

# Humidity Cell Testing of Virginia Formation Drill Core: Eleven Year Laboratory Experiment

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## 0. EXECUTIVE SUMMARY

The data and findings in this research report have been and will continue to be used to support the environmental review and mine permitting responsibilities of the Minnesota DNR. The information contained in this report is particularly useful for operations that are or may excavate rock from the Duluth Complex (DC) and Virginia Formation (VF). These regulatory activities require prediction of solute release from waste rock during mine operation and in the decades and centuries following mine closure. As a foundation for such predictions, the reactions occurring in waste rock (stockpiles, pit walls) and variables affecting these reactions must be understood. In the present project, laboratory studies were conducted for eleven years to examine solute release and variables affecting this release from VF waste rock.

The objectives of this report are to 1) characterize the solid phase composition and evaluate the drainage quality observed for the VF samples under test by the DNR, 2) compare the results from objective 1 to existing data sets from Northshore Mining (NSM) and PolyMet Mining (PM) tests of VF samples with similar sulfur content, and 3) compare the DNR VF data to the DC waste rock data set under test by the DNR.

Since 2004 the DNR has had five samples of VF drill core from NSM under kinetic test. These samples range in sulfur content from 0.22 to 0.81 and consist primarily of plagioclase, quartz, cordierite, biotite, and augite. Minimum leachate pH was typically in the range of 4.0 to 6.4 and tended to decrease with increasing sulfur content. Sulfate and major cation release rates tended to increase as a function of sulfur content. One exception to this was the 0.30%S sample which tended to have release rates lower than anticipated. Metal concentrations (Cu, Ni, Co, Zn) were analyzed less frequently over the eleven year period of record, however these data show a similar increasing trend with sulfur content.

The chemical composition and mineralogy of the DNR and NSM VF samples were fairly similar. However, drainage quality differed considerably between the two sample sets. Minimum drainage pH from the NSM samples was typically 0.5 to 1.5 units lower than the DNR samples. As a result, the NSM samples had sulfate release rates that were, on average, 1.3 to 2.6 times higher than the DNR samples. Likewise, copper and cobalt release rates in the NSM samples were, on average, 3 to 30 times higher than the DNR samples.

The DNR VF samples were also compared to the VF samples under test by PM. Chemical composition between these two samples sets was somewhat similar, however the mineralogy was very different. The PM samples consisted primarily of clinopyroxene, potassium feldspar, and mica. Minimum drainage pH from the DNR samples was typically 1 to 2 units lower than the PM samples. As a result, sulfate release rates were, on average, 3 to 5 times higher than the PM samples. In addition, peak copper and cobalt release rates in the DNR samples were as much as 250 to 700 times higher than the PM samples.

The DNR VF samples were also compared to the Duluth Complex waste rock (DCWR) samples with similar sulfur content under test by the DNR. Because these samples were from two distinctly different rock types, chemical composition, mineralogy and drainage quality were significantly different. Minimum drainage pH in the VF samples was typically 1 unit lower than

the DCWR samples. As a result, sulfate release rates in the VF samples were, on average, 2.5 times higher than the DCWR samples. Copper release in the DCWR samples, on average, was 13% higher than the VF samples. However, cobalt release in the VF samples, on average, was 44% higher than the DCWR samples. These differences in release rates were not reflective of the chemical compositions and may have had more to do with the sulfide minerals present in these samples.

These types of comparisons emphasize the importance of performing a thorough waste rock characterization program during environmental review and permitting. These programs should include all rock types that may be disturbed during mineral resource development of the DC and VF.

# 1. INTRODUCTION

## 1.1. Background

Several areas of the Duluth Complex (DC) are presently being considered for mineral resource development in Minnesota. In many instances a unit called the Virginia Formation (VF) is likely to be disturbed during development of the DC. Prior to development, potential mine wastes must be characterized (particle size, chemistry, mineralogy) and well-characterized samples must be subjected to kinetic testing. These tests assess the potential of mine wastes (e.g. waste rock, mine walls, tailings, and processing residues) to adversely impact water resources. The Minnesota Department of Natural Resources (DNR) is conducting kinetic testing on five well-characterized samples from the VF. The current period of record for these samples is 11 years.

This report describes the rock samples composition and evaluates the kinetic test leachate compositions of VF samples collected from Northshore Mining (NSM) drill core. A comparison of the test methods and leachate composition among the DNR, NSM, and PolyMet Mining (PM) kinetic test results is discussed. In addition, this report provides a comparison between the DNR VF and DC kinetic test results. The present report includes data collected over the first 580 weeks of testing.

## 1.2 Geology

The DC is one of the largest mafic intrusive complexes in the world. It covers roughly 6500 km<sup>2</sup>, ranging from the Duluth, MN area northward 240 km and is over 50 km wide at some points (Figure 1). Geologic contacts on the north and west are easily recognized, where the mafic intrusives and volcanics of the DC form the headwall of the contact, and metagreywackes and slates of the Animike Group form most of the footwall of the contact. The Animike Group is composed primarily of the VF and Biwabik Iron Formation (BIF) that dominate the Animike metasediments near the contact. The VF is a well-bedded sequence of argillaceous siltstone, carbonaceous shale, mudstone, fine-grained feldspathic greywacke, and minor limey-cherty interbeds all variably thermally metamorphosed by the DC. The BIF is a well bedded rock unit comprised of alternating, iron-oxide rich and cherty intervals, variably thermally metamorphosed by the DC. The Giants Range Batholith (GRB) is predominantly late Archean quartz monzonite, granite and monzodiorite, which also forms a portion of the western footwall.

## **2. OBJECTIVES**

The objectives of the present research on samples from the VF are as follows.

1. Determine the variation of leachate compositions and rates of solute release as a function of sulfur content and time.
2. Describe the similarities and differences between the DNR and NSM kinetic test results.
3. Describe the similarities and differences between the NR and PM kinetic test results.
4. Compare kinetic test results from the DNR VF and DC samples from the from the Mesaba (Babbitt) deposit.

### 3. METHODS

#### 3.1. Materials

The DNR in Hibbing, MN received five rock samples of VF rock of varying sulfur contents from NSM drill core. The drill core samples were prepared by RPC Research Laboratory in Fredericton, New Brunswick, Canada. The sulfur contents of the five rock samples were: 0.22, 0.25, 0.30, 0.42, and 0.81%  $S_{\text{Total}}$ . Samples for the humidity cells were prepared following the ASTM D5744 method. Each sample contained approximately 1010 to 1030 grams.

On June 22, 2004 five humidity cells were set up containing VF rock. Each of the five samples was put through a riffle splitter twice to be separated into 4 parts. A tray was zeroed on an analytical balance and the four bags representing one sample were layered into the tray one at a time. The weight was generally about 10 to 30 grams over the desired 1000-gram sample size. A plastic spoon was used to randomly remove the excess sample. The rock was then poured slowly into the cleaned and tared humidity cell. The plastic pan and spoon were rinsed with distilled water after each cell was filled. The cells with dry solids were weighed and the tare weight recorded.

#### 3.2. Apparatus

Cylindrical humidity cells (I.D. = 10.2 cm, h = 19.0 cm) constructed of acrylic plastic was used in the experiment. A 0.64-cm high acrylic sleeve was glued into the bottom of the cell to support a 0.16-cm thick PVC plate, which was perforated with 0.32-cm holes spaced 0.48 cm on center. The plate was covered with a polypropylene filter (National Filter Media Corporation, Polymax B, Style 226-075-2) that supported the solids. The bottom was sealed with an acrylic plate with a 0.85-cm outlet port in the center and a removable cover, with a 0.85-cm vent hole, was placed on top of the cell (Figure 2). Prior to filling, the cells were acid washed with 10%  $\text{HNO}_3$  and then rinsed three times with distilled water. The cells were weighed and the weight was recorded on the cell.

#### 3.3. Experimental Procedure

The solids were rinsed three times (week 0) to remove oxidation products that accumulated on the solids from the time they were processed until the beginning of the experiment. The rinsing procedure was to place a rubber cap on the outlet port and add 500 mL of distilled water to each cell. The water was slowly dripped into the cell, with the outlet capped, from a separatory funnel. The water remained in the cell for ten minutes after the last one was filled, and then the cells were uncapped and allowed to drain. The cells have since been rinsed weekly with one 500 mL volume of distilled water.

Leachate samples were weighed and analyzed for pH and specific conductance at the DNR laboratory. A portion of the leachate samples were collected and filtered for subsequent determinations of sulfate and metal concentrations. After filtration, samples to be analyzed for metals were preserved with 0.2 mL Baker Instra-Analyzed nitric acid per 50 mL sample. Samples were rinsed three times at the initiation of the experiment (week 0). The first of the

three rinses was analyzed for SO<sub>4</sub>, Ca, Mg, Na, K, and As at the Minnesota Department of Agriculture in St. Paul, MN (MDA).

### 3.4. Reaction Conditions

Between rinses the samples were retained in the cells to oxidize. The cells were stored in a room (8.5 x 10.5 x 9.5 ft.) in which temperature and humidity were controlled by commercially available equipment. Temperature was maintained by a thermostatically controlled heater (Lakewood 750) and humidity was maintained by a Holmes HM 3500 humidifier and a Sears Kenmore dehumidifier, both of which were controlled by Honeywell humidistats. Over the 580 week period of record temperature and relative humidity were measured three to four times a week with a Taylor wet-bulb, dry-bulb hygrometer.

Water retention in the humidity cells was determined by weighing. Weights were determined immediately before and one day after rinsing.

### 3.5 Analyses

#### 3.5.1. Solid Phase Analyses

Solid phase analyses were performed by Actlabs in Vancouver, BC. Samples were analyzed for total sulfur, carbon, sulfate, and carbon dioxide using ASTM E1915. Major oxides were determined using a lithium metaborate fusion method with analysis by ICP. Major and trace metals were determined using a sodium peroxide fusion method and analysis by ICP/MS or ICP/OES. Mineral identification and quantification was done using X-ray diffraction (XRD) analysis with Rietveld refinement.

#### 3.5.2. Drainage Quality Analyses

Water samples were analyzed for specific conductance, pH, and alkalinity or acidity at the DNR laboratory. Specific conductance was analyzed using a Myron L conductivity meter, and an Orion SA720 meter, equipped with a Ross combination pH electrode (8165), was used for pH analyses. Alkalinity (for pH 6.3) and acidity were determined using standard titration techniques for endpoints of 4.5 and 8.3, respectively (APHA et al., 1992). The remaining sample was filtered for metals and sulfate analyses.

Between June 2004 to April 2013, metals and sulfate samples were analyzed at MDA. Calcium, magnesium, sodium, and potassium were determined with a Varian 400 SPECTRAA; inductively coupled plasma mass spectrometry (ICP-MS, Hewlett Packard HP4500 Series, model #G1820A was used for arsenic analyses). Sulfate concentrations were determined using a Lachat QuickChem 8000 or, for [SO<sub>4</sub>] < 5 mg/L, a Dionex ion chromatograph. Samples collected after April 2013 was analyzed at Legend Technical Services in St Paul, MN. Ca, Mg, Na, K, Cu, Ni, Co, and Zn concentrations were determined using ICP-AES (EPA 6010B method) and SO<sub>4</sub> concentrations were determined using ion chromatography (EPA 9056(M) method). Occasionally, Si, Al, As, Cd, Cr, Pb, Se, Ag, Fe, Mn, Tl, B, Be, Sb, and V concentrations were determined using ICP-MS (EPA 6020, 6020A methods).

