rate than all other samples, and is at a concentration of 0.52 mg/L at week 7 versus the range of 0.005 to 0.21 mg/L seen in the other seven samples. The concentrations of samples 5 and 6 appeared to be below the calibration limit by week 4 as no values were returned.

The highest release rate calculated was 1.95 mg/kg seen in sample 7 in week 1, while the lowest release rate was observed in sample 2 of week 7 to be 0.0025 mg/kg. Initial release rates found in week 1 for samples 1 to 4 range from 0.088 to 0.22 mg/kg, while samples 5 to 8 show a range of 1.0 to 1.9 mg/kg; however, rates decrease significantly for all samples, generally by more than an order of magnitude. The decreasing trend in sample 8 is not as dramatic as in all other samples, as it progresses from a rate of 1.0 to 0.25 mg/kg, and shows the highest rates at the end of the experiment (see Figure 5-11).

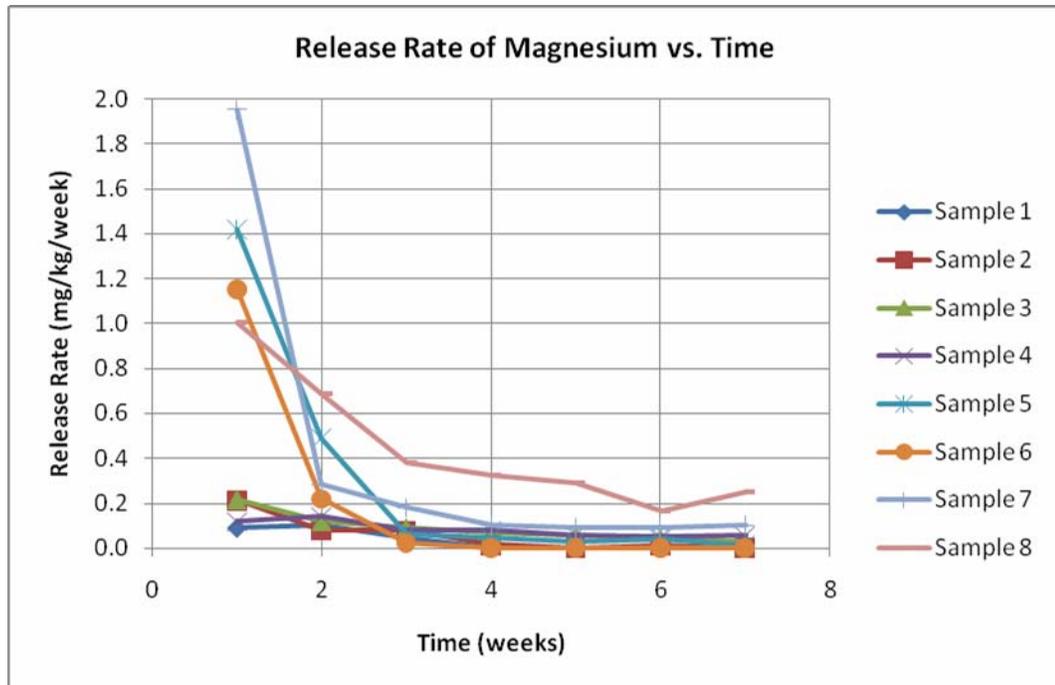


Figure 5-11: Magnesium Release Rate vs. Time

5.3.8 Manganese

No values for samples 1 to 4 were returned until samples for week 4. These concentrations were interpreted to be less than the calibration limit of 0.1 mg/L. Notably, all results were well below the calibration limit.

The maximum concentration of 0.19 mg/L appeared in sample 7 in week 0, and the minimum concentration of 0.001 mg/L appeared in sample 1 during week 5. Consistently, samples 1 and 4 show the lowest concentrations, ranging from 0.001 to 0.002 mg/L, while sample 8 shows the highest concentrations which range from 0.044 to 0.10 mg/L. If the anomalous maximum concentration of 0.19 mg/L in sample 7 is disregarded, sample 6 shows the highest concentrations initially, but decreases to lower concentrations in the range of 0.0095 to 0.012

mg/L by week 4. Concentrations in samples 1 to 7 appear to be stabilizing or increasing at the end of this experiment, while concentrations in sample 8 appear to be increasing.

The release rate for sample 7 during week 1 was the maximum at 0.055 mg/kg, while sample 4 showed the minimum rate at 0.009 mg/kg during week 7. Release rates ranged from 0.022 mg/kg in sample 8 to 0.055 mg/kg in sample 7 during week 1, and progressed to range from 0.009 mg/kg in sample 4 to 0.034 mg/kg in sample 8 by week 7. The release rates of manganese in samples 5 to 7 appear to be stabilizing after an initial decrease while the rates in samples 1 to 4 appear to be increasing. Release rates of sample 8 appear to be increasing at the end of this experiment, and are the highest of all samples by week 3. Manganese release rates are plotted against time in figure 5-12 below:

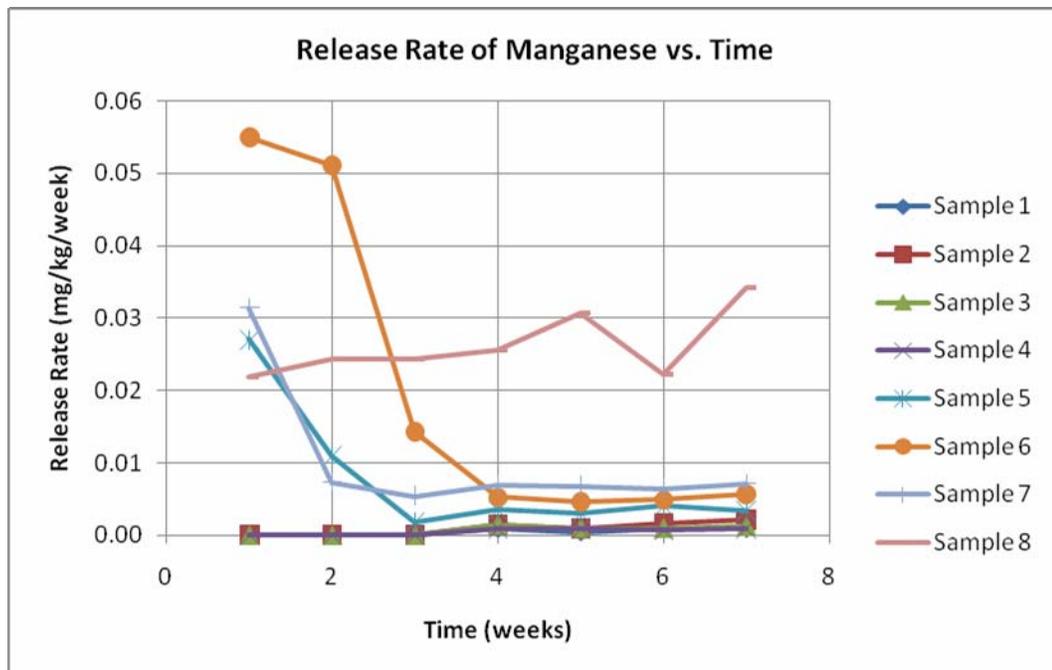


Figure 5-12: Manganese Release Rate vs. Time

5.3 Phreeqc Interactive Analysis

The results of the geochemical analysis was input into the computer modelling program Phreeqc Interactive Analysis to model the charge balance and saturation indices of the water samples. Samples 1-1 to 7-8 were analyzed, as other samples were not titrated and thus no alkalinity value was available to be modelled.

5.3.1 Charge Balance

The percentage error in charge balance is presented in Table 5-1 below. Results showed mostly positive errors, indicating that charge was dominated by cations over anions. The large positive error may be attributed to the fact that very few negatively charged elements were analyzed. Significant concentrations of chlorine and NO_3^- were expected, and along with other anions that were not analyzed, would have helped to contribute in decreasing the charge balance error. Large negative errors appeared in samples that showed a calcium concentration that was above the calibration limit, and was modelled as 50 mg/L. When modelled at a concentration of 100 mg/L, errors became slightly positive.

Sample	Error (%)						
EY 1-1	40.86	EY 2-7	20.53	EY 4-5	17.52	EY 6-3	22.59
EY 1-2	36.10	EY 2-8	14.83	EY 4-6	19.30	EY 6-4	22.86
EY 1-3	29.31	EY 3-1	32.07	EY 4-7	14.42	EY 6-5	17.89
EY 1-4	21.58	EY 3-2	33.95	EY 4-8	11.81	EY 6-6	20.96
EY 1-5	-14.25	EY 3-3	27.83	EY 5-1	3.51	EY 6-7	17.13
EY 1-6	-62.84	EY 3-4	25.46	EY 5-2	15.40	EY 6-8	14.81
EY 1-7	-20.92	EY 3-5	23.06	EY 5-3	33.68	EY 7-1	-5.99
EY 1-8	2.87	EY 3-6	16.87	EY 5-4	24.04	EY 7-2	12.86
EY 2-1	36.09	EY 3-7	12.66	EY 5-5	15.68	EY 7-3	19.72
EY 2-2	37.15	EY 3-8	11.00	EY 5-6	18.05	EY 7-4	19.30
EY 2-3	33.36	EY 4-1	6.65	EY 5-7	17.35	EY 7-5	18.18
EY 2-4	28.17	EY 4-2	17.88	EY 5-8	12.59	EY 7-6	18.52
EY 2-5	17.86	EY 4-3	26.76	EY 6-1	3.11	EY 7-7	18.73
EY 2-6	-32.87	EY 4-4	22.57	EY 6-2	17.17	EY 7-8	15.62

Table 5-1: Percent error in charge balance

5.3.2 Saturation Indices

All saturation indices were modelled (see Appendix F), and the saturation indices of calcite, gypsum, and dolomite (disordered) were plotted as they were the minerals of highest concern. Of the three minerals, calcite was the only to reach saturation, and only in samples 7 and 8 (see figure 5-13). Samples 5 to 8 show initial trends of increase that decrease over time, while samples 1 to 4 show an overall decreasing trend.

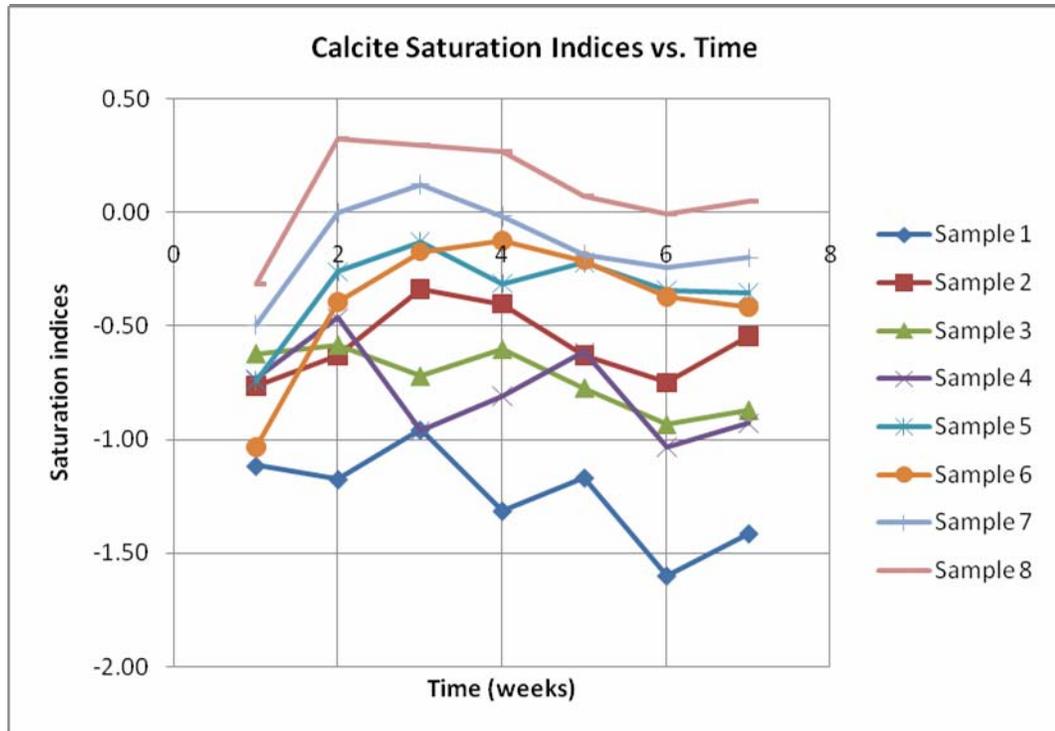


Figure 5-13: Calcite Saturation Indices vs. Time

The saturation indices of gypsum, plotted in figure 5-14 against time, shows a decreasing trend by the end of the experiment in samples 1 to 3, while trends in samples 4 to 8 may be increasing after an initial decrease. Disordered dolomite saturation indices, plotted in Figure 5-15, were highest in samples 8, 7, and 5, respectively. Samples 1 and 6 returned no data for the samples collected from week 4 onwards. Decreasing trends were visible by the end of this experiment.

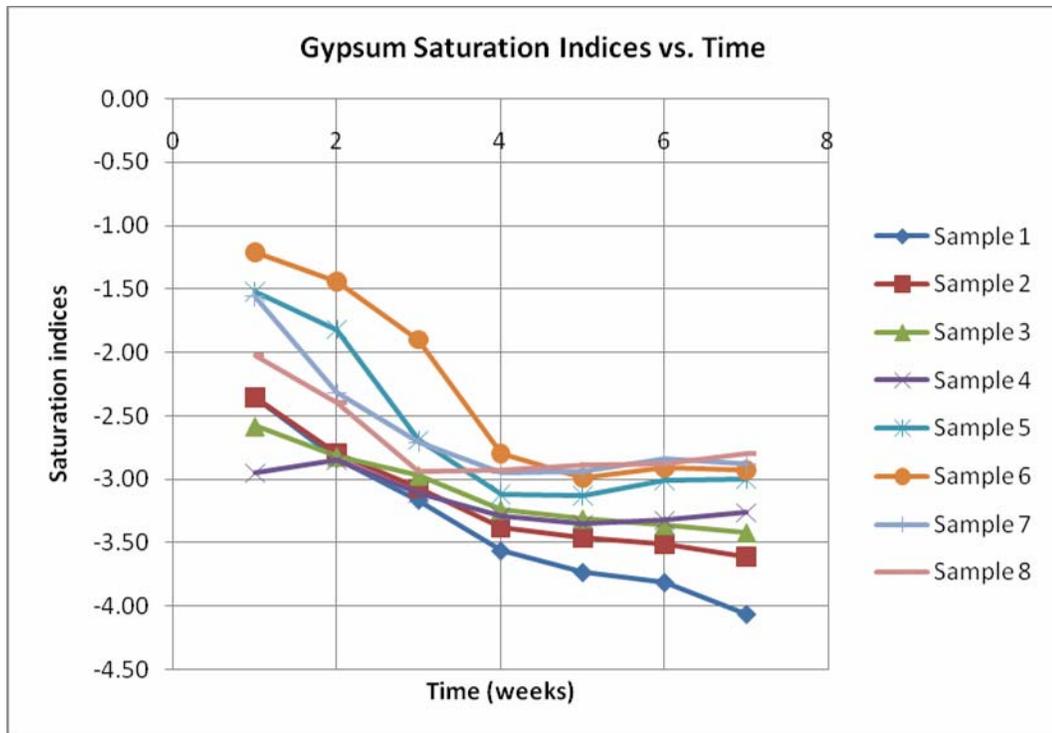


Figure 5-14: Gypsum Saturation Indices vs. Time

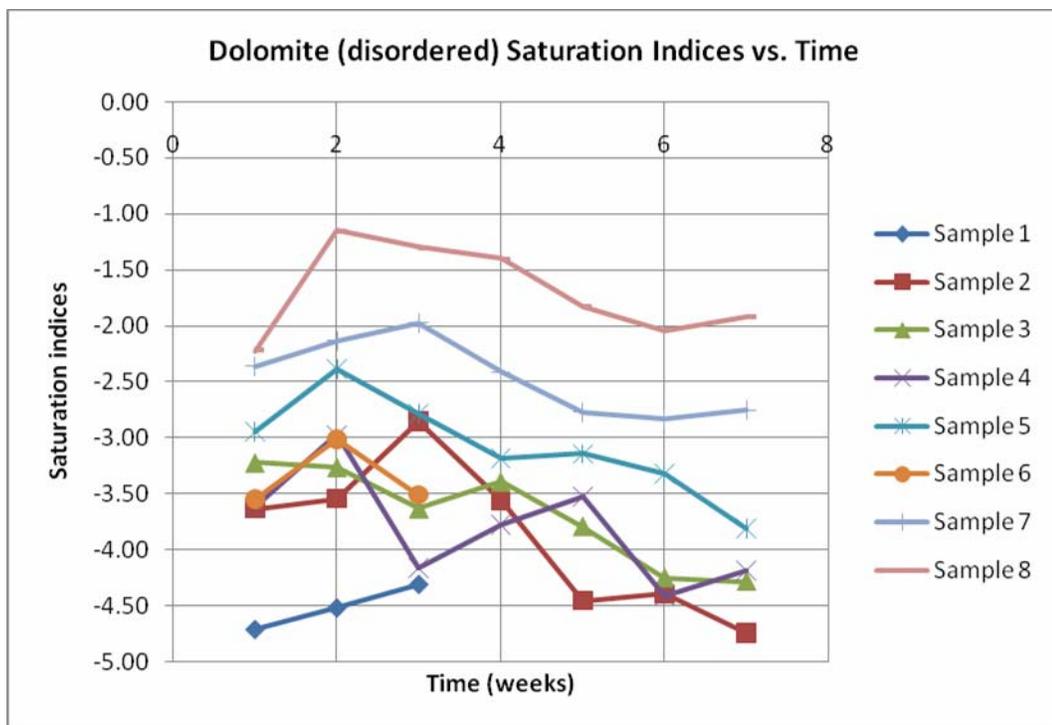


Figure 5-15: Dolomite (disordered) Saturation Indices vs. Time

6. CONCLUSIONS

Although the test samples and the conditions under which they were subjected do not truly represent the conditions found at the Antamina mine, results from this experiment help to increase the understanding the environmental impacts of the waste rock at the mine and of neutral drainage. It can be seen that elements of concern are leached from neutral drainage at significant concentrations. Furthermore, the effects of particle size on drainage quality were evident, along with the following conclusions:

- Concentrations and release rates of calcium, sulphur, molybdenum, magnesium, and manganese reveal that higher concentrations are seen the smaller the grain size of the waste rock
- Trends of increasing alkalinity and pH were observed with decreasing grain size
- Concentrations of copper, chromium, nickel, and iron were determined to be below the detection limit of 0.1 mg/L
- High initial concentrations in calcium, sulphur, zinc, arsenic, magnesium, and manganese were observed which decreased significantly over time
- Manganese and magnesium concentrations became the highest in the finest grained sample
- Molybdenum concentrations revealed that finer grained particles leach higher concentrations, with a maximum concentration of 0.038 mg/L
- Selenium concentrations range from 0.011 to 6.1 mg/L, but no clear trend was seen

- High positive charge balance error indicated that the analyzed parameters did not cover all elements necessary for a full analysis, and that anions at significant concentrations were absent from this experiment

7. RECOMMENDATIONS FOR FURTHER WORK

Although initial trends were observed, the characterisation of waste rock drainage over a long period of time is necessary in order to gain further understanding. Humidity cell experiments are a relatively simple way to help improve the management of waste rock and develop environmental mitigation techniques. This experiment was able to demonstrate the effect of particle size on drainage quality, and that finer grained samples show a significantly different characteristic than coarser grained samples, and the apparatus used and the samples collected from this experiment should be utilized to continue testing of the marble diopside waste rock in order to better understand these effects. Further characterization with lower calibration limits is needed for arsenic, zinc, molybdenum, selenium, copper, iron, nickel, and chromium, and could be performed on the preserved samples already collected. A higher calibration limit for the ICP-OES instruments is needed for calcium in order to better characterize the initial concentrations.

Improvements to the apparatus could be made, such as to cover the rock samples to prevent foreign material from entering, and to design better clamping of the samples so that less water sample is lost. Results from this experiment should be compared to other experiments currently testing the same type of rock in order to evaluate the validity of the experiment. Furthermore, results should be considered in the overall evaluation of waste rock management techniques.

ACKNOWLEDGEMENTS

The samples and samples list were obtained by Celedonia Aranda from the Antamina Mine in Peru. Technical assistance was provided by Olga Singurindy is preparing acid baths, titration acids, and ICP-OES calibration standards. The ICP-OES analysis was operated by Maureen Soon. Ongoing assistance was provided by Professor Uli Mayer. The writer thanks Professor Roger Beckie for his supervision, and Diane Moug, Rajiv Joiya, and Nick Edgar for their support and assistance.

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APPENDICES

Appendix A

Photos of Apparatus and Laboratory Cells



Sample 1



Sample 2



Sample 3



Sample 4



Sample 5



Sample 6



Sample 7



Sample 8



Sample 9



Sample 10

Apparatus:









Appendix B

List of Samples Collected from Antamina Mine



University of British Columbia
 Department of Mining Engineering
 "Assessment of waste rock weathering characteristics at the Antamina mine based on field cells experiment"

Project: Waste Rock Study at Antamina Mine
Material Type: Waste Rock
Rock Type: Marble and Hornfels - Class B
Test Types: As indicated
Description:

Prepared by:
Email:
Telephone:
Reviewed by:

Samples ID	Size		Sampling date (dd/mm/yy)	Rock Type	Sample Mass			Sample - combination of size fractions
	(US)	(mm)			Initial* (Kg)	For Column Test (Kg)	Subsample 2**** (Kg)	
FC-3-A	4"	100.0	07/07/06	Marble Diopside	0.00	0.00	No sample	
FC-3-B	3"	75.0	07/07/06	Marble Diopside	0.00	0.00	No sample	
FC-3-C	2"	50.0	07/07/06	Marble Diopside	17.80	8.90	0.15	
FC-3-D	1 1/2"	37.5	07/07/06	Marble Diopside	16.00	8.00	0.20	
FC-3-E	1"	25.0	07/07/06	Marble Diopside	20.10	10.05	0.19	
FC-3-F	3/4"	19.0	07/07/06	Marble Diopside	12.90	6.45	0.18	
FC-3-G	1/2"	12.5	07/07/06	Marble Diopside	16.70	8.35	0.16	
FC-3-H	3/8"	9.50	07/07/06	Marble Diopside	8.10	4.05	0.24	4.05
FC-3-I	1/4"	6.30	07/07/06	Marble Diopside	8.80	4.40	0.14	4.40
FC-3-J	#4	4.75	07/07/06	Marble Diopside	5.37	1.30	0.18	
FC-3-K	#6	3.35	07/07/06	Marble Diopside	4.54	1.10	0.15	2.40
FC-3-L	#8	2.36	07/07/06	Marble Diopside	3.51	0.85	0.12	
FC-3-M	#16	1.18	07/07/06	Marble Diopside	4.95	1.20	0.14	2.05
FC-3-N	#30	0.600	07/07/06	Marble Diopside	2.48	0.60	0.15	
FC-3-O	#50	0.300	07/07/06	Marble Diopside	2.57	0.30	0.16	0.90
FC-3-P	#100	0.150	07/07/06	Marble Diopside	3.43	0.40	0.22	
FC-3-Q	#140	0.106	07/07/06	Marble Diopside	2.14	0.25	0.15	0.65
FC-3-R	#200	0.075	07/07/06	Marble Diopside	2.14	0.25	0.12	
FC-3-S	#270	0.053	07/07/06	Marble Diopside	1.71	0.20	0.10	0.45
FC-3-T	#270	-0.053	07/07/06	Marble Diopside	6.74	0.79	0.19	0.79

Column No.

8

7

6

5

4

2

2

1

Appendix C

Measurements

Marble Diopside - Sample contents

Sample #	Soil	Sieve Size	Particle Size (mm)	Mass (kg)	Total mass (kg)
1	FC3-H	3/8"	9.500	0.800	0.800
2	FC3-I	1/4"	6.300	0.800	0.800
3	FC3-J	#4	4.750	0.433	0.800
	FC3-K	#6	3.350	0.367	
4	FC3-L	#8	2.360	0.332	0.800
	FC-M	#16	1.180	0.468	
5	FC3-N	#30	0.600	0.528	0.792
	FC3-O	#50	0.300	0.264	
6	FC3-P	#100	0.150	0.492	0.800
	FC3-Q	#140	0.106	0.308	
7	FC3-R	#200	0.075	0.444	0.800
	FC3-S	#270	0.053	0.356	
8	FC3-T	-#270	-0.053	0.801	0.801
9	FC3-P	#100	0.150	0.400	0.652
	FC3-Q	#140	0.106	0.252	
10	FC3-T	-#270	-0.053	0.226	0.226

Initial masses (kg)				
Sample #	Empty Small	Empty Large	Empty Large with stopper	Soil
1	0.07608	0.1279	0.15644	0.800
2	0.07612	0.1242	0.15246	0.800
3	0.07715	0.1251	0.15332	0.800
4	0.076553	0.1294	0.15698	0.800
5	0.07653	0.1292	0.15759	0.792
6	0.07607	0.1252	0.1536	0.800
7	0.07583	0.1291	0.1583	0.800
8	0.07652	0.1268	0.1563	0.801
9	0.07704	0.1289	0.15858	0.652
10	0.07746	0.1288	0.15714	0.226

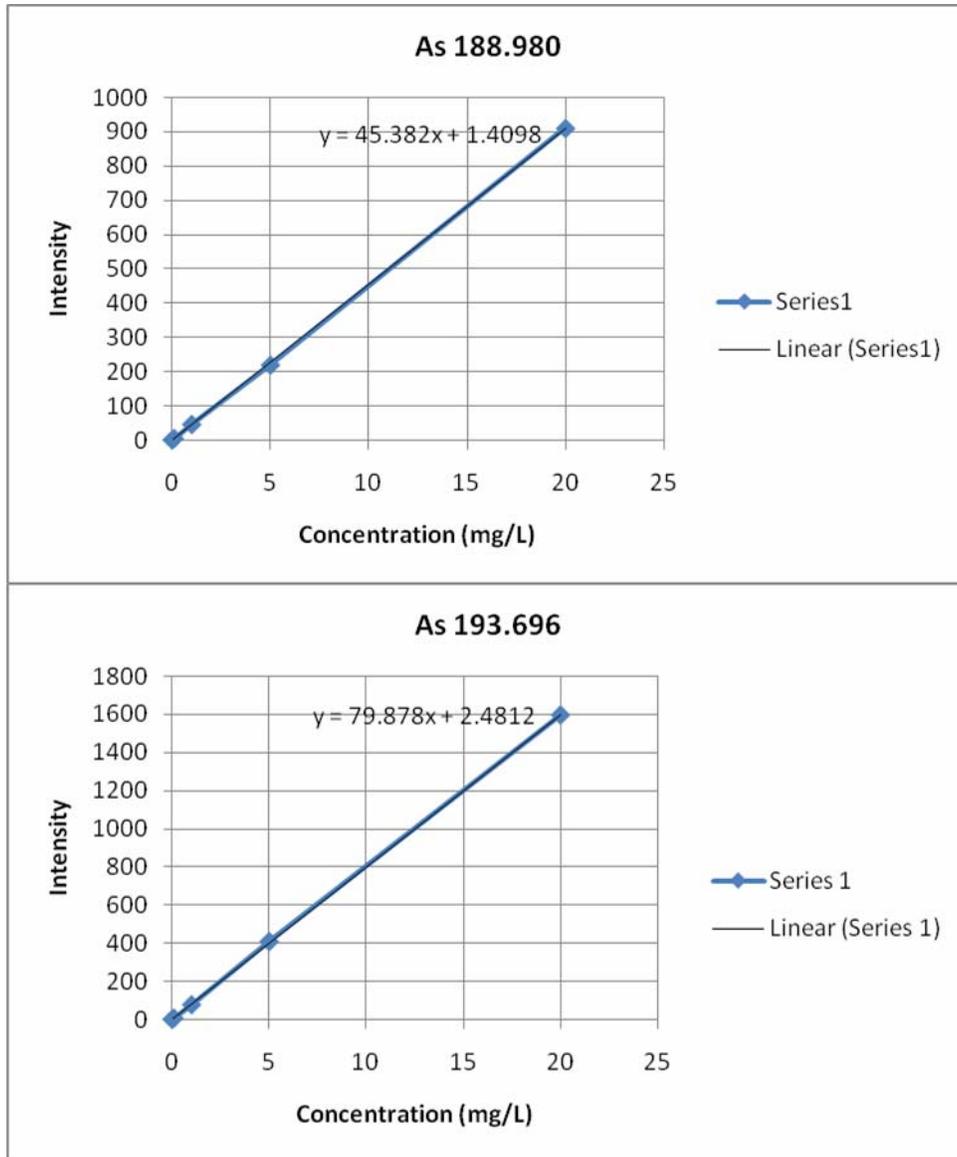
Initial pH							
	Week						
Sample #	1	2	3	4	5	6	7
1	7.46	7.72	8.07	7.60	7.81	7.33	7.51
2	7.73	8.26	8.68	8.55	8.38	8.08	8.16
3	7.98	8.25	8.09	8.37	8.3	7.91	7.97
4	7.84	8.22	7.77	7.97	8.23	7.76	7.78
5	7.53	7.93	8.20	8.05	8.18	7.94	7.99
6	7.30	7.70	7.87	8.13	8.09	7.92	7.86
7	7.38	7.80	8.02	8.09	7.97	7.9	7.98
8	7.40	7.99	8.14	8.18	8.03	8.01	8.07
9	7.40	7.79	n/m	n/m	n/m	n/m	8.05
10	7.72	8.16	n/m	n/m	n/m	n/m	8.22

Alkalinity (eq/L)								
	Sample #							
Week	1	2	3	4	5	6	7	8
1	3.00E-04	3.69E-04	3.78E-04	4.89E-04	5.31E-04	6.33E-04	1.33E-03	1.69E-03
2	2.38E-04	2.38E-04	2.78E-04	3.79E-04	5.73E-04	8.48E-04	1.28E-03	1.75E-03
3	2.33E-04	2.38E-04	3.21E-04	3.85E-04	6.48E-04	7.90E-04	1.33E-03	1.51E-03
4	3.92E-04	3.34E-04	2.82E-04	3.90E-04	7.06E-04	7.61E-04	1.00E-03	1.36E-03
5	3.81E-04	3.16E-04	2.29E-04	3.56E-04	6.81E-04	7.48E-04	9.13E-04	1.26E-03
6	4.09E-04	3.90E-04	3.59E-04	3.80E-04	7.72E-04	7.26E-04	9.21E-04	1.13E-03
7	4.60E-04	4.96E-04	3.76E-04	4.38E-04	7.05E-04	7.61E-04	8.67E-04	1.11E-03