### 3.6. Calculations

Weekly mass release and solute release rates were calculated as the product of the observed drainage concentrations and the drainage volume. Concentrations for the weeks in which no analysis were conducted were estimated by linear interpolation between the previous and subsequent measured concentrations. Rates of release and rate periods were based on visual examination of cumulative release plots. Linear regression was conducted on periods in which the rate was relatively uniform. Mass release and rates were calculated from the third initial rinse at week 0 to week 580.

During a three week period (July 1 to July 21, 2011) the VF samples were not rinsed due to the State of Minnesota shutdown. Because of this change to the rinsing frequency, adjustments were made to the associated release rate calculations. Observed  $\text{SO}_4$ , Ca, Mg, Na, K, and As release after the shutdown (weeks 367-369) were divided by four in order to account for accumulated mass in the samples. For cumulative mass release calculations, zero mass release was entered for the weeks during the shutdown and the higher observed release measured after the shutdown was retained. For concentration vs. time figures (Appendix 3, Figures A3.1-A3.10) no adjustment was made. The disruption of the rinsing frequency accounted for less than a 1% change of the measured values during the entire period of record and had minimal effect on the overall release rate calculations.

## 4. RESULTS

### 4.1. Introduction

In June 2004, DNR initiated kinetic test work of VF samples from NSM drill core. Sulfur and CO<sub>2</sub> (measured in carbonate) content ranged were 0.22 to 0.81% and 0.03 to 0.09%, respectively. Five -0.25 inch (d < 6.35 mm) samples were tested in humidity cells using ASTM method D5744 (ASTM, 2007). These experiments remain in operation and the following reporting represents an assessment of the data through week 580.

### 4.2. Solid Phase Analysis

The average major whole rock components were SiO<sub>2</sub> (55.7%), Al<sub>2</sub>O<sub>3</sub> (16.3%), Fe<sub>2</sub>O<sub>3</sub> (7.8%), MgO (4.8%), and CaO (4.6%) (Table 1). Average copper, nickel, cobalt and zinc contents were determined as 0.019, 0.015, 0.0038, and 0.023%, respectively. Mineral contents were 33-47% plagioclase, 7-30% quartz, 1-16% cordierite, 8-24% biotite, 4-19% augite, and 5-12% amorphous material. Potassium feldspar, orthopyroxene, chlorite, ilmenite, and rutile were also reported, on average, at 1-8%. Sulfur weight % concentrations corresponding to sulfide mineral contents were below instrument detection levels. Additional solid phase data can be found in Appendix 1.

### 4.3. Reaction Conditions

#### 4.3.1. Temperature and Relative Humidity

Over the 580-week period of record temperature and relative humidity (in the room in which humidity cells were stored) were measured three to four times a week with a Taylor wet-bulb, dry-bulb hygrometer. Average weekly values for temperature ranged from 20 to 28°C, averaging 24°C (s.d. = 1.6 °C, n = 571). The corresponding range for relative humidity was 42 to 75%, averaging 58% (s.d. = 4.0%, n = 571) (Appendix 2, Table A2.1).

#### 4.3.2. Water Retention

Average water retention before the rinse ranged from 86 to 128 grams. Average water retention after the rinse ranged from 96 to 142 grams (Table 2). Humidity cells 2 and 5 typically had water retention values that were, on average, 35% higher than the other humidity cells. Additional analysis was performed to assess the extent of a low-permeability layer formation at the top of the sample or particle aggregation within humidity cell 4 (0.42 %S) (Appendix 2, Attachment A2.1).

#### 4.3.3. Leachate Volume

Leachate volume remained fairly consistent over the 11 year period of record. Average leachate volumes for the five humidity cells ranged from 476 to 484 mL (Appendix 3, Tables A3.1-A3.5).



#### 4.4. Kinetic testing of DNR VF rock

##### 4.4.1. Drainage pH

Minimum drainage pH was typically in the range of 4.0-6.4 and was reached after 100-300 weeks. Drainage pH typically decreased as solid-phase sulfur content increased (Figure 3). Whereas this trend seems reasonable, it is somewhat at odds with one aspect of the observed sulfate concentrations. In particular, sulfate concentrations from the 0.30% S sample were lower than those from the 0.25% S sample for about 200 weeks, and values were subsequently roughly equal. Based on this observation, pH from the 0.25% S sample would be expected to be lower, but the opposite was distinctly the case. This suggests that the neutralization capacity of the 0.25% S sample was greater than that for the 0.30% S sample. However the CO<sub>2</sub> content of the 0.30% S sample was slightly higher than the 0.25% S sample, 0.03 and 0.05% respectively, and the estimated neutralization potential (NP) based on cumulative mass release was very similar between these samples (Table 4).

##### 4.4.2. Sulfate Release

Sulfate release rates from the VF samples generally increased with increasing solid-phase sulfur content (Table 3, Figure 4). Sulfate release peaked at different times. The 0.81% S sample peaked within the first 10 weeks, and the 0.22, 0.25, and 0.42% S samples all peaked between weeks 100 and 125. Sulfate release from the 0.30% S increased steadily until around week 225, and then declined. Sulfate release rates from the 0.30% S sample were somewhat lower than expected based on its sulfur content. They were lower than those from the 0.22% S sample through about week 100 and reached those from the 0.25% S sample only after about 200 weeks of reaction. It appears that total sulfate release from the 0.30% S sample after almost 580 weeks was intermediate to that from the 0.22% S and 0.25% S samples (Table 4). Sulfur depletion for these five samples over the 580 week period of record ranged from 26-48% (Table 5).

##### 4.4.3. Major Cation Release

Molar concentrations of major cations decreased in the order  $Ca > Mg > K > Na$  (Table 4). Release rates tended to parallel those of sulfate, which typically peaked during weeks 100 and 200 and decreased for the remainder of the period of record (Figures 5, 6, 8). The one exception to this was sodium release which peaked during the initial flush and decreased for the duration of the period of record (Figure 7). As discussed above, the NP of the 0.25% S sample appeared to be greater than the 0.30% S based on drainage pH. Total NP was calculated as the sum of  $Ca + Mg + 0.5(Na+K)$ . Based on this calculation, total NP of the 0.25% S was approximately 50% higher than the 0.30% S sample (Table 4).

Sodium release for a period of approximately one year (weeks 284-336) displayed unusual behavior. Sodium decreased in all humidity cells by year 6 to concentrations in the range of 0.1-0.2 mg/L. However, during weeks 284-336 sodium concentrations increased by a factor of 2 to 3. Due to the consistent nature of this increase in all humidity cells and corresponding to similar increases in sodium release in other DNR experiments, it was determined these values were due

to analytical error and were considered anomalous for the purposes of this report. These anomalous values can be found in Appendix 3, Table A3.0.

#### 4.4.4. Metal Release

Intermittent metal analyses of copper and cobalt were performed during the period of record and were regularly analyzed starting at week 465, along with nickel and zinc. In general, copper and cobalt concentrations increased and peaked around weeks 100 to 300 and began to plateau by week 360 (Figures 9, 10). Nickel and zinc concentrations from weeks 465-580 increased with increasing solid-phase sulfur content and release rates were fairly steady over the 115 week period of analysis (Figures 11, 12).

Arsenic concentrations from the VF samples generally increased with decreasing solid-phase sulfur content (Figure 13). This is because arsenic is an oxyanion and typically is more soluble as drainage pH increases. Arsenic release was highest in all samples between weeks 0 and 3 and then decreased for the remainder of the period of record. After approximately 100 weeks all measured arsenic concentrations were below the detection limit of 0.002 mg/L.

## 5. DISCUSSION

### 5.1. Introduction

The general objective of this experiment was to correlate rock composition with rock leachate composition to aid in predicting potential impacts to water resources and assist waste management for mining operations excavating VF rock in Northeastern Minnesota. Growing interest in mining of these resources highlights the importance of long-term studies, like this one, that will aid in determining rock leachate compositions from mine wastes over time scales of decades to centuries.

Five samples of VF rock have been tested at the DNR (580 weeks), 19 samples have been tested by NSM (580 weeks), and 11 VF samples have been tested by PM (440 weeks). In addition, the DNR has conducted long-term kinetic testing of ten samples from the DC (400 weeks). The following section provides a comparison of solid phase and leachate composition of the DNR VF samples with 1) NSM VF samples, 2) PM VF samples, and 3) DNR DC waste rock samples.

### 5.2. Comparison of DNR and NSM VF samples

#### 5.2.1. Introduction

Test results from NSM's humidity cell program were used to compare laboratory weathering behavior to DNR's VF samples. In order to assess water quality impacts from Type II VF waste rock, NSM placed 19 samples under kinetic testing between January 2003 and May 2004 (Golder Associates, 2012). These samples ranged from 0.06 to 0.42 %S and included three groupings, metasedimentary (MS), diabase sill (DS), and bedded (BD). Six of these humidity cells (No. 1-4, 11, 13) were terminated after 65 weeks and will not be used in this comparison. The remaining humidity cells were still running as of the time of this report. It should be noted that for seven of these humidity cells (No. 5-10, 12) the rinse frequency was switched from weekly to monthly after 57 to 69 weeks. For release rate calculations, these rates have been divided by 4 to adjust for this deviation from the humidity cell ASTM method. It should also be noted that for a number of weeks during kinetic test work, many of the samples had a significant charge imbalance. For comparison with DNR samples, this report will only utilize NSM samples between  $0.22 \leq \%S \leq 0.42$  that had a charge imbalance of  $\pm 10\%$ .

#### 5.2.2. Solid Phase Analyses

Whole rock chemistry and metal composition between the DNR and NSM samples were similar (Table 6). One exception to this was the NSM samples had arsenic content, on average, 5 times higher than the DNR samples. Average Cu, Ni, Co, Zn content was typical within 30% for both sample sets, although average Zn content was approximately twice as high in the DNR samples.

Mineral content of the NSM samples were determined by XRD. Mineralogy between the DNR and NSM samples was also fairly similar. A few exceptions to this were the DNR samples had, on average, 40% higher plagioclase content and a few samples had augite/diopside minerals

present. Conversely, the NSM samples had, on average, 80% higher biotite content, and amorphous content that was, on average, three times higher than the DNR samples.

### 5.2.3. Solute Release

#### 5.2.3.1. Drainage pH

Drainage pH from the NSM samples tended to be lower than the DNR samples. For a specified sulfur content, the minimum drainage pH from the NSM samples was typically 0.5-1.5 pH units lower than the DNR samples (Figure 14). Minimum pH in the DNR samples tended to occur between weeks 250 to 350 (except for the 0.42 %S which reached minimum pH after 100 weeks). Similarly, minimum pH in the NSM samples occurred during weeks 240 to 300 (Figure 18).

#### 5.2.3.2 Sulfate Release

Unlike the DNR VF humidity cells, the NSM cells did not show a strong relationship between  $dSO_4/dt$  and %S (Figure 15). When compared to the DNR samples with similar sulfur contents, the NSM cells typically had similar sulfate release rates for the first 100-300 weeks. After this point,  $dSO_4/dt$  increased significantly in the NSM cells to rates 4 to 7 times higher than the DNR cells after 300-350 weeks (Figure 19). Overall, the NSM samples had sulfate release rates, on average, that were 1.3 to 2.6 times higher than DNR samples with similar sulfur content (Table 7). It should be noted that these NSM samples were all classified as metasedimentary samples, similar to the samples DNR put under test.

In general, average sulfate release rates in the NSM cells were highest for the bedded samples, followed by the metasedimentary samples, and then the diabase sill samples (Table 7). For comparison, one sample from each rock type (BD, MS, DS) was put under test with sulfur contents of 0.32, 0.29, and 0.30, respectively. For these samples, sulfate release was relatively close for almost 200 weeks, at which point rates from the bedded sample increased to roughly three times those of the sill and metasedimentary samples (Figure 16). Oxidation of sulfide minerals occurring along bedding planes and consequent replacement by less dense iron oxides might explain the increased reactivity of the bedded sample. These processes would result in expansion along the bedding plane with a concomitant exposure of additional sulfide minerals for oxidation and the resultant pH depression (Figure 17). It should be noted that the bedded sample had C as carbonate content of 0.20 weight percent, followed by the sill (0.08%) and metasedimentary samples (0%). It does not appear that these differences were highly influential. It is possible that the presence of some less reactive form of carbonate kept the leachate pH from the bedded sample from decreasing further.

### 5.2.3.3 Major Cation Release

Similar to the DNR samples, molar concentrations of major cations decreased in the order  $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$  in the NSM samples (Table 8). Ca and Mg release rates tended to parallel those of sulfate, where release rates typically peaked during weeks 200-400 and decreased for the remainder of the period of record (Figures 20, 21). NSM calcium and magnesium release rates were typically similar to DNR rates for the first 100-300 weeks and then NSM rates increased 3 to 6 times higher than DNR rates. Na release rates tended to decrease after 100 weeks and then peak between weeks 300-400 (Figure 22). NSM sodium rates increased 40 to 100 times higher than DNR rates during minimum drainage pH. NSM potassium release rates tended to be similar to DNR rates for the first 100 weeks and then NSM rates increased 3 to 10 times higher than DNR rates (Figure 23). Similar to sulfate release rates, NSM major cation release rates did not show a strong relationship with sulfur content (Table 7).

### 5.2.3.4 Metal Release

For comparison with NSM's VF samples, the DNR had intermittent Cu and Co analyzed throughout the 580 period of record, but only analyzed Ni and Zn for the last 115 weeks. In the NSM samples, copper release gradually increased for the first 300-400 weeks and then rapidly peaked to rates that were 10 to 30 times higher than DNR rates (Figure 24). Cobalt release rates in the NSM samples tended to be similar to the DNR samples for the first 100 weeks, but then NSM rates increased to values that were 3 to 12 times higher than DNR rates (Figure 25). Based on these significantly higher Cu and Co release rates in the NSM samples one would expect that metal composition would be considerably higher in the NSM samples, however this was not the case. Average copper and cobalt content for the DNR and NSM samples were 0.016-0.019% and 0.0026-0.0038%, respectively. This disparity may have more to do with the sensitivity of metal release to drainage pH, which tended to be lower in all of the NSM samples throughout the 580 week period of record.

Unfortunately there was not enough nickel and zinc data from the DNR samples to draw a strong comparison with the NSM samples. However, Ni and Zn release rates tended to be about twice as high in the NSM samples during this period of analysis. Arsenic release in the NSM samples initially was similar to DNR samples, where rates dropped within the first 25-50 weeks and reached values close to the detection limit (Figure 26). However unlike the DNR samples, arsenic release in the NSM samples tended to oscillate over the 580 period of record to rates as high as  $0.2 \mu\text{mol}/\text{kg}\cdot\text{wk}$ .

## 5.3. Comparison of DNR and PM VF samples

### 5.3.1. Introduction

Test results from PM humidity cell program were compared to the DNR's VF kinetic test results. In order to assess water quality impacts from DC waste rock, PM placed 89 samples under kinetic testing (11 VF samples) starting in August 2005 (SRK, 2007). These samples ranged from 0.24-5.68% S. This comparison will focus on three samples from PM that were between 0.24-0.55 % S.

### 5.3.2. Solid Phase Analyses

Whole rock chemistry and metal composition between the DNR and PM samples was somewhat similar (Table 9). A few exceptions to this were that the PM samples had arsenic content, on average, three times higher than the DNR samples and CaO content, on average, twice as high as the DNR samples (especially humidity cell #5 which had CaO content of 20.1%). In addition the PM samples, on average, had CO<sub>2</sub> contents that were 8 times higher than the DNR samples. Also, the DNR samples had cobalt content, on average, twice as high as the PM samples.

Mineral abundances for the PM samples were determined by microprobe analyses of individual silicate and sulfide grains. Mineralogy between the DNR and PM samples were very different (Table 9). The DNR samples had, on average, 41% plagioclase, 17% quartz, 17% biotite, 9% cordierite, 8% amorphous, 5% potassium feldspar, and 4% clinopyroxene. Alternatively, the PM samples had, on average, 39% clinopyroxene, 30% potassium feldspar, 20% mica, and 3% biotite. The PM samples also had chlorite, graphite, and carbonate content that were not identified in the DNR samples. The PM samples did not identify any plagioclase, which was the dominate silicate mineral in the DNR samples. Sulfides were identified in the PM samples ranging from 1–2%. The primary sulfides detected were pyrrhotite and sphalerite.

### 5.3.3. Solute Release

#### 5.3.3.1. Drainage pH

Drainage pH from the DNR samples tended to be significantly lower than the PM VF samples (Figure 27). For a specified sulfur content, drainage pH from the PM samples was typically 1 to 2 pH units higher than the DNR samples. Minimum pH in the DNR samples typically occurred between weeks 250-350 (except for the 0.42 %S which reached minimum pH after 100 weeks). However, minimum pH in the PM samples tended to occur during the first 50-100 weeks. The significantly higher drainage pH observed in the PM samples may have been due to neutralization from the additional CO<sub>2</sub> content in these samples.

#### 5.3.3.2 Sulfate Release

Sulfate release behavior tended to be somewhat similar among DNR and PM samples. Sulfate release tended to increase for the first 100-200 weeks, peaked, and then gradually decreased over the period of record (Figure 28). DNR samples typically had dSO<sub>4</sub>/dt rates that were 3 to 5 times higher than PM samples during peak release (Table 10, Figure 28). Peak release tended to be more gradual in the PM samples as well.

#### 5.3.3.3 Major Cation Release

Molar concentrations of major cations decreased in the order Ca > Na > K > Mg (Table 11). There did not appear to be a strong correlation between major cation release and sulfur content (Table 10). Calcium release behavior tended to parallel sulfate release, where rates increased for the first 100-200 weeks, peaked and then gradually declined (Figure 29). PM samples tended to be 2 to 3 times higher than DNR samples. Alternatively, Mg, Na, and K release behavior did not

parallel sulfate release in the same manner as calcium. Release rates tended to decrease steadily for the first 100-200 weeks and then leveled off. DNR magnesium release rates tended to be 8 to 40 times higher than PM rates (Figure 30). Likewise, DNR potassium release rates were, on average, 2 to 4 times higher than PM rates (Figure 32). DNR and PM samples tended to have similar sodium release rates for the 440 week period of record (Figure 31).

#### 5.3.3.4 Metal Release

Copper release remained fairly steady in the PM samples for the first 200 weeks and then decrease by approximately 75%. At peak release, DNR rates were 20 to 250 times higher than PM rates (Figure 33). Cobalt had similar behavior, although rates did not decrease as much after 200 weeks. At peak release, DNR Co rates were also orders of magnitude (100-700) times higher than PM rates (Figure 34). These large discrepancies in Cu and Co release between the two sample sets cannot be accounted for by copper and cobalt composition, where average Cu = 0.012, 0.014% and Co = 0.0019, 0.0040% for the PM and DNR samples, respectively. This discrepancy was likely a function of lower drainage pH in the DNR samples.

DNR did not have Ni and Zn data that coincided with the period of record available for the PM samples, so no comparison could be drawn at this time. Arsenic release in the PM samples displayed similar behavior to the DNR samples, where rates decreased significant in the first 100 weeks and then leveled off (Figure 35). Arsenic release in the PM samples was typically 4 to 10 times higher than the DNR samples. This appears to be in agreement with PM arsenic composition, which on average was at least 4 times higher than DNR samples (Table 9).

### 5.4. Comparison of DNR VF and DC waste rock samples

#### 5.4.1. Introduction

Results from DNR test work on Duluth Complex waste rock (DCWR) from the Mesaba (Babbitt) deposit (Lapakko et al., 2013) were used to compare solid phase and drainage quality data to the DNR's VF samples. The DCWR experiment looked at ten samples under test for 400 weeks in humidity cells, with sulfur contents ranging from 0.13–1.36. For this exercise, the comparison will focus on samples with similar sulfur contents to the VF samples, specifically 0.13–0.72% S (5 samples in total, HC9-HC14).

#### 5.4.2. Solid Phase Analyses

The composition and mineralogy of the VF and DCWR samples were very different (Table 12). The DCWR samples tended to have less SiO<sub>2</sub> content and greater CaO and MgO content. The DCWR samples had metal compositions (Cu, Ni, Co) that were, on average, 3 to 10 times higher than the VF samples. One exception to this was Zn content, which was about two times higher in the VF samples on average.

Mineral abundances for the DCWR samples were determined by microprobe analyses of individual silicate and sulfide grains. The DCWR samples had, on average, 50% plagioclase, 21% olivine, 7% augite, 6% ilmenite, and 3% biotite. This differs considerably from the VF

samples which had on average, 40% plagioclase and 16% biotite and significant amounts of quartz, cordierite, and amorphous minerals not found in the DCWR samples. Sulfides were identified in the DCWR samples ranging from 1–3%. The primary sulfides detected were cubanite, pyrrhotite, and chalcopyrite.

### 5.4.3. Solute Release

#### 5.4.3.1. Drainage pH

Drainage pH from the VF samples tended to be lower than the DCWR samples. For a specified sulfur content, the minimum leachate pH from the DCWR samples was roughly 1 pH unit higher than that from the VF samples (Figure 36). Unlike the DCWR samples which were mainly circumneutral (Figure 44), VF samples with sulfur content as low as 0.25% generated acidic leachate within 300 weeks of reaction.

#### 5.4.3.2 Sulfate Release

VF and DCWR samples both showed a strong correlation between sulfate release and sulfur content (Figure 37). However, sulfate release behavior in the DCWR samples was not similar to the VF samples. Sulfate release rates in the DCWR samples slowly decreased over the course of the 400 period of record (Figure 45). Rates typically only decreased by 40 to 60% during this period, whereas VF samples typically peaked within the first 200 weeks and then quickly declined. Overall, the VF samples had sulfate release rates that were 2.5 times higher than DCWR samples (Table 13, Figure 37).