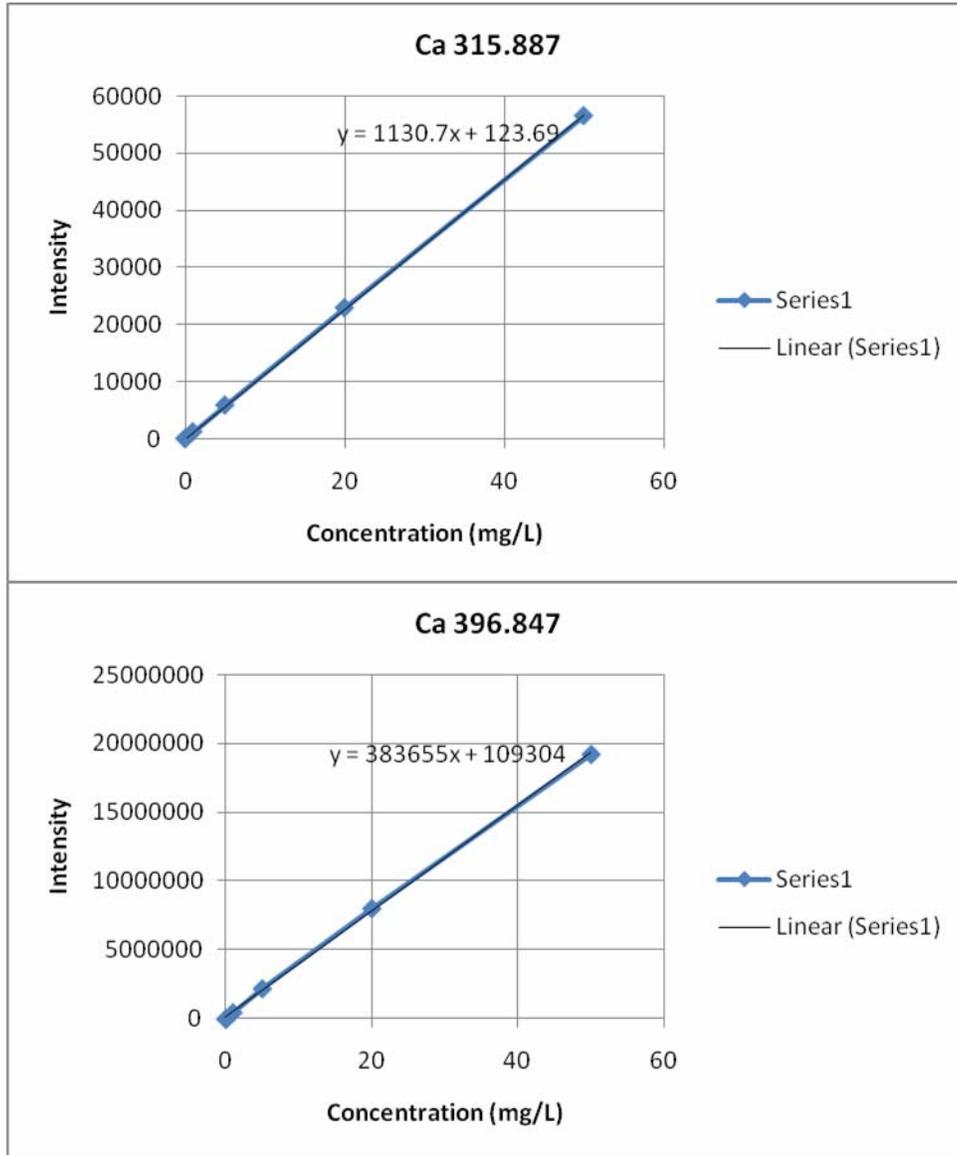
Appendix D

ICP-OES Analysis Calibration Curves

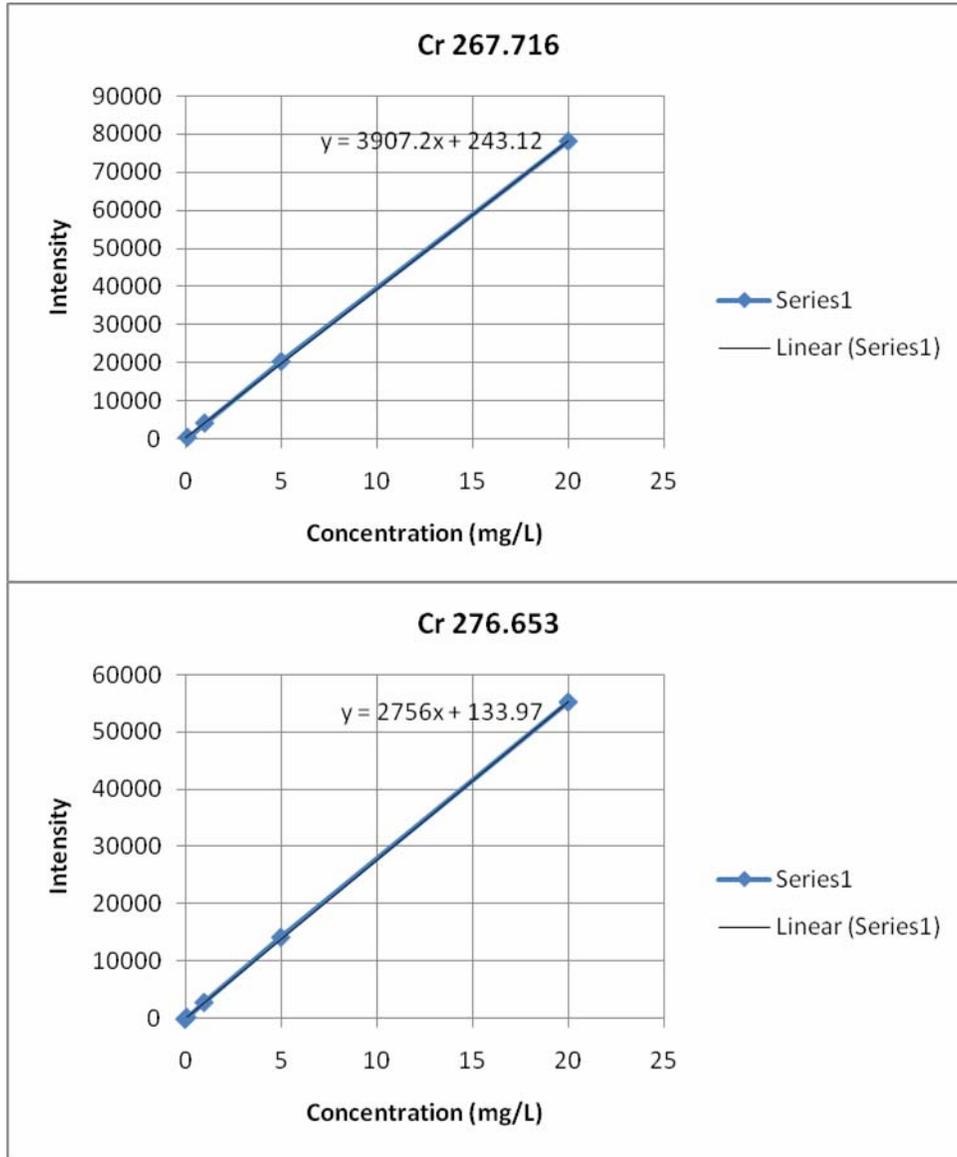
Arsenic:



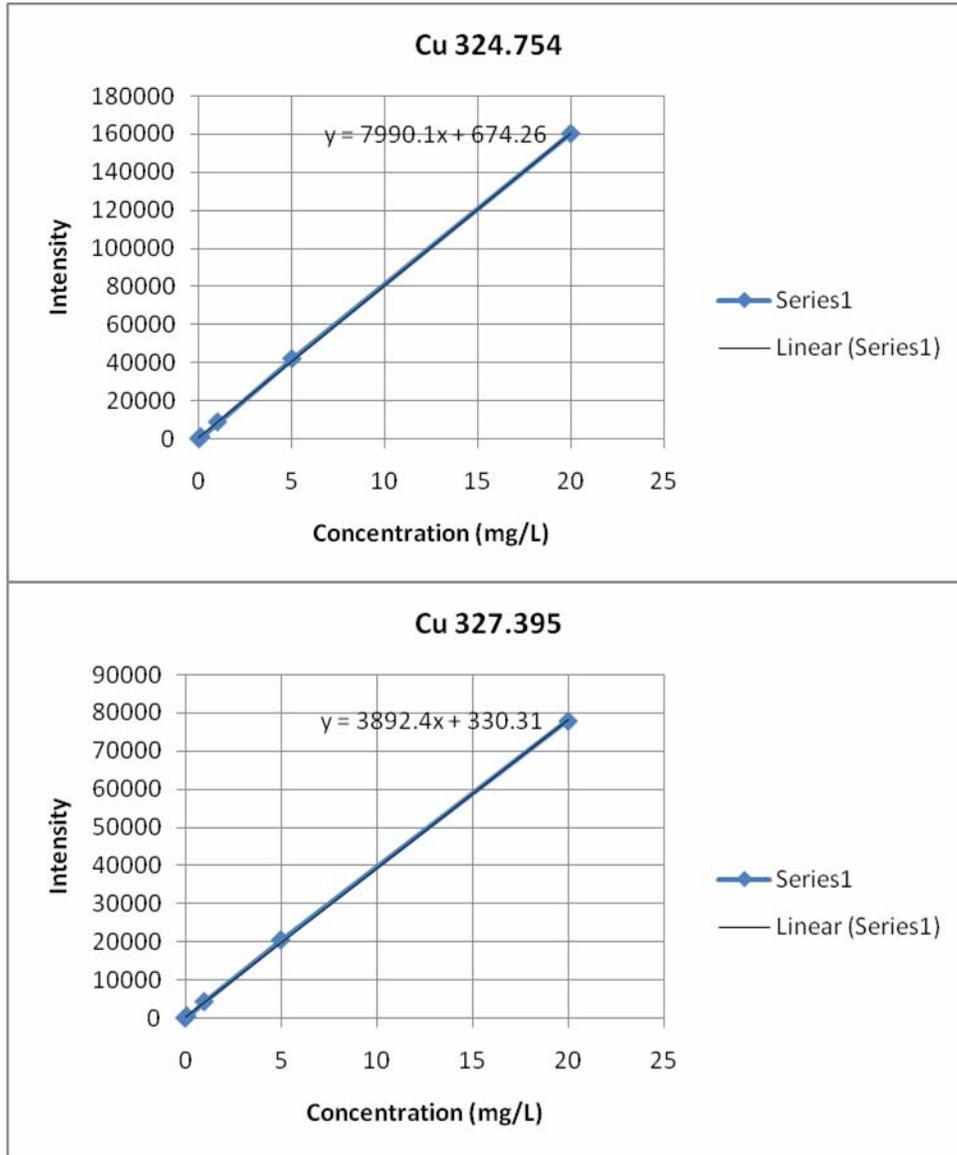
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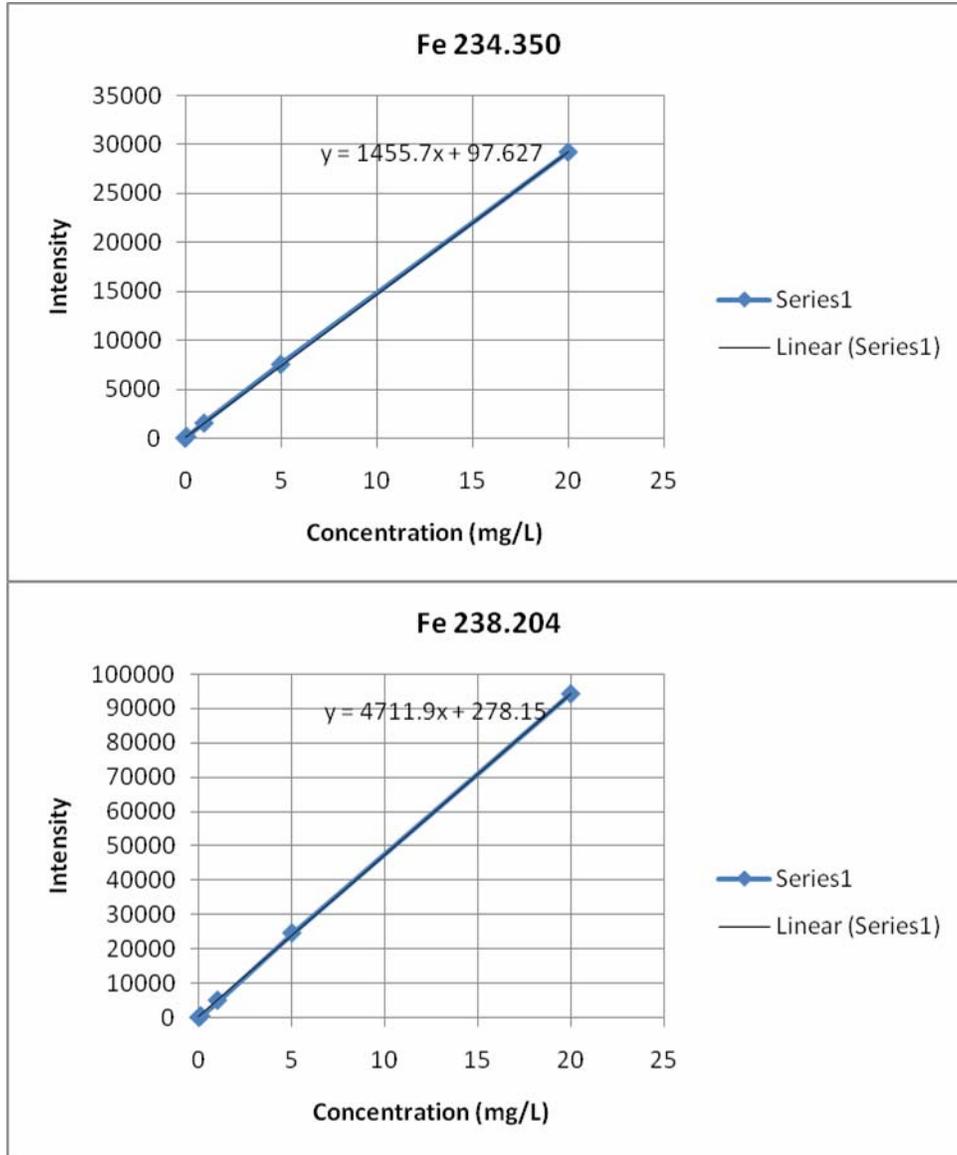
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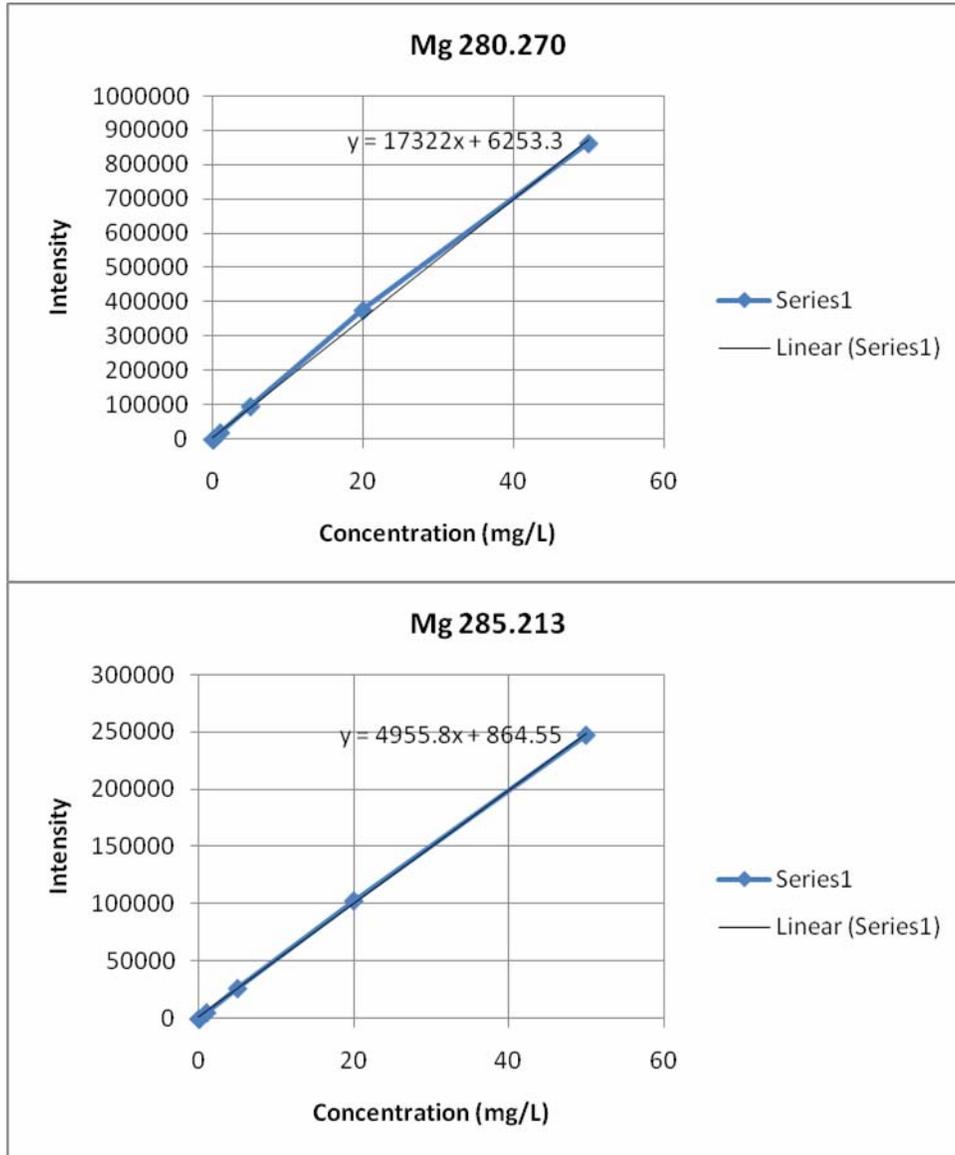
Copper:



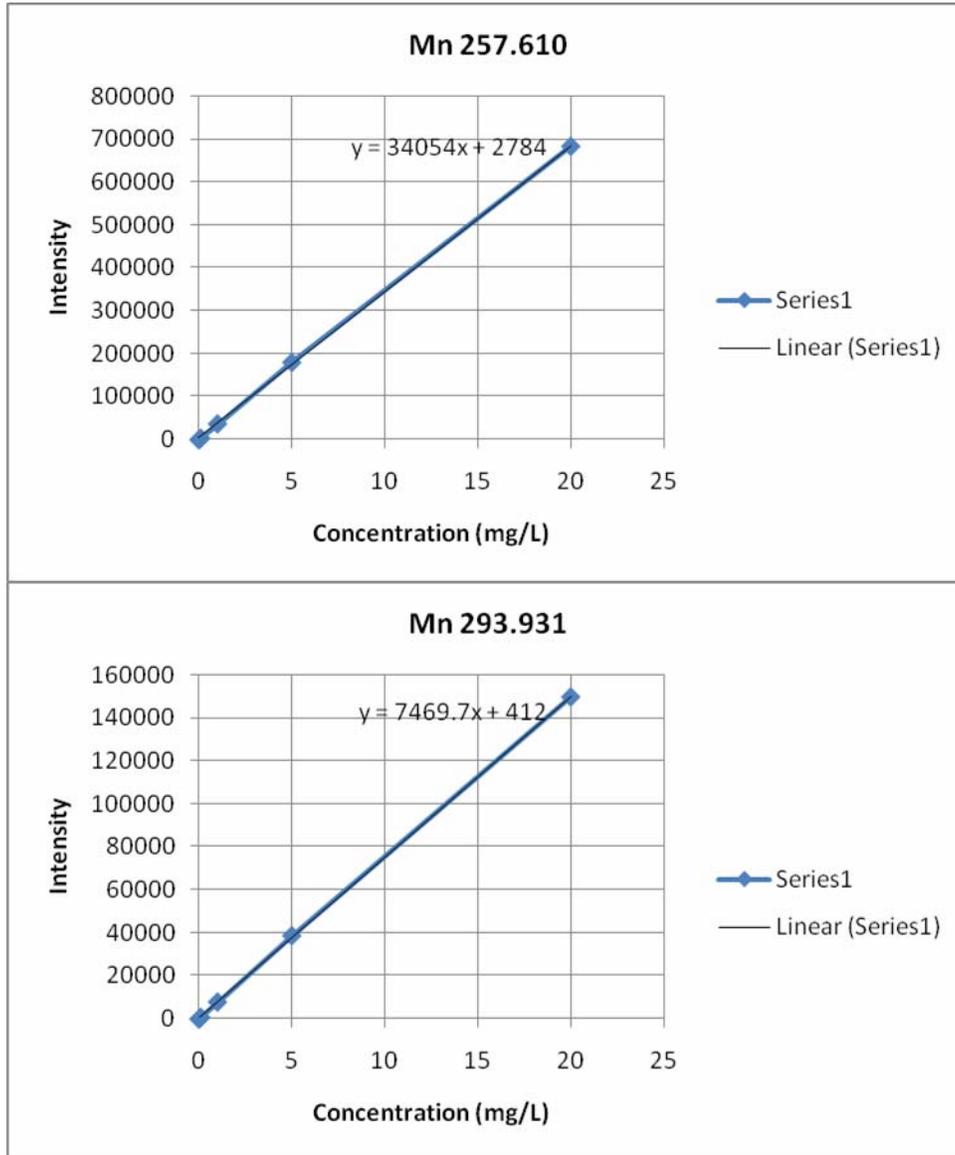
Iron:



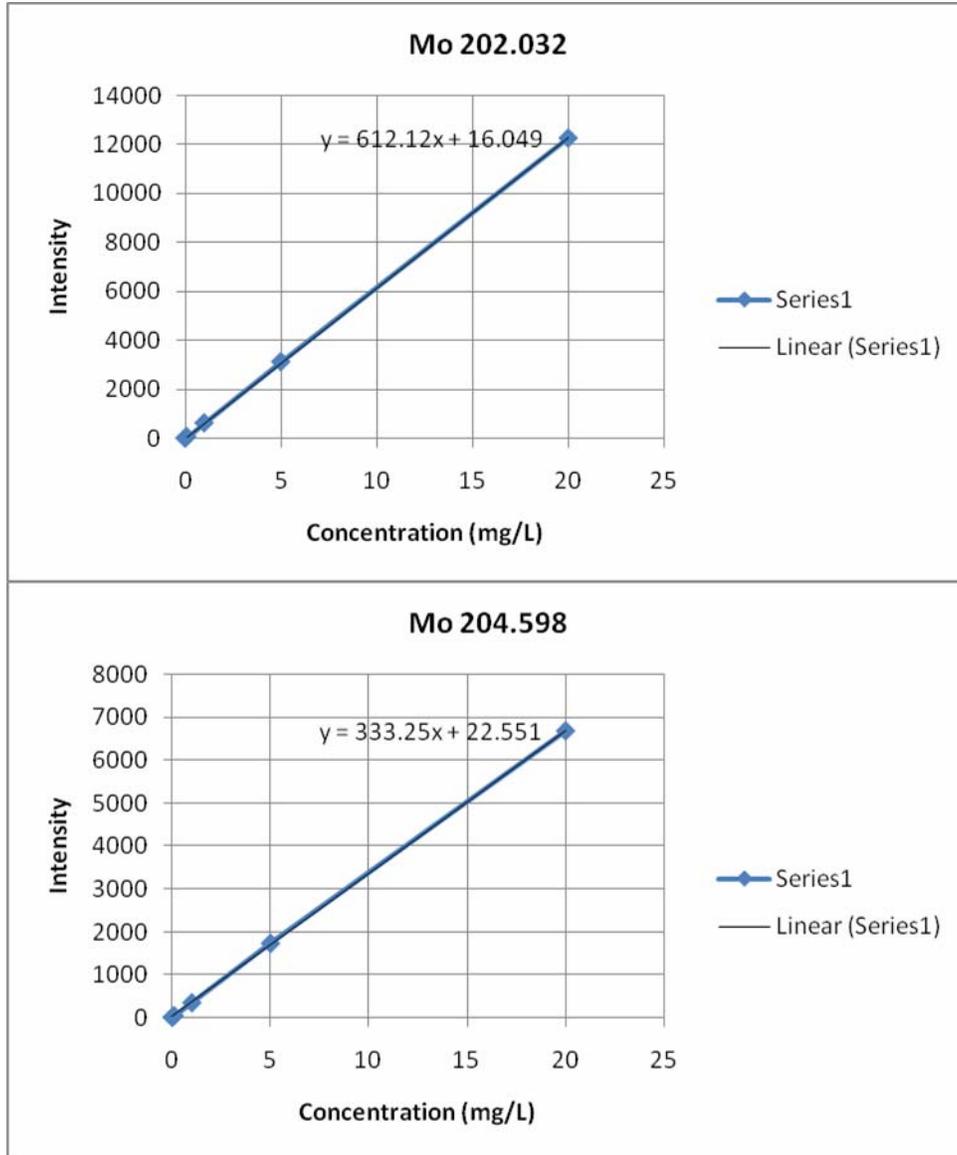
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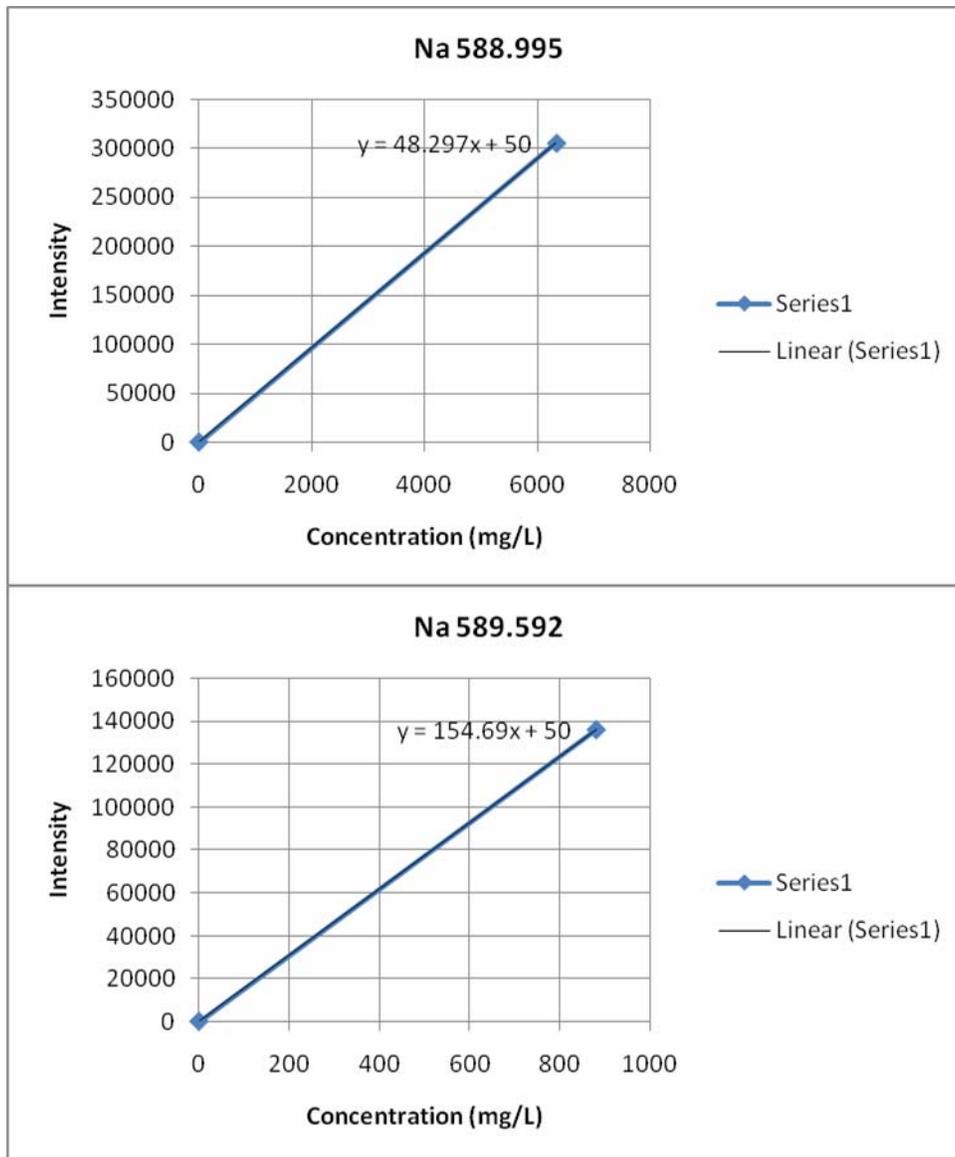
Manganese:



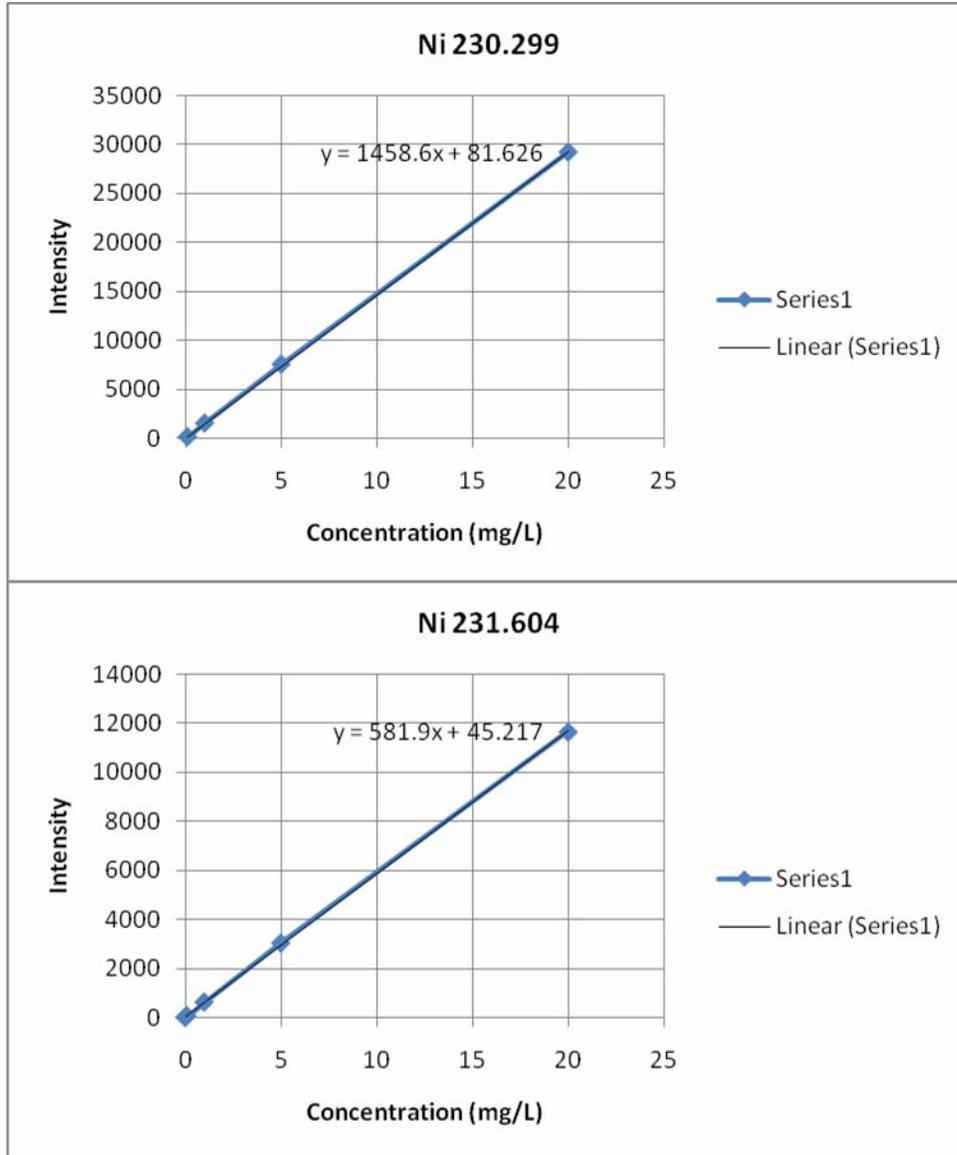
Molybdenum:



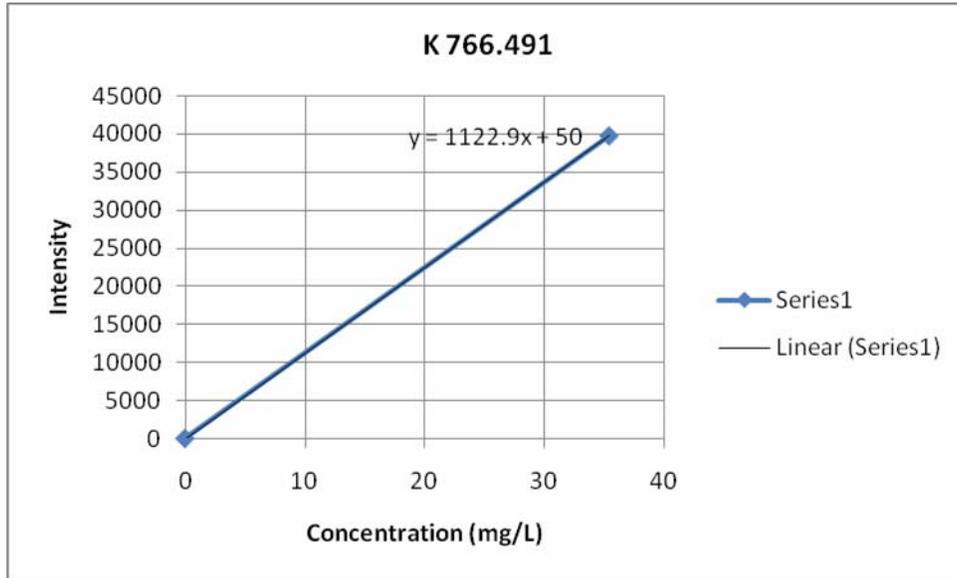
Sodium:



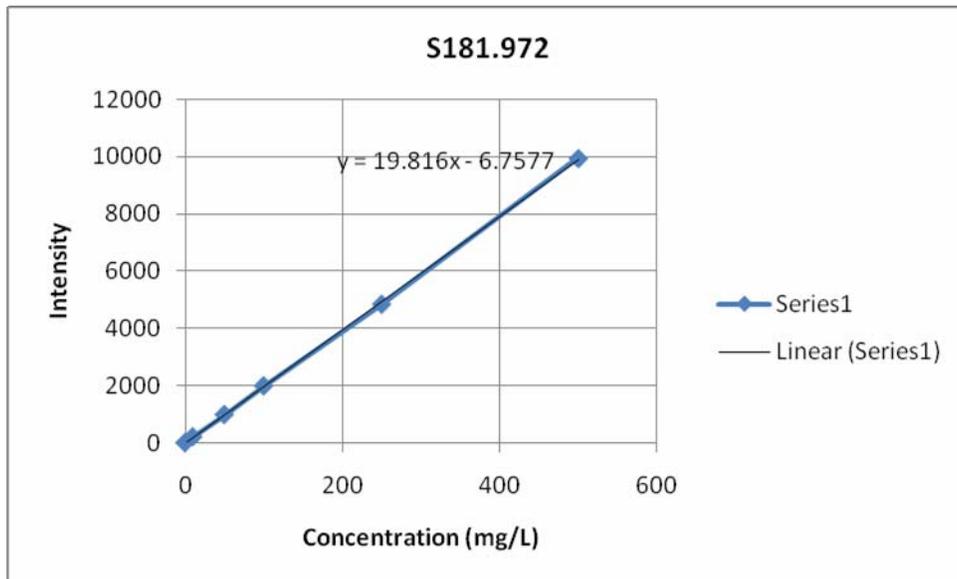
Nickel:

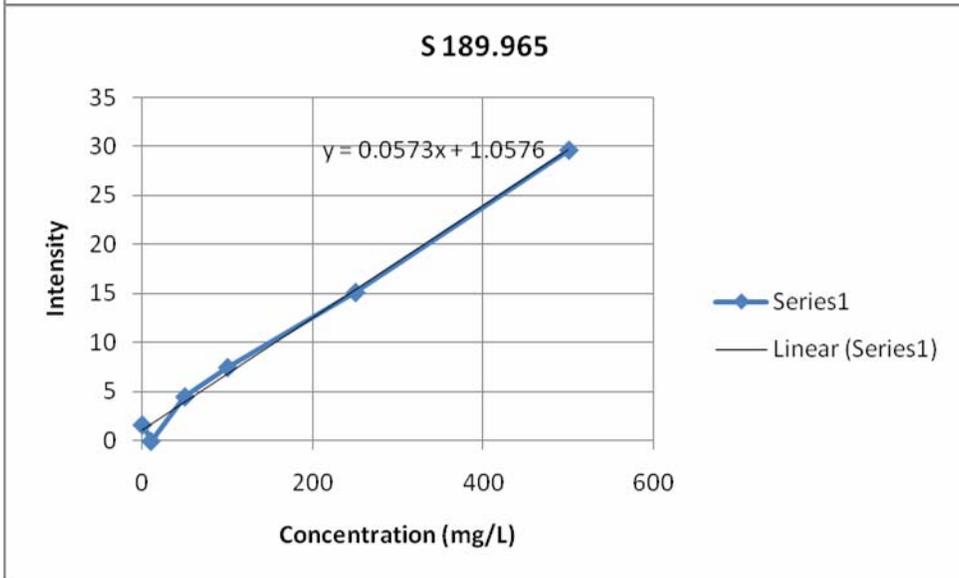
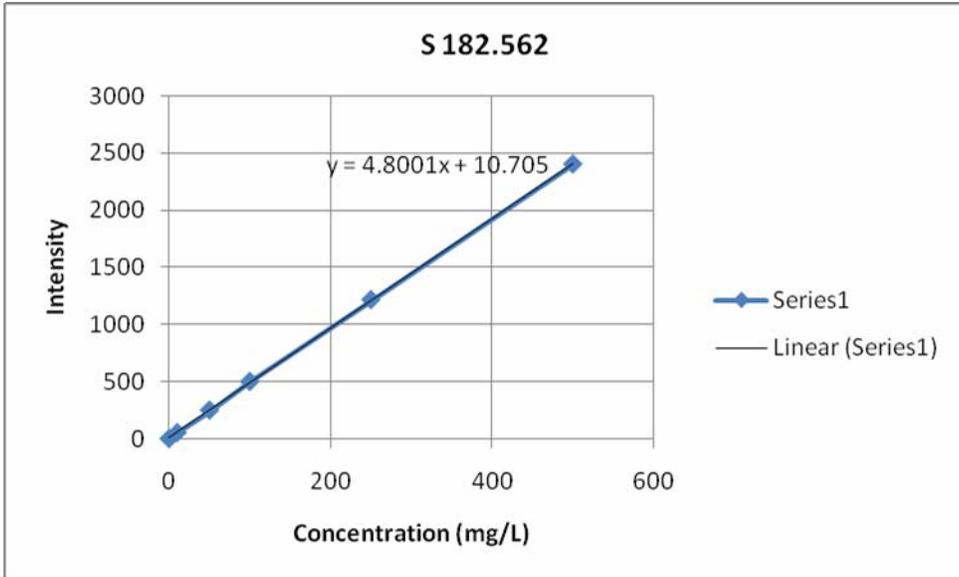


Potassium:

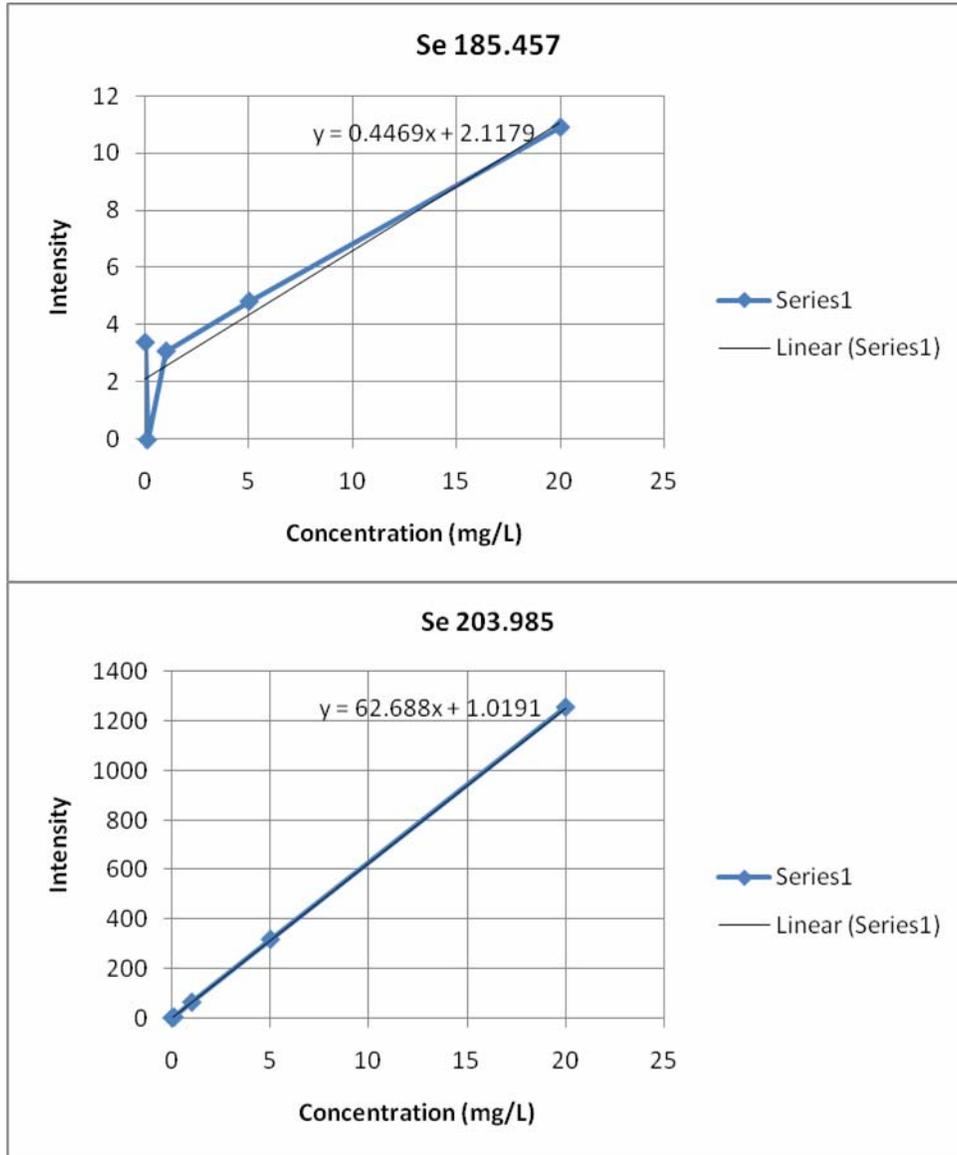


Sulphur:

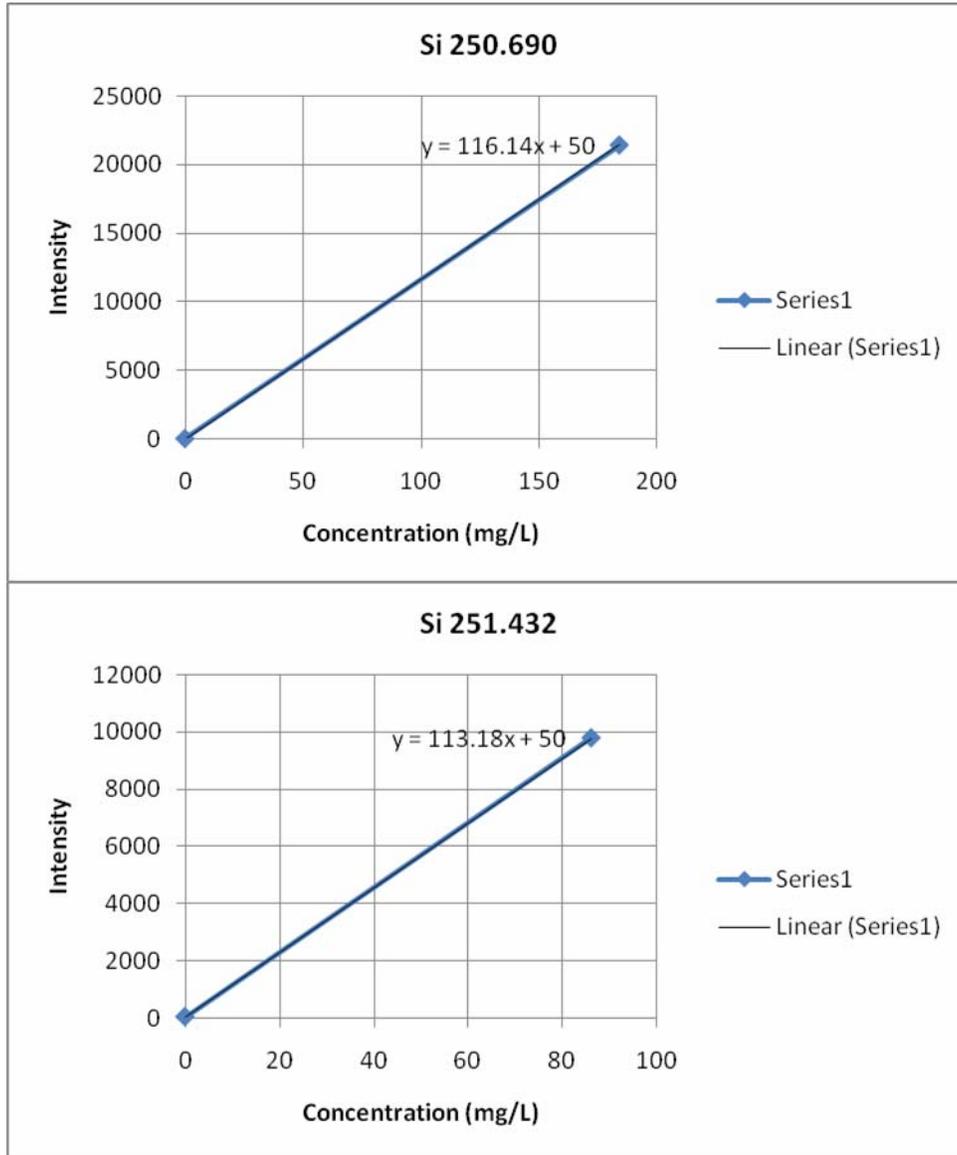




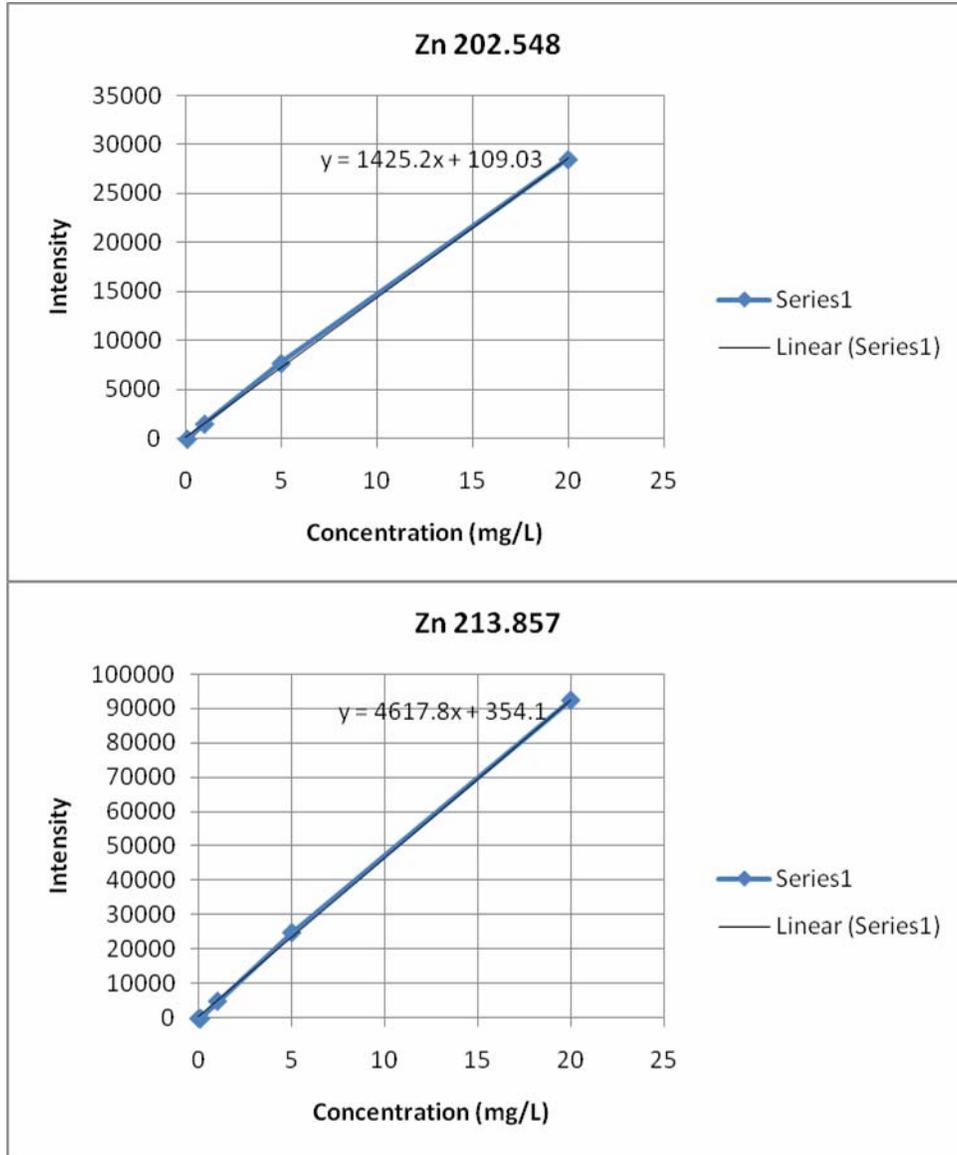
Selenium:



Silicon:

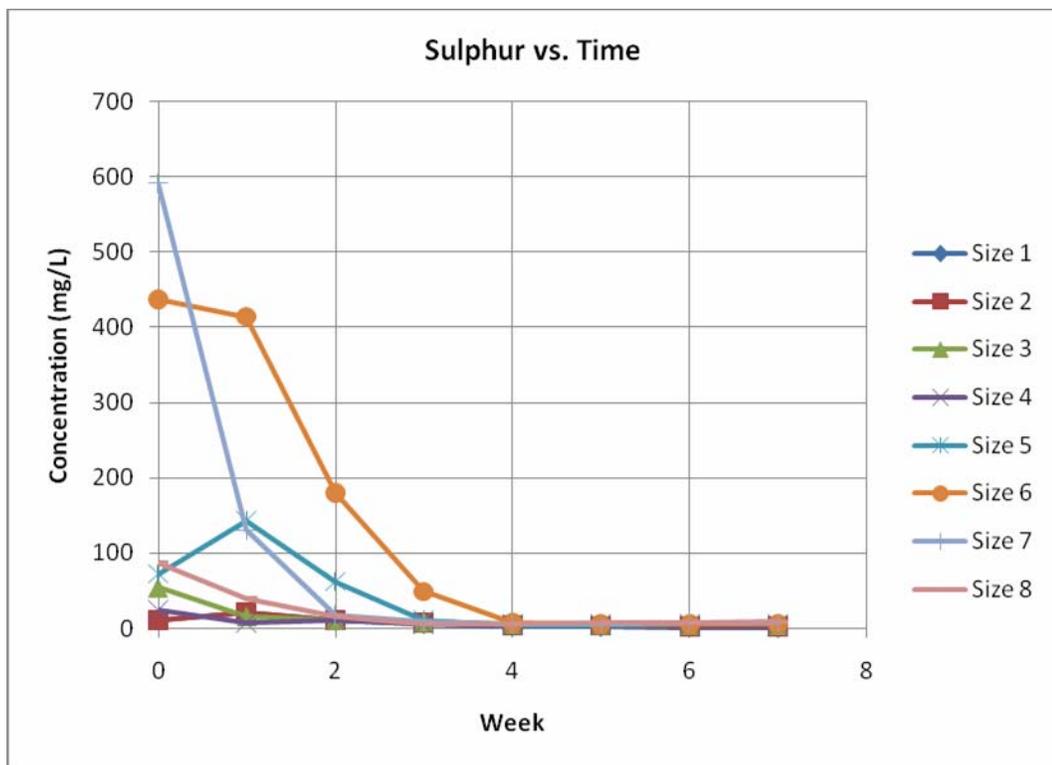
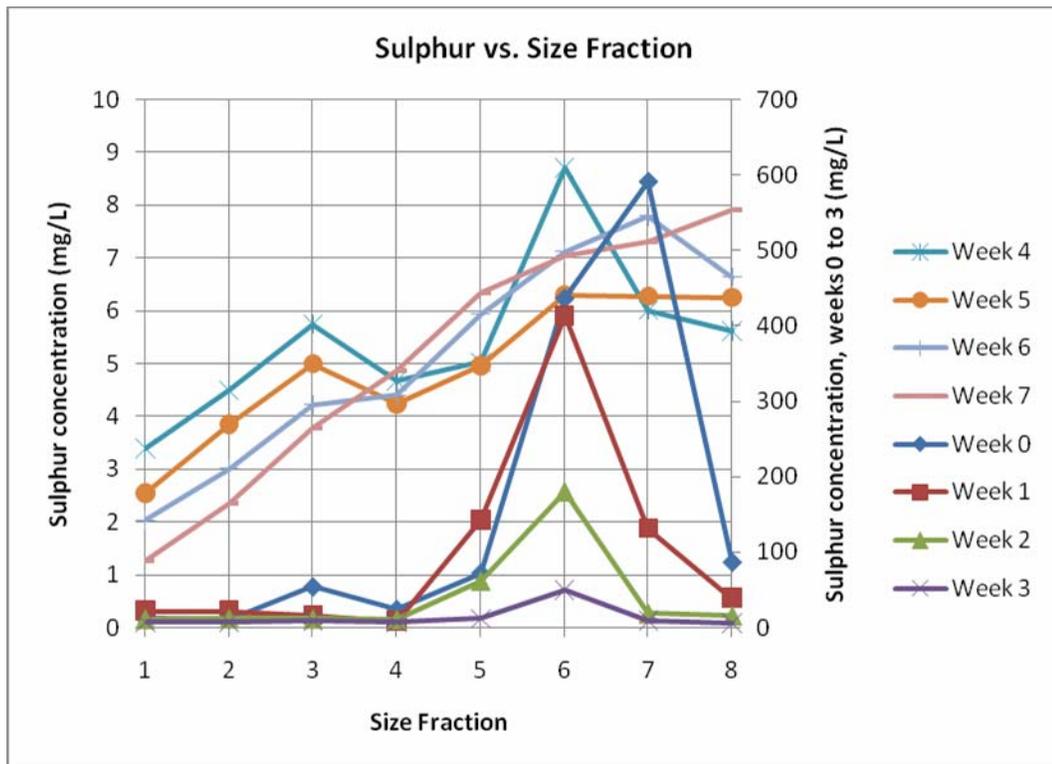


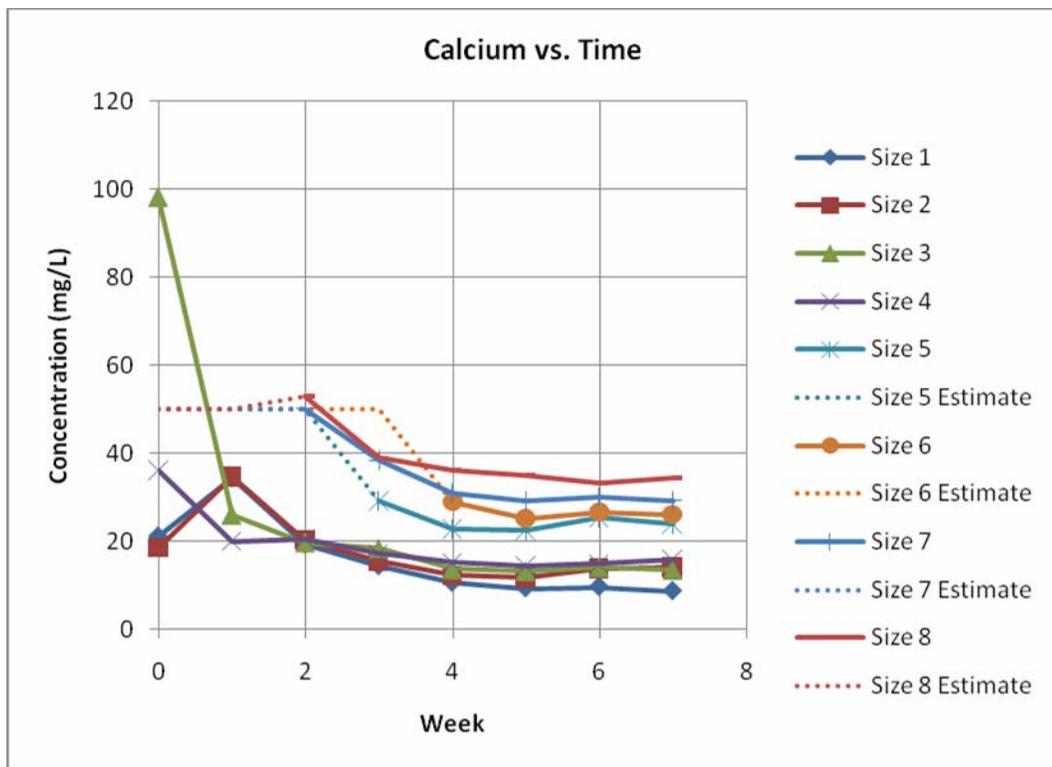
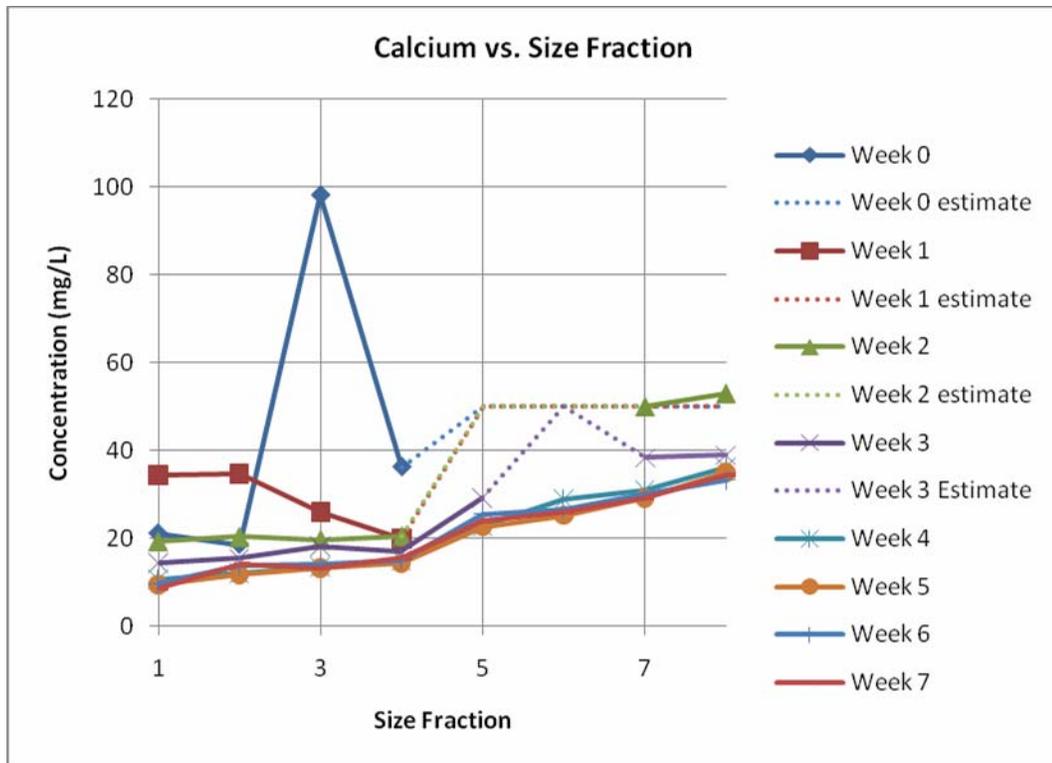
Zinc:

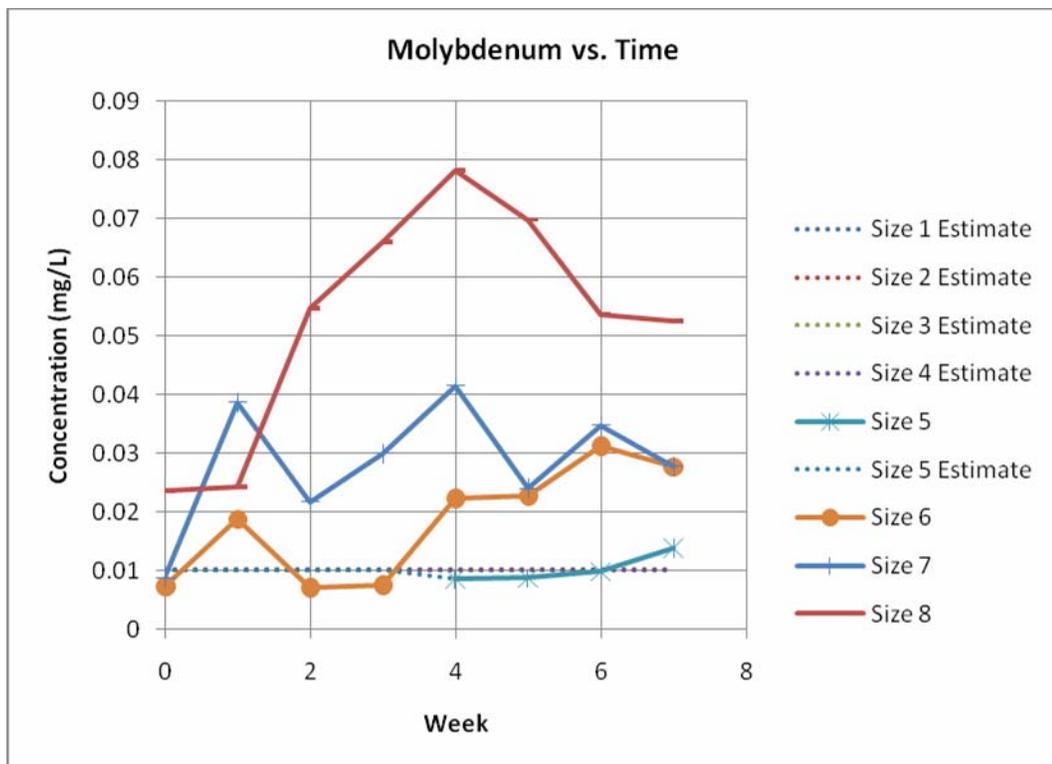
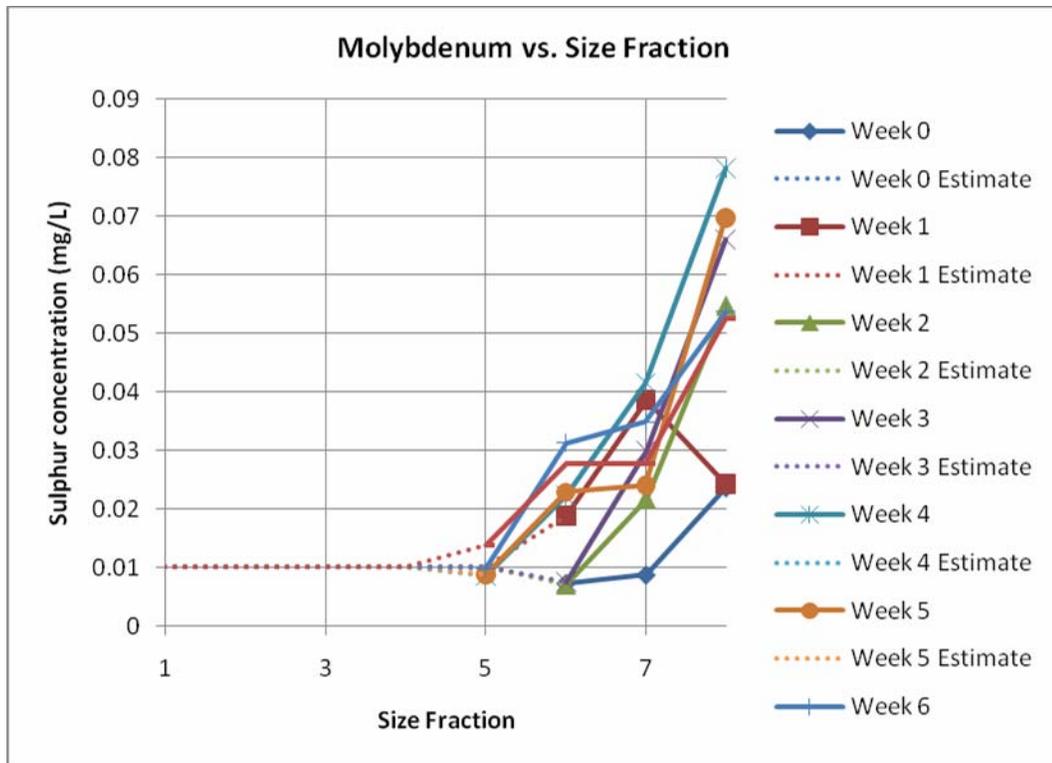