On average, the DCWR samples had sulfide mineral abundances that decreased in the order of cubanite > pyrrhotite > chalcopyrite > pentlandite (2.9%, 1.9%, 1.5%, 0.8%, respectively). This is in general agreement with literature values on the DC (Ripley and Alawi, 1986; Theriault and Barnes, 1998). Although XRD analysis performed by Actlabs did not identify sulfide minerals in the DNR VF samples, NSM did detect sulfide mineral abundances in similar samples in order of pyrrhotite > chalcopyrite > pyrite (4%, 1%, <1%, respectively). Because Fe-sulfides are generally regarded as more reactive than Cu- and Ni-sulfides (Jambor, 1994), the lower leachate pH of the VF samples is likely due to the greater abundance of Fe-sulfides.

#### 5.4.3.3 Major Cation Release

Molar concentrations of major cations in the DCWR samples decreased in the order Mg > Ca > K > Na (Table 14). Calcium and magnesium release had a strong correlation with sulfur content (Figures 38, 39). Alternatively, sodium and potassium release had a much weaker correlation (Figures 40, 41). Major cation release rates tended to steadily decrease over the 400 week period of record, similar to  $dSO_4/dt$ , where rates decreased by about 50% during this period of record (Figures 46-49). Ca and Mg release rates in the VF samples, on average, were 4 and 2 times higher, respectively, than the DCWR samples (Figures 38, 39). Average Na and K release rates tended to be about twice as high in the VF samples.



#### 5.4.3.4 Metal Release

Similar to the VF samples, Cu and Co release rates correlated well with sulfur content (Figures 42, 43). For a specified sulfur content, copper release rates were 13% higher than the VF samples (Figure 42). Alternatively, cobalt release rates in the VF samples were 44% higher than the DCWR samples (Figure 43). These differences in release rates were not reflective of the metal compositions, where average Cu and Co content for the VF and DCWR samples were 0.019, 0.21% and 0.0038, 0.0077%, respectively. DCWR copper and cobalt release rate behavior tended to be similar to the VF samples. Copper release tended to increase steadily over the 400 week period of record for both data sets (Figure 50). Cobalt release increased for the first 100 to 200 weeks, peaked, and decreased for the remaining period of record (Figure 51). DNR did not have nickel and zinc data for the VF samples that coincided with the period of record available for the DCWR samples, so no comparison could be drawn at this time. Arsenic was not measured in the DCWR samples for comparison with the VF samples.

## 6. SUMMARY

In June 2004 laboratory kinetic tests were initiated on five VF samples provided by NSM. These samples ranged in sulfur content from 0.22 to 0.81. All samples were characterized with respect to chemical composition and mineral content. This experiment remains in progress and the present report analyzed and summarized data collected through week 580.

Leachate pH in the VF samples tended to decrease with increasing sulfur content. Minimum leachate pH was in the range of 4.0 to 6.4. In general, release rates for sulfate, metals (copper, cobalt) and major cations (calcium, magnesium, sodium, potassium) tended to increase with increasing sulfur content. One exception to this was the 0.30%S sample, which tended to have sulfate and major cation release rates lower than expected based on its sulfur content.

Solid phase and leachate composition data from the DNR VF samples was compared to VF samples from NSM and PM. In general, both static and kinetics test results differed considerably between these sample sets. Leachate pH was the highest for the PM samples (min pH ~ 6.7) and the lowest for the NSM samples (min pH ~ 3.5). Sulfate release from the NSM samples, on average, were 35% higher than the DNR samples, and as much as 5 times higher than the PM samples. In addition, the NSM VF samples displayed varying release rates as a function of rock type.

A similar comparison was also made to the DCWR samples under test by the DNR. These two sample sets displayed significant differences in sulfate and cation release rates. Leachate pH from the VF samples were typically at least 1 pH unit lower than the DCWR samples and sulfate release rates were on average 2.5 times higher. These comparisons demonstrate the importance of a thorough waste rock characterization program for all rock types that may be disturbed during mineral resource development of the DC and VF.

## **7. ACKNOWLEDGMENTS**

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Table 1. Whole rock chemistry, metal composition, and mineralogy for DNR VF humidity cells (d<6.35 mm). Additional details in Appendix 1.

HC	1	2	3	4	5	Average
%S	0.22	0.25	0.30	0.42	0.81	
Whole rock chemistry (%) performed by Actlabs						
CO <sub>2</sub>	0.09	0.03	0.05	0.05	0.07	0.06
SiO <sub>2</sub>	50.77	54.9	59.18	54.54	58.85	55.65
Al <sub>2</sub> O <sub>3</sub>	15.37	16.25	17.1	18.11	16.33	16.63
Fe <sub>2</sub> O <sub>3</sub>	10.99	12.54	8.53	10.78	7.84	10.14
MnO	0.166	0.103	0.071	0.083	0.078	0.10
MgO	7.66	3.7	4.23	5.18	3.38	4.83
CaO	8.48	3.91	3.29	3.58	3.72	4.60
Na <sub>2</sub> O	1.8	2.91	2.04	2.32	1.71	2.16
K <sub>2</sub> O	2.15	2.39	3.51	2.96	3.12	2.83
TiO <sub>2</sub>	1.216	2.188	0.855	1.094	0.855	1.24
LOI	1.63	1.48	1.57	1.44	4.11	2.05
Metal composition (%) performed by Actlabs						
Al	8.22	8.46	9.0	9.8	8.6	8.8
As	< 0.0005	< 0.0005	< 0.0005	< 0.0005	0.0052	0.0014
Co	0.00512	0.00343	0.00332	0.00424	0.00296	0.00381
Cu	0.0179	0.0124	0.0104	0.0149	0.0399	0.0191
Fe	7.87	8.72	6.01	7.53	5.63	7.15
Mn	0.14	0.08	0.0552	0.0628	0.0603	0.0797
Ni	0.018	0.007	0.009	0.013	0.028	0.015
Zn	0.02	0.022	0.02	0.029	0.025	0.023
Mineralogy (modal %) performed by Actlabs						
Plagioclase	44.1	46.7	32.7	40.1	32.5	39.2
K-feldspar		2.9	7	4.9	7.5	5.6
Quartz	6.6	21	21.3	20	30.2	19.8
Augite	18.9				3.7	11.3
OPX	5.1	3.4		3.7		4.1
Cordierite	5.4	1.2	12.5	16	4.3	7.9
Biotite	7.7	23.8	20.2	14.7	14	16.1
Chlorite		trace	1.4	trace	trace	1.4
Ilmenite	0.6	1				0.8
Rutile				0.5	trace	0.5
Amorphous	11.6		4.9		7.7	8.1

Table 2. Water retention (g) for the DNR VF rock humidity cells for weeks 1-580.

HC	% S	Water retention before rinse <sup>1</sup>					Water retention after rinse				
		count	min	max	mean	SD	count	min	max	mean	SD
1	0.22	576	82	141	102.9	6.9	576	90	165	109.1	8.3
2 <sup>2</sup>	0.25	575	112	138	126.8	2.7	575	115	149	136.4	3.6
3	0.30	576	70	130	92.6	5.4	576	75	127	101.0	6.2
4	0.42	576	71	127	85.6	3.4	575	75	144	95.7	5.4
5	0.81	576	110	164	127.8	6.2	576	113	165	141.8	7.3
Avg		576	89	140	107.1	4.9	576	93.6	150	116.8	6.2
St Dev		0.4	20.3	14.6	19.3	1.4	0.5	19.5	13.7	20.6	1.4

<sup>1</sup> To calculate water retention the original mass of the reactor and dry solids (at the beginning of the experiment) was subtracted from the mass before the rinse.

<sup>2</sup> Missing water retention data from week 526

Table 3. Page 1 of 2. Minimum pH and average annual rates of release for sulfate, calcium, magnesium, sodium, and potassium in  $\mu\text{mol} \cdot (\text{kg rock} \cdot \text{week})^{-1}$ . Period of record is 6 – 580 weeks. During the first seven years, 13-14 concentrations were sampled for each parameter. Sampling frequency for subsequent years decreased to approximately 6-7 per year.

ID	Year	min pH <sup>1</sup>	Sulfate		Calcium		Magnesium		Sodium		Potassium	
			rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.
Humidity cell 1 0.22 %S	1	7.27	43.5	14.0	32.0	10.7	11.7	4.4	70.8	74.2	17.3	3.2
	2	6.93	56.1	6.0	38.8	4.1	16.9	2.0	5.5	1.5	19.7	2.4
	3	6.75	47.9	9.1	31.6	4.7	16.8	2.0	4.2	1.6	18.6	2.9
	4	6.65	36.2	5.5	21.3	3.5	13.9	1.6	1.5	0.7	13.6	1.7
	5	6.61	27.1	2.8	15.9	2.0	12.1	0.9	1.4	0.6	11.1	0.9
	6	6.42	26.8	7.2	15.8	3.2	13.2	2.7	1.8	0.7	11.8	2.0
	7	6.53	20.2	1.9	12.2	1.0	10.7	0.7	1.5	0.6	10.5	2.0
	8	6.58	16.4	1.7	9.3	1.2	8.9	1.2	1.0	0.1	9.0	4.4
	9	6.68	19.7	4.9	12.2	2.6	10.4	2.0	1.1	0.004	8.8	0.9
	10	6.65	22.0	6.8	11.2	2.7	11.8	3.1	1.1	0.01	8.7	0.8
	11 <sup>2</sup>	6.63	21.5	5.5	10.9	2.1	12.1	2.4	1.6	0.6	9.2	0.9
Total <sup>3</sup>	6.56	33.2	14.6	21.3	11.0	12.9	3.3	11.5	35.2	13.5	4.6	
Humidity cell 2 0.25 %S	1	7.05	34.8	9.1	17.6	7.1	7.3	4.0	48.5	42.6	17.8	4.1
	2	6.53	76.8	15.6	43.4	7.8	22.4	5.9	6.3	0.9	26.6	2.4
	3	6.19	101.9	13.0	53.1	11.4	37.8	4.1	5.0	1.1	28.7	3.5
	4	5.89	100.3	9.2	41.4	5.0	38.8	2.5	3.2	0.7	22.4	1.3
	5	5.70	82.6	7.0	31.0	4.4	37.9	2.8	3.2	0.3	18.3	1.8
	6	5.54	71.9	10.3	26.0	3.5	36.2	5.9	3.6	0.4	17.9	2.7
	7	5.54	53.6	4.8	18.1	2.5	28.1	3.1	3.1	0.3	15.4	2.0
	8	5.67	42.9	8.8	13.4	2.7	22.4	4.6	2.7	0.7	11.5	3.2
	9	5.70	44.3	11.8	15.4	4.4	24.5	6.4	1.9	1.1	13.1	2.1
	10	5.73	49.0	9.6	14.6	3.4	26.7	5.7	1.1	0.006	12.9	1.6
	11 <sup>2</sup>	5.76	45.3	7.5	12.6	2.3	23.5	3.9	3.3	0.7	12.8	1.1
Total <sup>3</sup>	5.64	68.0	25.4	28.8	14.7	28.3	10.9	9.7	21.8	19.2	6.0	
Humidity cell 3 0.30 %S	1	6.95	28.9	4.7	23.0	3.4	7.6	0.6	29.0	26.2	22.7	2.6
	2	6.27	38.8	6.2	21.5	2.3	8.2	1.2	5.7	1.1	21.9	1.8
	3	5.67	53.7	4.3	30.1	3.8	14.0	2.0	4.8	0.9	21.3	3.1
	4	4.60	80.1	14.6	36.8	6.5	22.0	5.8	3.8	0.5	16.7	1.0
	5	4.54	97.3	14.4	37.2	7.2	32.2	4.4	4.6	0.5	15.1	2.5
	6	4.47	63.5	15.1	25.7	4.7	22.4	5.5	4.1	1.0	11.5	2.2
	7	4.77	35.3	4.4	16.4	2.3	11.1	1.9	2.7	0.3	7.0	1.2
	8	4.97	24.7	6.7	11.2	3.0	7.3	2.0	2.1	0.8	4.5	1.4
	9	5.12	21.8	5.0	12.2	2.7	6.2	1.5	1.3	0.6	4.2	0.6
	10	5.20	21.9	3.6	10.7	1.8	6.7	1.3	1.1	0.01	4.4	0.5
	11 <sup>2</sup>	5.34	17.7	1.7	8.0	0.7	5.0	0.4	1.3	0.5	4.0	0.2
Total <sup>3</sup>	5.28	49.5	27.1	23.8	10.3	14.7	9.4	7.0	12.9	14.0	7.3	

<sup>1</sup> 5th percentile value

<sup>2</sup> Year 11 represented by weeks 521-580

<sup>3</sup> Average and standard deviation for entire period of record

Table 3. Page 2 of 2. Minimum pH and average annual rates of release for sulfate, calcium, magnesium, sodium, and potassium in  $\mu\text{mol} \cdot (\text{kg rock} \cdot \text{week})^{-1}$ . Period of record is 6 – 580 weeks. During the first seven years, 13-14 concentrations were sampled for each parameter. Sampling frequency for subsequent years decreased to approximately 6-7 per year.

ID	Year	min pH <sup>1</sup>	Sulfate		Calcium		Magnesium		Sodium		Potassium	
			rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.	rate	s.d.
Humidity cell 4 0.42 %S	1	6.31	60.4	16.3	31.6	4.1	21.3	4.3	13.9	8.8	19.0	1.7
	2	4.85	127.8	32.7	58.6	14.1	51.1	16.1	6.1	1.0	21.0	2.2
	3	4.34	152.3	60.7	59.3	24.7	71.4	24.4	7.1	1.9	17.3	5.3
	4	4.57	91.5	15.3	30.7	5.0	33.7	6.5	4.1	1.0	8.0	1.2
	5	4.63	64.3	8.0	23.9	4.0	23.4	6.4	3.6	0.4	5.4	0.7
	6	4.53	54.7	6.4	21.6	2.4	19.9	2.2	3.7	0.5	5.5	0.6
	7	4.70	42.0	2.8	17.5	1.7	14.4	1.5	3.2	0.1	4.7	0.7
	8	4.76	35.5	9.9	13.9	4.0	11.1	3.3	2.9	0.8	3.4	1.1
	9	4.81	35.1	6.9	16.7	3.1	11.0	2.1	2.2	1.1	3.3	0.4
	10	4.86	37.0	7.5	15.5	3.3	12.0	2.6	1.8	2.1	3.9	0.4
	11 <sup>2</sup>	4.89	29.5	3.3	11.8	1.3	8.8	0.6	3.1	0.4	3.5	0.1
Total <sup>3</sup>	4.52	74.4	46.6	30.8	19.2	28.5	21.4	5.5	4.9	10.1	7.2	
Humidity cell 5 0.81 %S	1	4.57	375.5	75.4	151.3	38.8	190.8	28.6	24.7	16.8	26.0	5.4
	2	4.37	290.5	27.8	101.3	9.4	138.8	17.6	9.3	0.8	16.4	2.1
	3	4.31	232.7	48.4	87.4	20.9	101.1	30.9	8.2	1.9	11.9	2.7
	4	4.22	175.0	23.4	59.3	6.1	45.7	7.4	5.2	1.4	6.1	0.6
	5	4.16	149.0	15.1	53.0	4.8	30.9	4.7	4.6	1.8	4.2	1.0
	6	4.04	129.7	19.2	49.9	5.7	27.7	3.9	4.7	0.5	5.1	1.5
	7	4.19	95.1	4.6	40.4	3.5	18.7	2.4	4.0	0.3	4.3	0.7
	8	4.27	80.1	23.8	33.3	9.9	14.1	4.5	3.5	1.0	3.0	1.1
	9	4.29	79.4	10.3	40.3	4.5	13.9	1.6	2.9	1.1	2.9	0.4
	10	4.37	76.8	8.6	35.5	4.7	14.7	2.5	2.1	1.4	3.7	0.3
	11 <sup>2</sup>	4.41	65.3	7.1	26.8	2.3	10.7	0.9	3.8	0.5	3.1	0.1
Total <sup>3</sup>	4.17	180.7	104.9	69.1	40.7	65.8	63.7	8.0	9.3	9.2	7.9	

<sup>1</sup> 5th percentile value

<sup>2</sup> Year 11 represented by weeks 521-580

<sup>3</sup> Average and standard deviation for entire period of record



Table 4. Total mass release for DNR VF humidity cells after 580 weeks (mmol)

HC	%S	SO <sub>4</sub>	Ca	Mg	Na	K	Total NP <sup>1</sup>	NP/AP
1	0.22	18.00	11.25	7.37	6.84	7.36	25.72	1.43
2	0.25	37.28	15.14	16.17	4.83	10.45	38.94	1.04
3	0.30	25.54	12.26	7.49	4.14	7.06	25.35	0.99
4	0.42	38.47	15.90	14.57	3.03	5.07	34.53	0.90
5	0.81	92.88	36.14	32.19	4.34	4.70	72.85	0.78

<sup>1</sup> Total neutralization potential (NP) = Ca + Mg + 0.5(Na + K)

Table 5. Annual sulfur depletion and remaining percent sulfur for DNR VF humidity cells after 580 weeks

Year	HC1, 0.22%S		HC2, 0.25%S		HC3, 0.30%S		HC4, 0.42%S		HC5, 0.81%S	
	% depl	% remain	% depl	% remain	% depl	% remain	% depl	% remain	% depl	% remain
1	96.6%	0.212	97.5%	0.244	98.2%	0.295	97.5%	0.409	92.0%	0.745
2	92.4%	0.203	92.5%	0.231	96.1%	0.288	92.6%	0.389	86.0%	0.697
3	88.7%	0.195	85.7%	0.214	93.1%	0.279	86.5%	0.363	81.1%	0.657
4	86.0%	0.189	79.0%	0.198	88.8%	0.266	82.8%	0.348	77.5%	0.628
5	83.9%	0.185	73.4%	0.184	83.3%	0.250	80.2%	0.337	74.4%	0.603
6	81.9%	0.180	68.6%	0.172	79.7%	0.239	78.0%	0.328	71.7%	0.581
7	80.3%	0.177	65.0%	0.163	77.8%	0.233	76.4%	0.321	69.8%	0.565
8	78.8%	0.173	61.8%	0.154	76.3%	0.229	74.8%	0.314	68.0%	0.551
9	77.3%	0.170	58.8%	0.147	75.1%	0.225	73.4%	0.308	66.4%	0.538
10	75.6%	0.166	55.6%	0.139	73.8%	0.222	72.0%	0.302	64.8%	0.525
11 <sup>1</sup>	73.7%	0.162	52.1%	0.130	72.7%	0.218	70.6%	0.297	63.2%	0.512

<sup>1</sup> Year 11 represented by weeks 521-580

Table 6. Whole rock chemistry, metal composition, and mineralogy for NSM VF humidity cells (d<6.35 mm). Page 1 of 2.

HC	5	6	7	8	9	10	12
%S	0.12	0.3	0.32	0.25	0.22	0.16	0.29
Whole rock chemistry (%)							
SiO <sub>2</sub>	48.93	60.19	62.06	59.05	58.17	53.26	59.67
TiO <sub>2</sub>	1.31	0.77	0.79	0.79	0.77	1.13	0.82
Al <sub>2</sub> O <sub>3</sub>	13.55	11.21	15.5	16.77	16.44	14.28	17.18
Fe <sub>2</sub> O <sub>3</sub>	11.94	7.949	8.255	10.2	9.953	10.1	9.431
MgO	9.44	6.707	3.441	4.04	3.987	6.762	3.815
MnO	0.1	0	0	0	0	0	0
CaO	10.63	6.366	2.483	1.76	1.737	8.15	1.676
K <sub>2</sub> O	0.9	1.39	3.62	5.03	4.99	1.86	3.32
Na <sub>2</sub> O	0.93	1.2	1.4	1.25	1.22	1.59	1.69
Metal composition (%)							
As	0.011	0.008	0.006	0.005	0.005	0.009	0.005
Cr	0.062	0.124	0.102	0.155	0.148	0.13	0.101
Co	0.004	0.002	0.002	0.003	0.003	0.003	0.002
Cu	0.011	0.018	0.018	0.009	0.009	0.013	0.014
Mo	0.002	0.005	0.007	0.007	0.008	0.005	0.007
Ni	0.017	0.018	0.01	0.01	0.01	0.013	0.009
Sr	0.031	0.023	0.02	0.017	0.018	0.029	0.015
Zn	0	0.002	0.023	0.017	0.017	0.006	0.012
Mineralogy (modal %) performed by CTG Pyrometallurgy							
Quartz	-	25.1	25.7	14	26.5	11	25.5
Biotite	4.7	29.9	29.5	55.1	28.5	13.9	39.7
Amphibole	65.1	21.8	1.7	-	7.1	30.5	-
Plagioclase	27.5	20.2	21.6	14.1	20.3	36.9	23
K-spar	-	1.2	8.4	11.4	9.6	6.4	<1
Augite	-	-	-	-	-	-	-
Cordierite	-	-	11.1	3.5	6.2	-	9.7
Chlorite	2.4	2.6	-	0.6	-	1.3	2.1

Table 6. Whole rock chemistry, metal composition, and mineralogy for NSM VF humidity cells (d<6.35 mm). Page 2 of 2.

HC	14	15	16	17	18	19	Average
%S	0.22	0.25	0.17	0.42	0.31	0.15	
Whole rock chemistry (%)							
SiO <sub>2</sub>	55.17	54.77	50.47	52.98	58.92	59.68	56.41
TiO <sub>2</sub>	2.26	2.21	1.18	1.12	0.86	0.9	1.15
Al <sub>2</sub> O <sub>3</sub>	15.56	15.91	16.11	17.82	16.88	12	15.32
Fe <sub>2</sub> O <sub>3</sub>	12.32	12.64	10.47	10.83	8.829	8.073	10.08
MgO	3.647	3.886	7.643	5.391	4.406	6.382	5.35
MnO	0.11	0.1	0.12	0.07	0.07	0.08	0.05
CaO	4.045	3.915	7.704	3.86	3.448	8.336	4.93
K <sub>2</sub> O	2.55	2.11	2.2	2.55	3.43	1.74	2.75
Na <sub>2</sub> O	2.43	2.64	1.33	1.71	1.61	0.83	1.53
Metal composition (%)							
As	0.009	0.009	0.009	0.007	0.008	0.009	0.008
Cr	0.014	0.014	0.037	0.032	0.024	0.042	0.076
Co	0.003	0.003	0.003	0.003	0.002	0.002	0.003
Cu	0.022	0.023	0.023	0.019	0.017	0.011	0.016
Mo	0.001	0.002	0.002	0.004	0.004	0.002	0.004
Ni	0.004	0.004	0.012	0.013	0.01	0.013	0.011
Sr	0.02	0.022	0.034	0.025	0.022	0.029	0.023
Zn	0.019	0.02	0.011	0.016	0.015	0.005	0.013
Mineralogy (modal %) performed by CTG Pyrometallurgy							
Quartz	13.7	9.8	-	9.5	26.4	25.5	19.3
Biotite	60.9	50.8	37.9	26.9	36.6	15.6	33.1
Amphibole	-	-	-	-	-	11.9	23.0
Plagioclase	24.6	37.9	42.9	40.6	21.9	35.2	28.2
K-spar	<1	<1	5.3	5.8	3.6	6.8	5.1
Augite	-	-	9.9	-	-	-	9.9
Cordierite	0.5	-	2.8	16.4	9.1	-	7.4
Chlorite	-	0.4	0.7	0.4	2.1	4.1	1.7

Table 7. Minimum pH and average release rates for NSM VF humidity cells (d<6.35 mm) in  $\mu\text{mol}*(\text{kg rock}*\text{week})^{-1}$ . Period of record is 6 – 580 weeks.