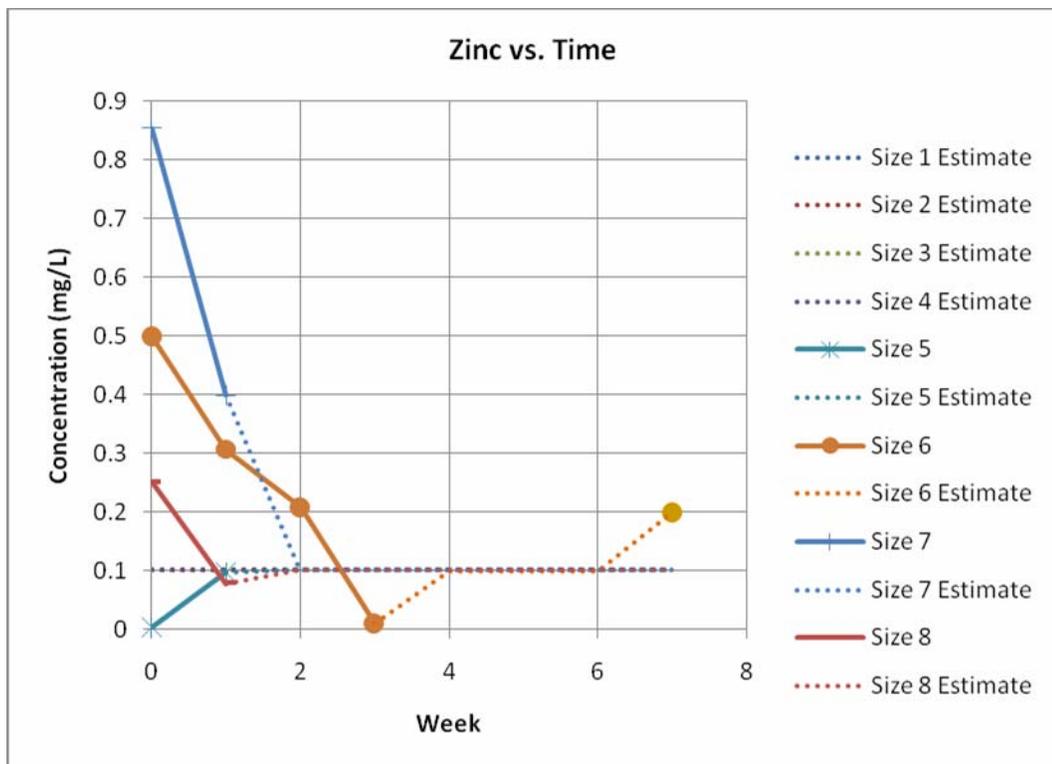
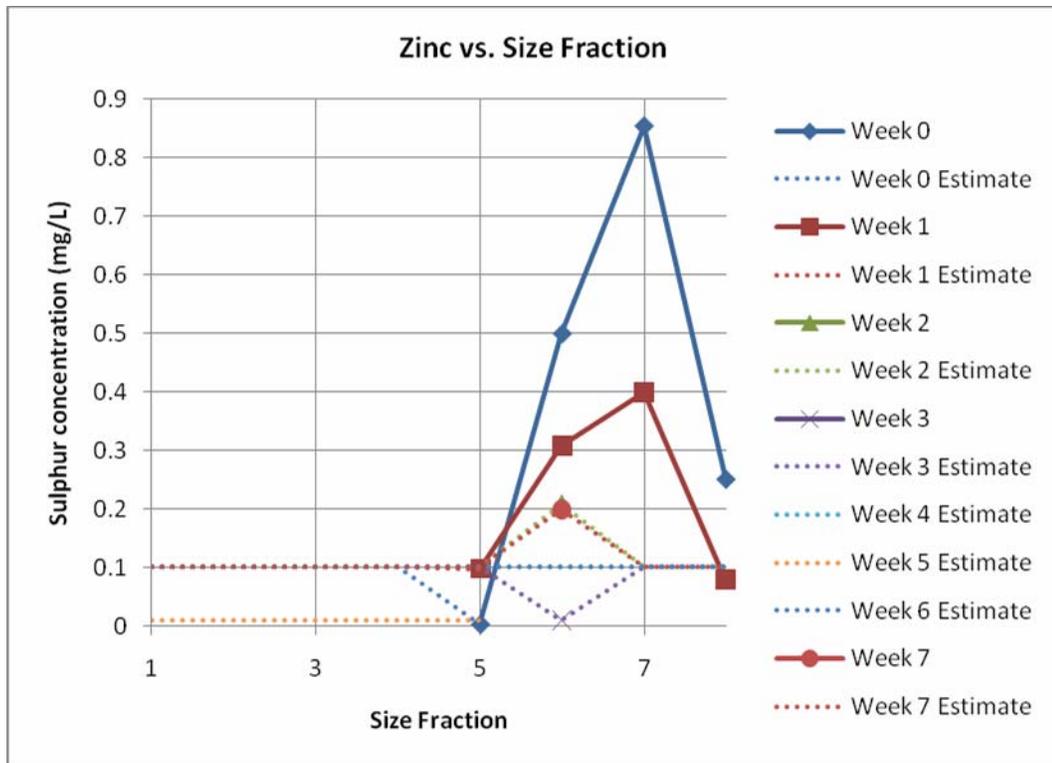
Appendix E

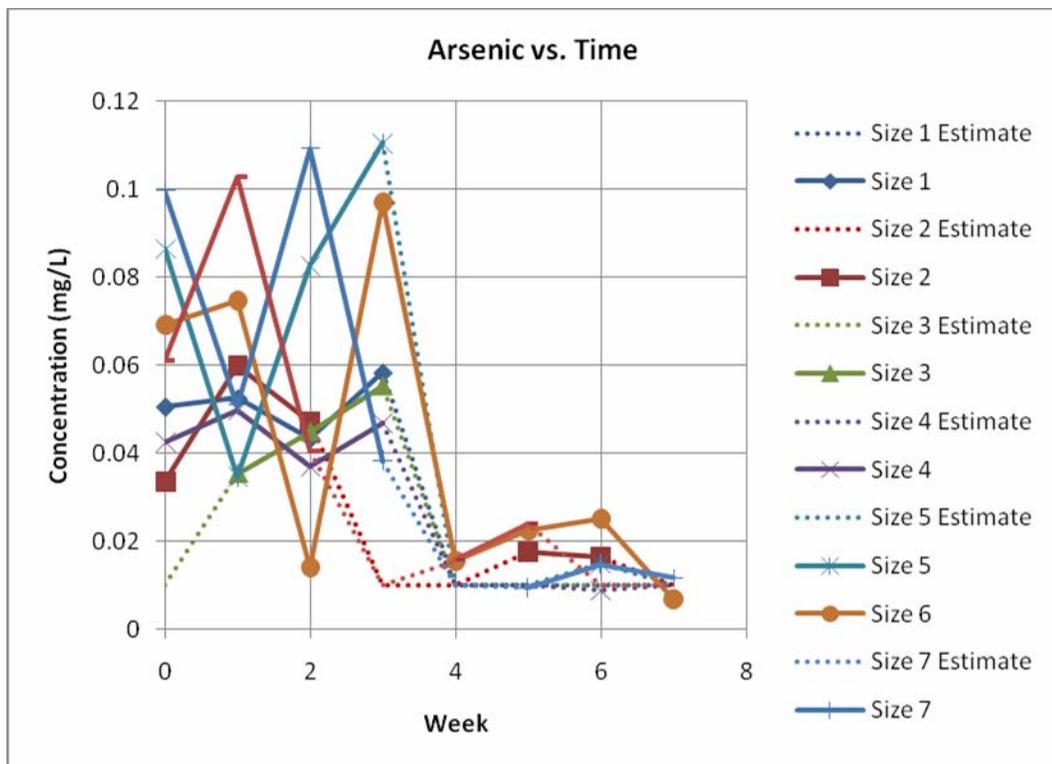
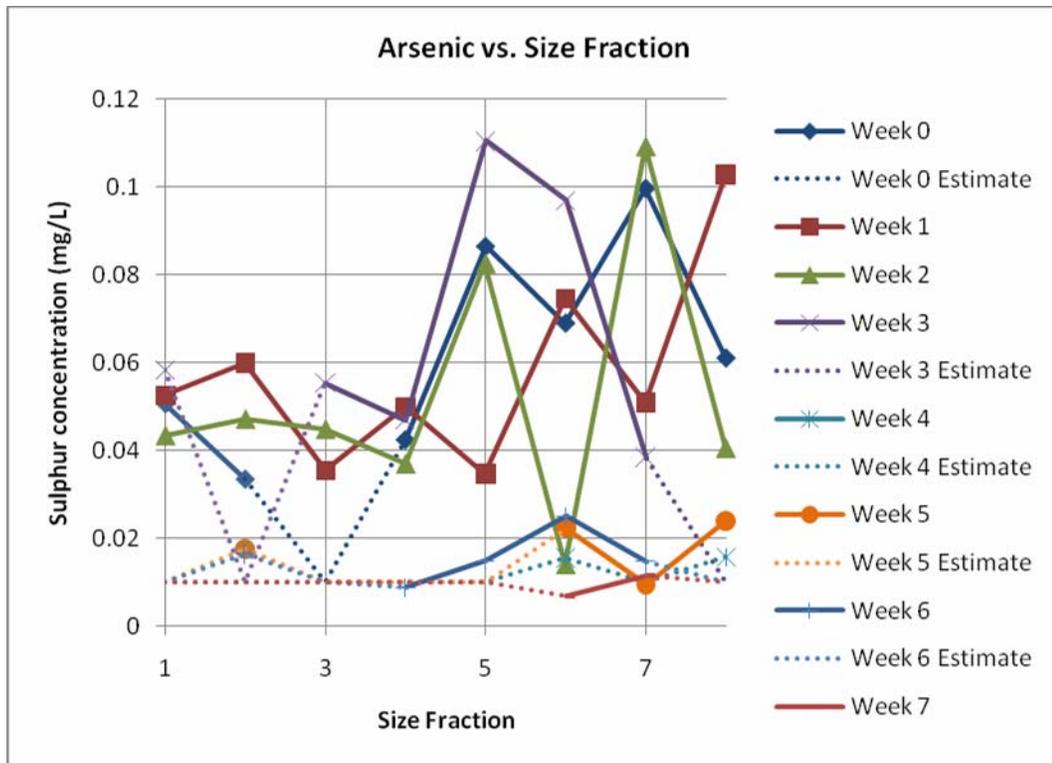
ICP-OES Analysis Concentrations vs. Sample Size and Time

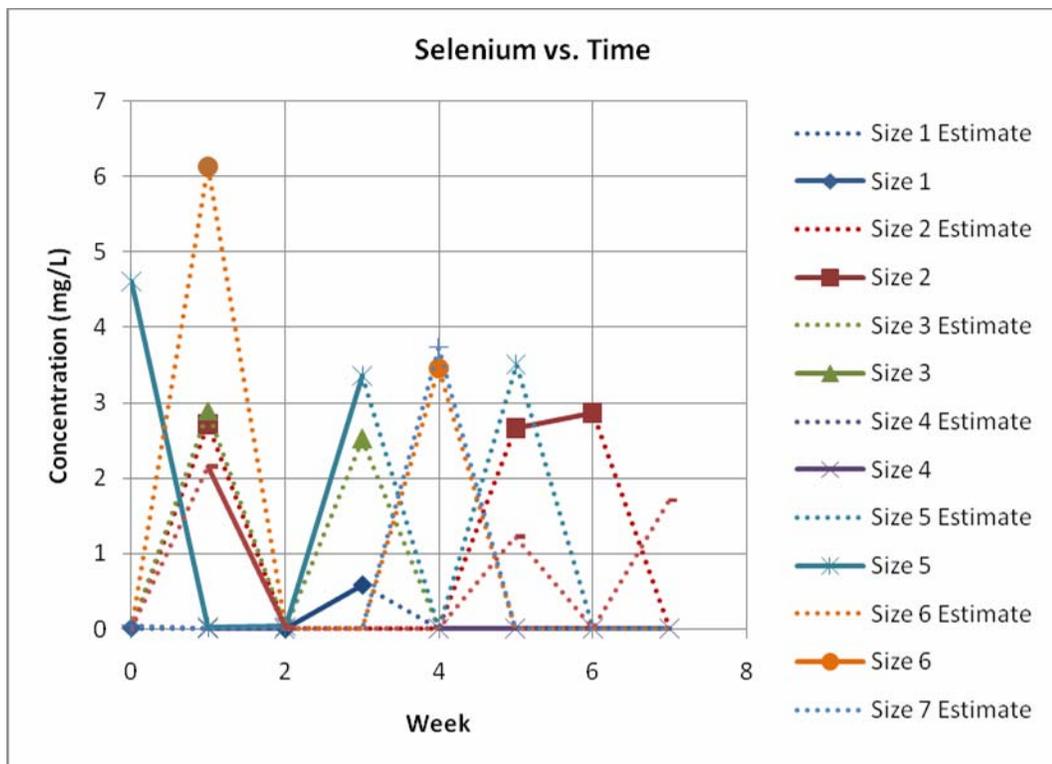
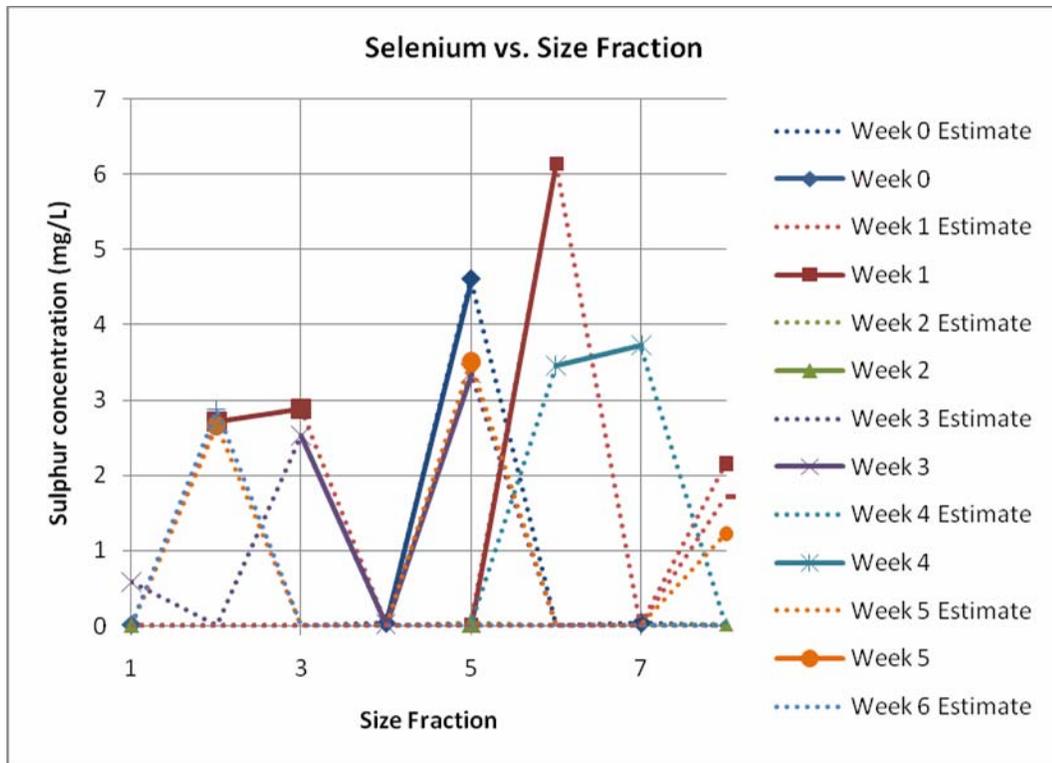