ID	Rock type	%S	CO <sub>2</sub>	Min pH <sup>2</sup>	SO <sub>4</sub>	Ca	Mg	Na	K
5 <sup>1</sup>	diabase sill	0.12	0.01	5.40	6.57	11.04	2.06	10.00	7.72
6 <sup>1</sup>	diabase sill	0.30	0.08	3.83	74.65	45.09	8.40	9.25	9.93
7 <sup>1</sup>	bedded	0.32	0.20	3.48	119.84	26.70	12.83	7.30	3.80
8 <sup>1</sup>	bedded	0.25	0.13	4.79	34.02	21.48	13.53	6.38	7.57
9 <sup>1</sup>	diabase sill	0.22	0	3.63	95.24	24.63	12.36	9.60	5.67
10 <sup>1</sup>	diabase sill	0.16	0.07	5.01	11.18	17.13	2.71	4.76	6.05
12 <sup>1</sup>	metasedimentary	0.29	0	3.72	68.03	16.45	27.99	8.69	7.93
14	metasedimentary	0.22	0.06	4.51	86.14	30.30	42.34	16.00	22.38
15	metasedimentary	0.25	0	4.95	85.54	34.60	36.97	21.96	27.16
16	metasedimentary	0.17	0	4.99	24.90	21.54	12.44	20.28	16.64
17	metasedimentary	0.42	0.14	3.64	132.74	38.63	44.16	15.27	14.57
18	metasedimentary	0.31	0.01	4.01	79.37	28.68	20.90	14.17	17.60
19	metasedimentary	0.15	0.03	5.22	14.49	43.13	4.36	11.20	16.06

<sup>1</sup> Rinse frequency change to monthly after 57-69 weeks

<sup>2</sup> 5<sup>th</sup> percentile value

Table 8. Total mass release after 580 weeks for NSM VF humidity cells under test in mmol/kg rock.

ID	Rock type	%S	Min pH <sup>2</sup>	SO <sub>4</sub>	Ca	Mg	Na	K	Total NP <sup>3</sup>	NP/AP
5 <sup>1</sup>	diabase sill	0.12	5.40	3.39	5.07	0.98	5.32	3.95	10.68	0.32
6 <sup>1</sup>	diabase sill	0.3	3.83	44.71	26.31	5.00	5.20	5.66	36.74	1.22
7 <sup>1</sup>	bedded	0.32	3.48	69.48	15.97	7.69	4.28	2.69	27.14	2.56
8 <sup>1</sup>	bedded	0.25	4.79	19.60	11.65	7.80	3.65	4.13	23.34	0.84
9 <sup>1</sup>	diabase sill	0.22	3.63	51.50	14.48	7.07	10.78	4.55	29.21	1.76
10 <sup>1</sup>	diabase sill	0.16	5.01	6.52	8.33	1.34	3.71	3.04	13.04	0.50
12 <sup>1</sup>	metasedimentary	0.29	3.72	41.37	9.84	16.98	5.59	4.90	32.07	1.29
14	metasedimentary	0.22	4.51	43.68	15.00	21.70	7.84	11.58	46.42	0.94
15	metasedimentary	0.25	4.95	46.05	18.15	20.72	13.70	14.73	53.09	0.87
16	metasedimentary	0.17	4.99	14.93	11.36	7.64	12.23	9.96	30.09	0.50
17	metasedimentary	0.42	3.64	78.70	22.89	25.60	10.46	8.99	58.21	1.35
18	metasedimentary	0.31	4.01	49.00	17.49	12.72	10.12	11.22	40.88	1.20
19	metasedimentary	0.15	5.22	9.08	25.16	2.49	8.97	9.88	37.07	0.24

<sup>1</sup> Rinse frequency change to monthly after 57-69 weeks

<sup>2</sup> 5<sup>th</sup> percentile value

<sup>3</sup> Total neutralization potential (NP) = Ca + Mg + 0.5(Na + K)

Table 9. Whole rock chemistry, metal composition, and mineralogy for PM VF humidity cells (d<6.35 mm) with sulfur content  $\leq 0.55$ .

HC	9	10	11	Average
%S	0.24	0.44	0.55	
Whole rock chemistry (%)				
CO <sub>2</sub>	1	0.3	0.2	0.50
SiO <sub>2</sub>	48	59.1	51.8	53.0
Al <sub>2</sub> O <sub>3</sub>	14.3	15.95	18.3	16.2
Fe <sub>2</sub> O <sub>3</sub>	8.3	6.81	10.6	8.57
CaO	20.1	4.23	5.34	9.89
MgO	3.82	3.77	5.64	4.41
Na <sub>2</sub> O	1.2	2.23	1.98	1.80
K <sub>2</sub> O	0.63	3.44	2.7	2.26
Cr <sub>2</sub> O <sub>3</sub>	0.03	0.03	0.04	0.03
TiO <sub>2</sub>	0.74	0.92	1.19	0.95
MnO	0.35	0.19	0.15	0.23
P <sub>2</sub> O <sub>5</sub>	0.13	0.15	0.02	0.10
SrO	0.04	0.03	0.03	0.03
BaO	0.09	0.09	0.11	0.10
Metal composition (%)				
As	0.0014	0.0027	0.0011	0.0017
Cr	0.0151	0.0196	0.026	0.0202
Co	0.0025	0.0024	0.0034	0.0028
Cu	0.0098	0.0146	0.0142	0.0129
Mo	0.0002	0.001	0.0008	0.0007
Ni	0.0104	0.0122	0.0144	0.0123
Sr	0.0326	0.0222	0.0269	0.0272
Zn	0.0168	0.0225	0.0399	0.0264
Mineralogy (%)				
Quartz			30.0	30.0
Biotite		5.0	0.5	2.8
K-spar	10.0	55.0	25.0	30.0
Cordierite		5.0		5.0
Chlorite			10.0	10.0
CPX	48.0		30.0	39.0
White Mica	10.0	30.0		20.0
Graphite	1.0	2.0	1.0	1.3
Carbonates	25.0			25.0
Vesuvianite/ Idocrase	5.0			5.0
Oxides		1.0	2.0	1.5
Sulfides	1.0	2.0	1.5	1.5

Table 10. Minimum pH and average release rates for PM VF ( $d < 6.35$  mm) in  $\mu\text{mol} \cdot (\text{kg rock} \cdot \text{week})^{-1}$  with sulfur content  $\leq 0.55$ . Period of record is 6 – 440 weeks.

ID	%S	Min pH <sup>1</sup>	SO <sub>4</sub>	Ca	Mg	Na	K
5	0.24	7.24	26.24	108.59	1.60	7.86	6.29
6	0.44	6.89	42.76	75.95	7.99	9.25	8.92
7	0.55	6.73	44.23	62.17	6.60	16.09	7.84

<sup>1</sup> 5<sup>th</sup> percentile value

Table 11. Total mass release after 440 weeks for PM VF humidity cells under test with sulfur content  $\leq 0.55$  in mmol/kg rock.

ID	%S	Min pH <sup>1</sup>	SO <sub>4</sub>	Ca	Mg	Na	K	Total NP <sup>2</sup>	NP/AP
5	0.24	7.24	11.65	44.17	0.59	3.80	2.31	47.82	4.11
6	0.44	6.89	18.49	30.35	2.88	4.66	3.47	37.30	2.02
7	0.55	6.73	18.93	25.03	2.49	6.85	3.27	32.59	1.72

<sup>1</sup> 5<sup>th</sup> percentile value

<sup>2</sup> Total neutralization potential (NP) = Ca + Mg + 0.5(Na + K)

Table 12. Whole rock chemistry, metal composition, and mineralogy for DNR DCWR humidity cells (d<6.35 mm).

HC	9	10	11	12	14	Average
%S	0.13	0.21	0.33	0.55	0.72	
Whole rock chemistry (%) performed by Lerch Brothers Inc. and ALS USA Inc.						
CO <sub>2</sub>	0.05	0.08	0.08	0.08	0.08	0.07
SiO <sub>2</sub>	45	45.4	44.8	44.2	43.7	44.6
Al <sub>2</sub> O <sub>3</sub>	18.15	17.3	18	16.65	14.95	17.0
Fe <sub>2</sub> O <sub>3</sub>	12.6	13.4	13.2	13.7	16.5	13.9
CaO	8.6	8.66	8.68	8.09	7.25	8.26
MgO	9.29	8.14	7.42	9.24	10.05	8.83
Na <sub>2</sub> O	2.4	2.58	2.57	2.37	2.26	2.44
K <sub>2</sub> O	0.42	0.62	0.58	0.63	0.65	0.58
Cr <sub>2</sub> O <sub>3</sub>	0.02	0.02	0.02	0.01	0.02	0.02
TiO <sub>2</sub>	0.96	2.25	1.69	1.84	1.85	1.72
MnO	0.14	0.15	0.15	0.15	0.17	0.15
P <sub>2</sub> O <sub>5</sub>	0.13	0.18	0.17	0.2	0.22	0.18
SrO	0.04	0.03	0.04	0.03	0.03	0.03
BaO	0.01	0.02	0.02	0.02	0.02	0.02
Metal composition (%) performed by ALS USA Inc.						
Ag	<0.00005	<0.00005	<0.00005	<0.00005	0.00006	0.00005
As	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005	<0.0005
Cd	<0.00005	<0.00005	<0.00005	<0.00005	<0.00005	<0.00005
Co	0.0071	0.0067	0.0069	0.0078	0.0101	0.0077
Cu	0.0779	0.1175	0.157	0.281	0.393	0.205
Mo	<0.0001	0.0001	<0.0001	<0.0001	0.0001	0.0001
Ni	0.0436	0.0426	0.0456	0.0612	0.0986	0.0583
Pb	<0.0002	0.0003	0.0002	0.0002	0.0006	0.0003
Sc	0.0009	0.0017	0.0012	0.0013	0.0014	0.0013
Zn	0.0095	0.0104	0.0106	0.0104	0.013	0.0108
Mineralogy (%) performed by McSwiggen and Associates						
Plagioclase	44.2	47.9	61	52.2	43.6	49.8
Olivine	38.3	20.2	11.9	13.9	21.4	21.1
Augite	4.2	7.6	4.2	8.7	10.3	7.0
OPX	2.5	5	3.4	4.3	0	3.0
Biotite	1.7	2.5	6.8	0.9	4.3	3.2
K-spar	0	1.7	0.8	2.6	0	1.0
Ilmenite	1.7	10.1	5.1	7	4.3	5.6
Sulfides	3.3	4.2	2.5	3.5	7.7	4.2

Table 13. Minimum pH and average release rates for DNR’s DCWR humidity cells in  $\mu\text{mol}^*(\text{kg rock}*\text{week})^{-1}$ . Period of record is 6 – 400 weeks.

ID	%S	Min pH <sup>1</sup>	SO <sub>4</sub>	Ca	Mg	Na	K
9	0.13	6.42	21.8	13.1	16.7	2.52	4.89
10	0.21	6.18	35.5	18.1	20.6	3.56	5.6
11	0.33	5.31	45	19.7	20.3	5.94	7.63
12	0.55	5.70	59.1	24.7	31.9	4.73	6.64
14	0.72	5.43	87.7	25.4	50.5	6.58	7.49

<sup>1</sup> 5<sup>th</sup> percentile value

Table 14. Total mass release after 400 weeks for DNR’s DCWR humidity cells in mmol/kg rock.

ID	%S	Min pH <sup>1</sup>	SO <sub>4</sub>	Ca	Mg	Na	K	Total NP <sup>2</sup>	NP/AP
9	0.13	6.42	9.1	5.43	7	1.28	1.99	14.07	1.55
10	0.21	6.18	14.7	7.44	8.63	1.74	2.27	18.08	1.23
11	0.33	5.31	18.6	8.09	8.5	2.64	3.14	19.48	1.05
12	0.55	5.70	24.5	10.2	13.3	2.22	2.71	25.97	1.06
14	0.72	5.43	36.1	10.5	20.8	2.81	3.04	34.23	0.95

<sup>1</sup> 5<sup>th</sup> percentile value

<sup>2</sup> Total neutralization potential (NP) = Ca + Mg + 0.5(Na + K)



Figure 1. Map of DC, VF, and GRB in Northeast Minnesota (Miller et al., 2002). Note that NSM is designated on the map with a star and PM deposit is designated on the map with a square.

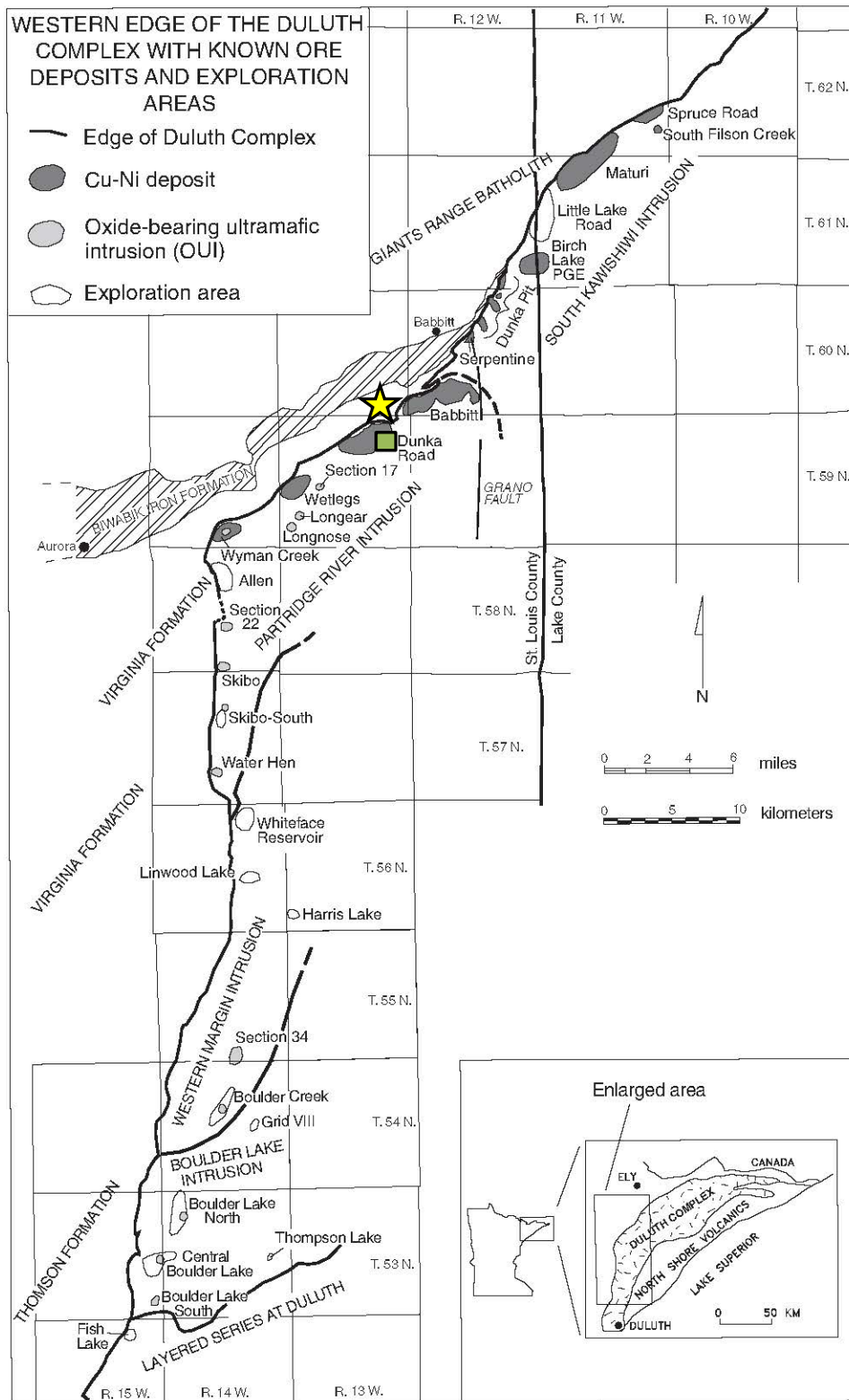


Figure 2. Schematic and photo of humidity cell apparatus. All humidity cell materials are acrylic except the perforated plate (polyvinyl chloride) and the outlet pipe (high density polyethylene).

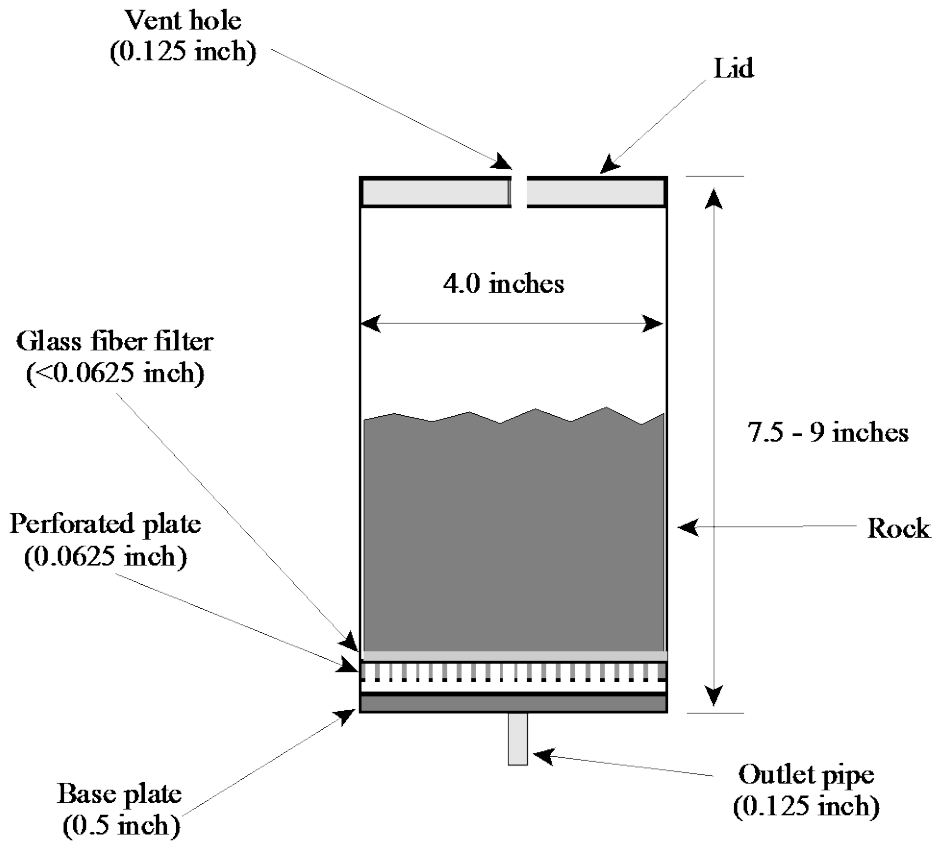


Figure 3. Drainage pH vs time for DNR VF humidity cells. Weeks 0-5 excluded to improve resolution.

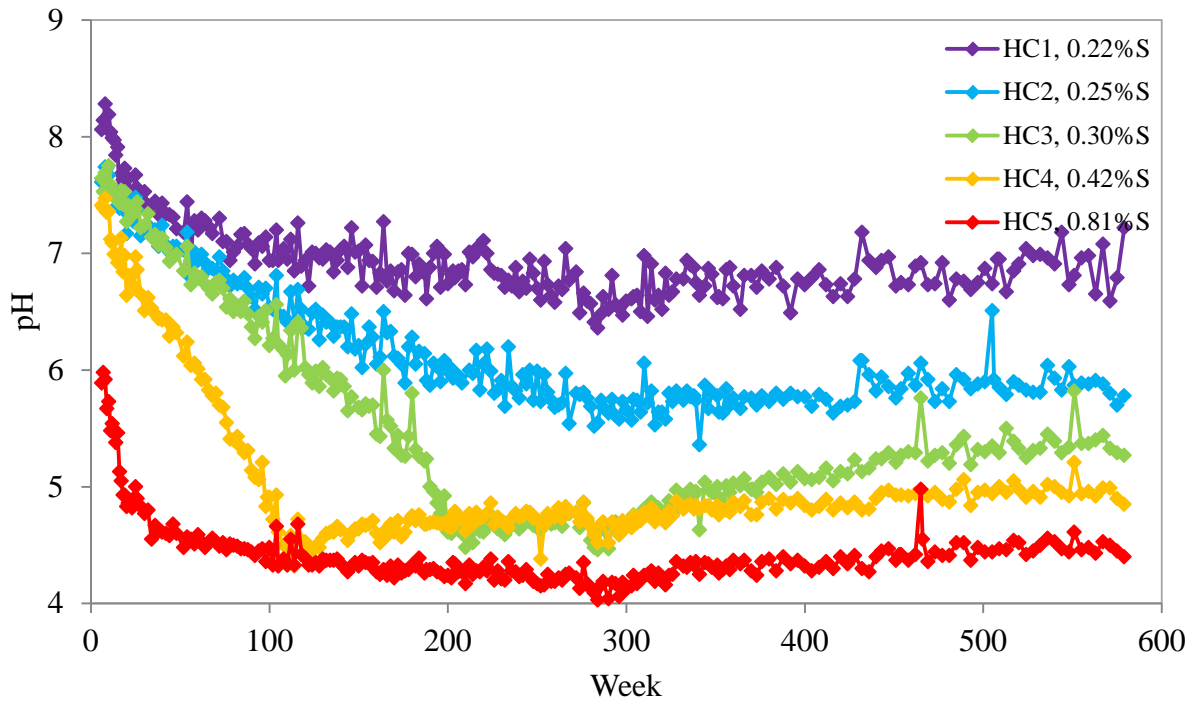


Figure 4. Sulfate release vs time for DNR VF humidity cells. Weeks 0-5 excluded to improve resolution.