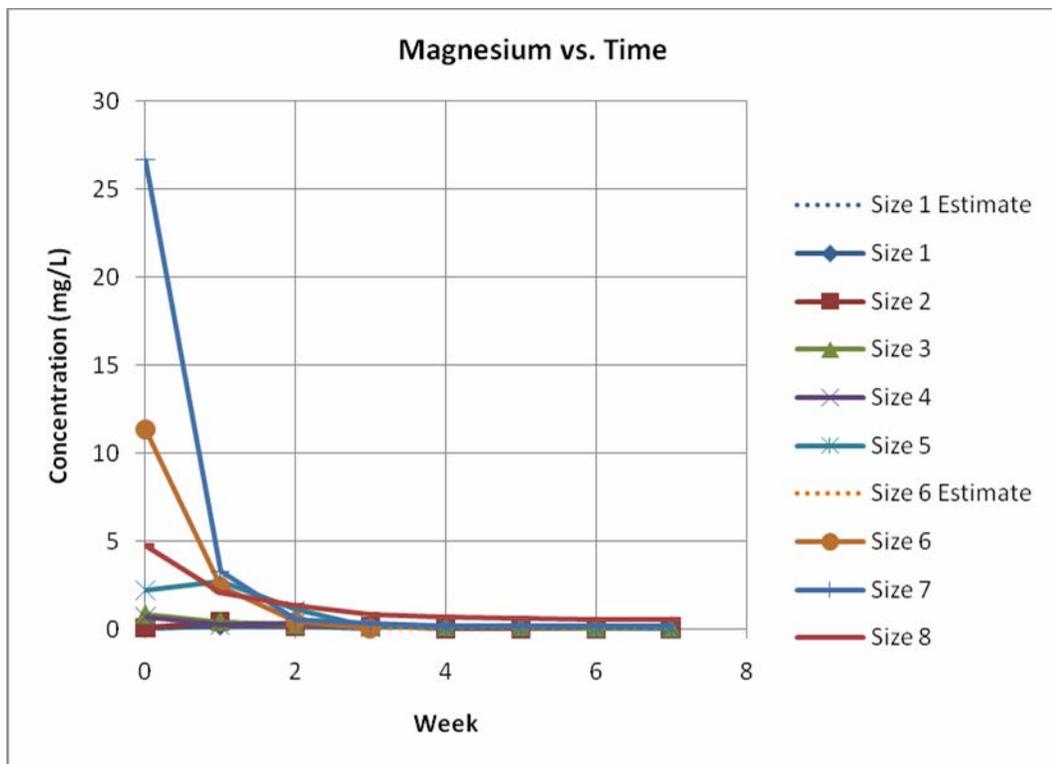
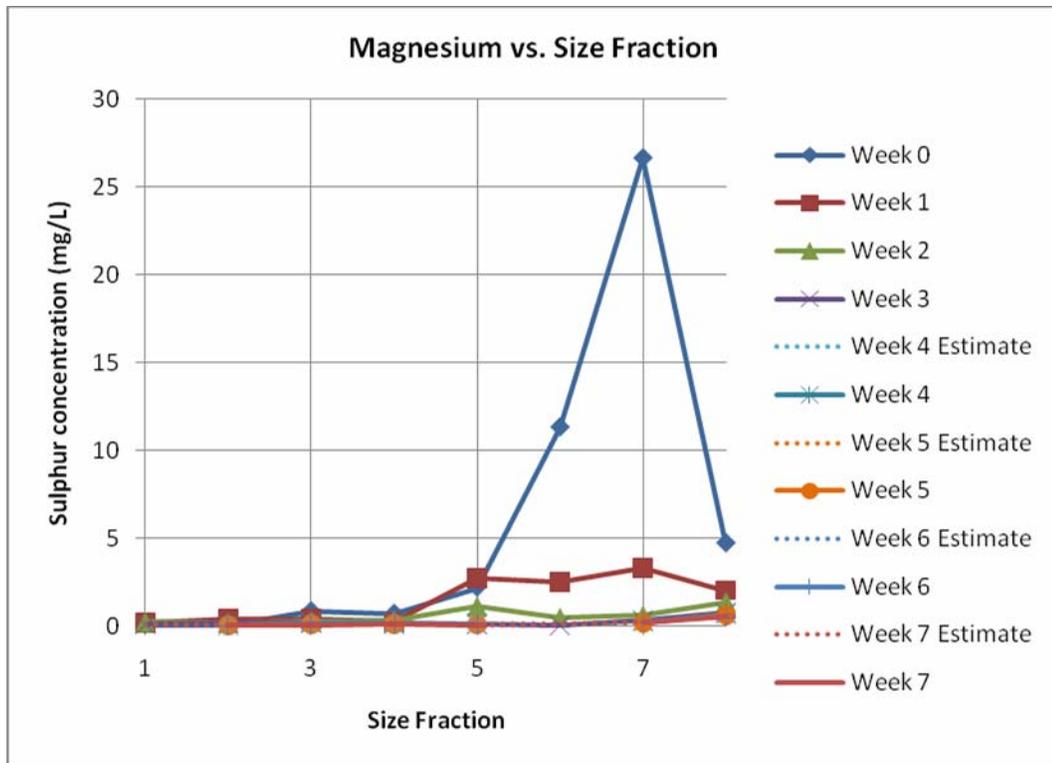


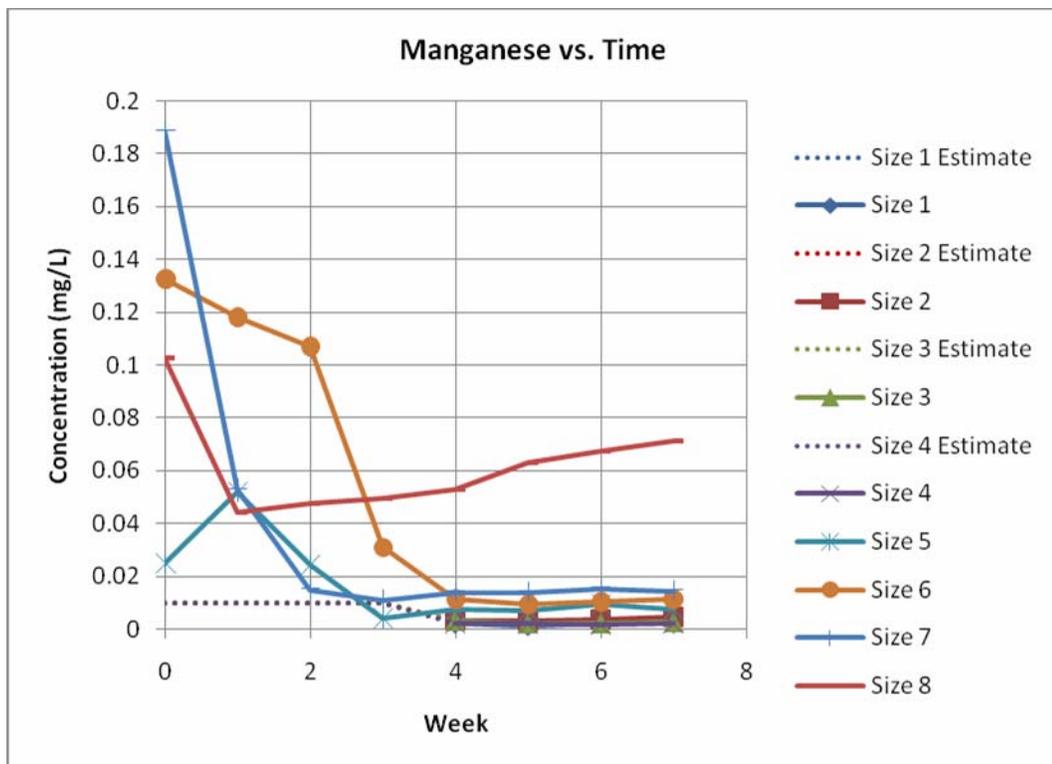
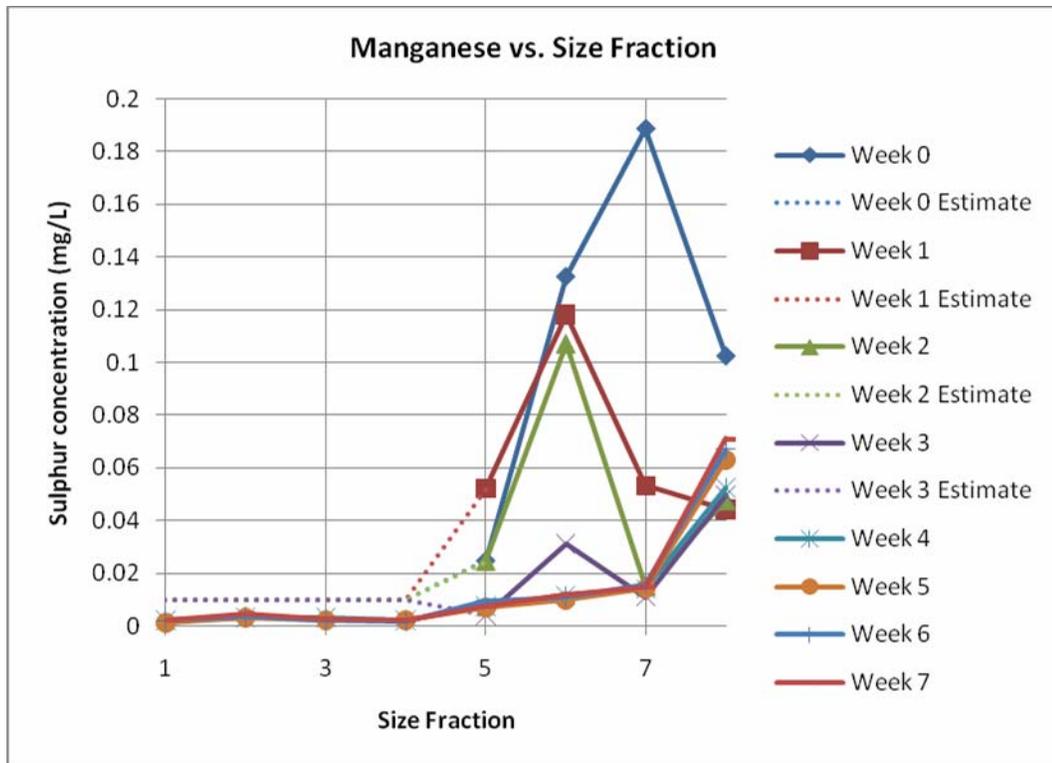












Appendix F

Phreeqc Results: Charge Balance and Saturation Indices

Sample	Solution	Charge	% error	SI Calcite	SI Gypsum	SI Dolomite
EY 1-1	11	0.000969	40.86	-1.12	-2.35	-4.71
EY 1-2	12	0.000906	36.10	-0.77	-2.35	-3.63
EY 1-3	13	0.000587	29.31	-0.62	-2.58	-3.22
EY 1-4	14	0.000353	21.58	-0.73	-2.95	-3.62
EY 1-5	15	-0.000780	-14.25	-0.74	-1.52	-2.94
EY 1-6	16	-0.006610	-62.84	-1.03	-1.21	-3.55
EY 1-7	17	-0.001278	-20.92	-0.50	-1.56	-2.36
EY 1-8	18	0.000141	2.87	-0.32	-2.02	-2.22
EY 2-1	21	0.000508	36.09	-1.18	-2.83	-4.52
EY 2-2	22	0.000542	37.15	-0.63	-2.79	-3.54
EY 2-3	23	0.000489	33.36	-0.58	-2.82	-3.26
EY 2-4	24	0.000447	28.17	-0.46	-2.85	-2.97
EY 2-5	25	0.000726	17.86	-0.26	-1.82	-2.38
EY 2-6	26	-0.002067	-32.87	-0.40	-1.44	-3.01
EY 2-7	27	0.000837	20.53	0.00	-2.32	-2.13
EY 2-8	28	0.000686	14.83	0.32	-2.39	-1.15
EY 3-1	31	0.000347	32.07	-0.96	-3.16	-4.31
EY 3-2	32	0.000389	33.95	-0.34	-3.07	-2.85
EY 3-3	33	0.000396	27.83	-0.72	-2.97	-3.63
EY 3-4	34	0.000346	25.46	-0.96	-3.11	-4.16
EY 3-5	35	0.000534	23.06	-0.13	-2.69	-2.78
EY 3-6	36	0.000676	16.87	-0.17	-1.90	-3.51
EY 3-7	37	0.000425	12.66	0.12	-2.71	-1.97
EY 3-8	38	0.000387	11.00	0.30	-2.94	-1.30
EY 4-1	39	0.000065	6.65	-1.31	-3.56	
EY 4-2	40	0.000181	17.88	-0.40	-3.38	-3.56
EY 4-3	41	0.000286	26.76	-0.60	-3.24	-3.39
EY 4-4	42	0.000278	22.57	-0.81	-3.29	-3.77
EY 4-5	43	0.000336	17.52	-0.31	-3.12	-3.18
EY 4-6	44	0.000456	19.30	-0.12	-2.80	
EY 4-7	45	0.000385	14.42	-0.02	-2.95	-2.41
EY 4-8	46	0.000383	11.81	0.26	-2.93	-1.40
EY 5-1	47	0.000031	3.51	-1.17	-3.73	
EY 5-2	48	0.000154	15.40	-0.63	-3.46	-4.45
EY 5-3	49	0.000330	33.68	-0.77	-3.31	-3.79
EY 5-4	50	0.000275	24.04	-0.62	-3.35	-3.52
EY 5-5	51	0.000301	15.68	-0.22	-3.13	-3.14
EY 5-6	52	0.000377	18.05	-0.21	-2.99	

EY 5-7	53	0.000426	17.35	-0.19	-2.94	-2.77
EY 5-8	54	0.000392	12.59	0.07	-2.89	-1.83
EY 6-1	55	0.000029	3.11	-1.60	-3.81	
EY 6-2	56	0.000200	17.17	-0.75	-3.51	-4.39
EY 6-3	57	0.000256	22.59	-0.93	-3.36	-4.25
EY 6-4	58	0.000274	22.86	-1.03	-3.32	-4.41
EY 6-5	59	0.000380	17.89	-0.34	-3.01	-3.32
EY 6-6	60	0.000451	20.96	-0.37	-2.91	
EY 6-7	61	0.000435	17.13	-0.24	-2.84	-2.83
EY 6-8	62	0.000428	14.81	-0.01	-2.88	-2.04
EY 7-1	63	-0.000055	-5.99	-1.41	-4.06	
EY 7-2	64	0.000158	12.86	-0.54	-3.61	-4.74
EY 7-3	65	0.000220	19.72	-0.87	-3.42	-4.28
EY 7-4	66	0.000253	19.30	-0.93	-3.26	-4.18
EY 7-5	67	0.000362	18.18	-0.35	-3.00	-3.81
EY 7-6	68	0.000401	18.52	-0.42	-2.93	
EY 7-7	69	0.000456	18.73	-0.20	-2.88	-2.75
EY 7-8	70	0.000464	15.62	0.05	-2.80	-1.92