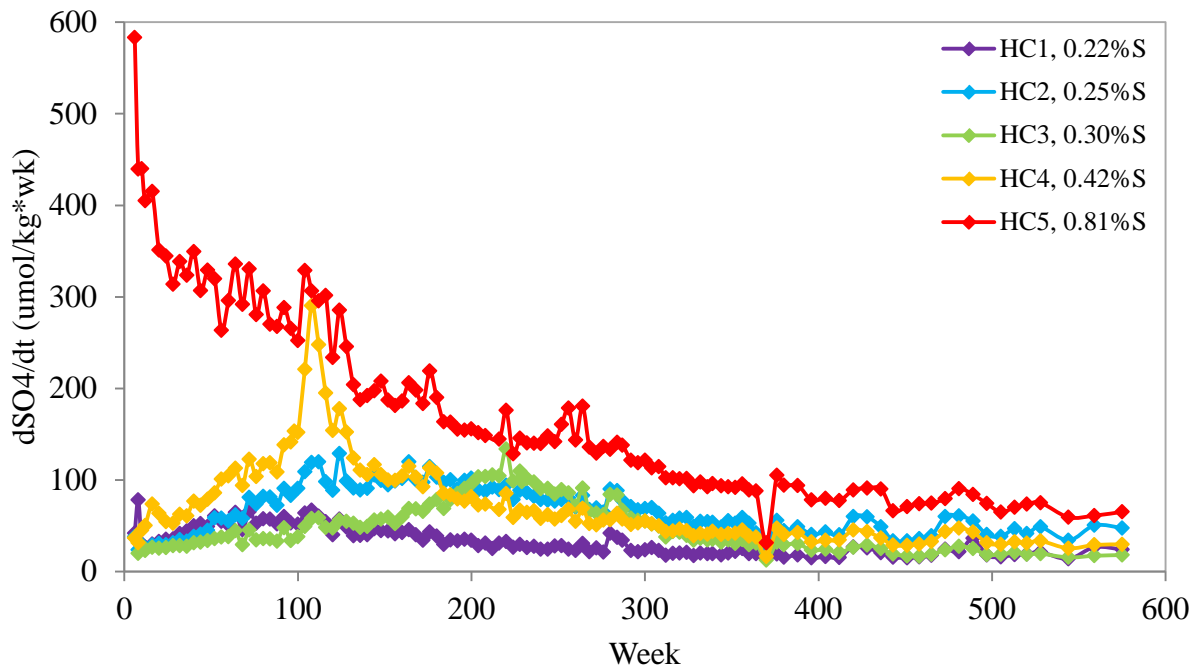


Figure 5. Calcium release vs time for DNR VF humidity cells. Weeks 0-5 excluded to improve resolution.

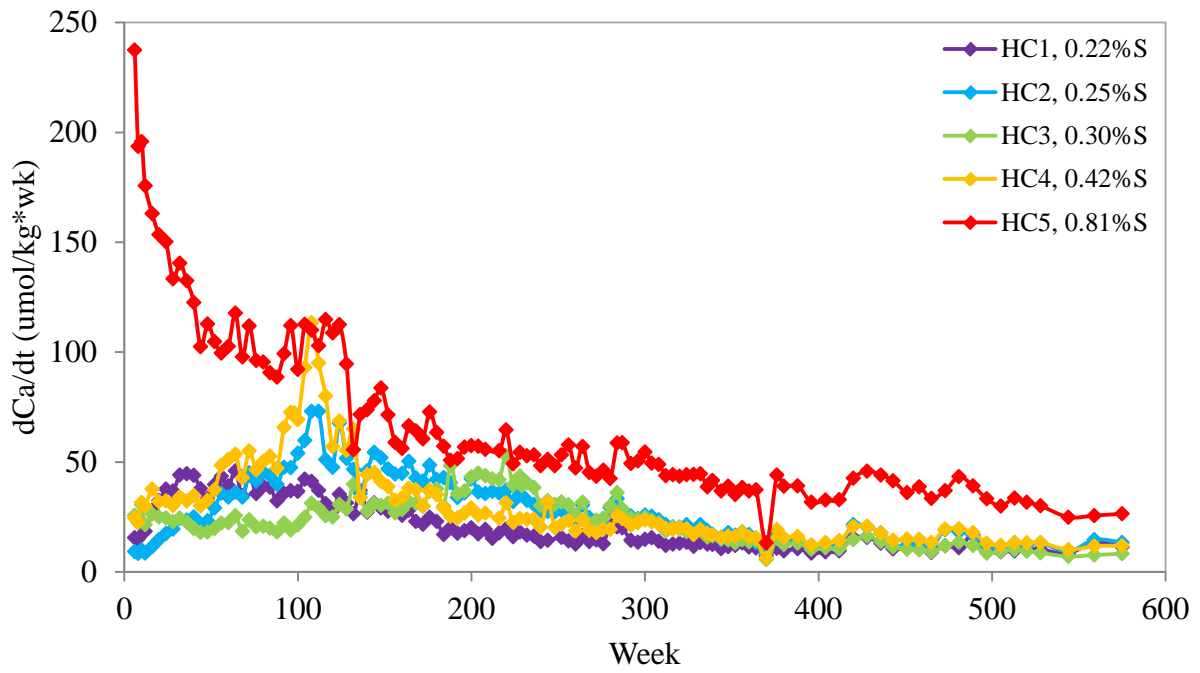


Figure 6. Magnesium release vs time for DNR VF humidity cells. Weeks 0-5 excluded to improve resolution.

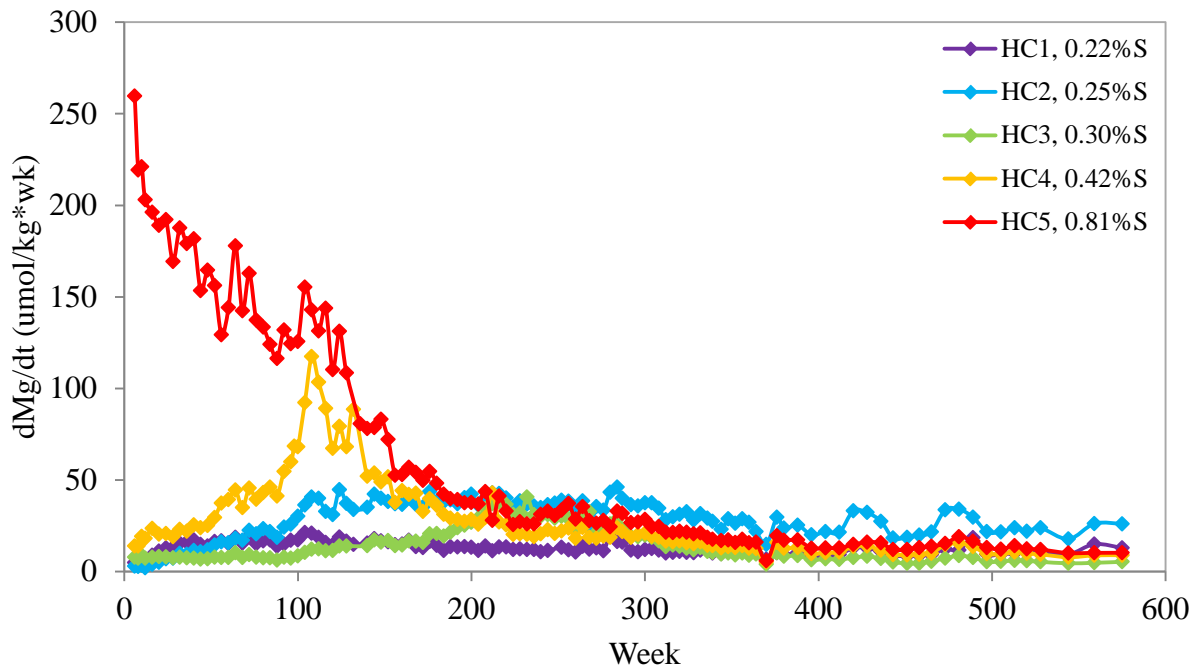


Figure 7. Sodium release vs time for DNR VF humidity cells. Na release greater than 20  $\mu\text{mol}/\text{kg}\cdot\text{wk}$  excluded to improve resolution.

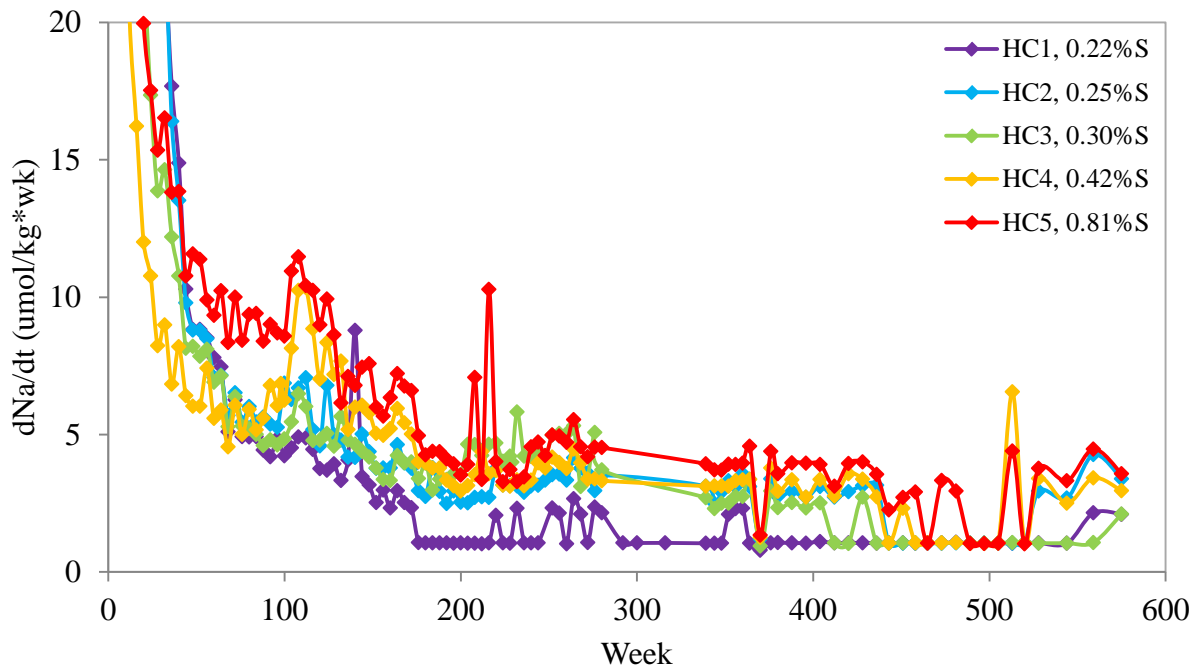


Figure 8. Potassium release vs time for DNR VF humidity cells. Weeks 0-5 excluded to improve resolution.

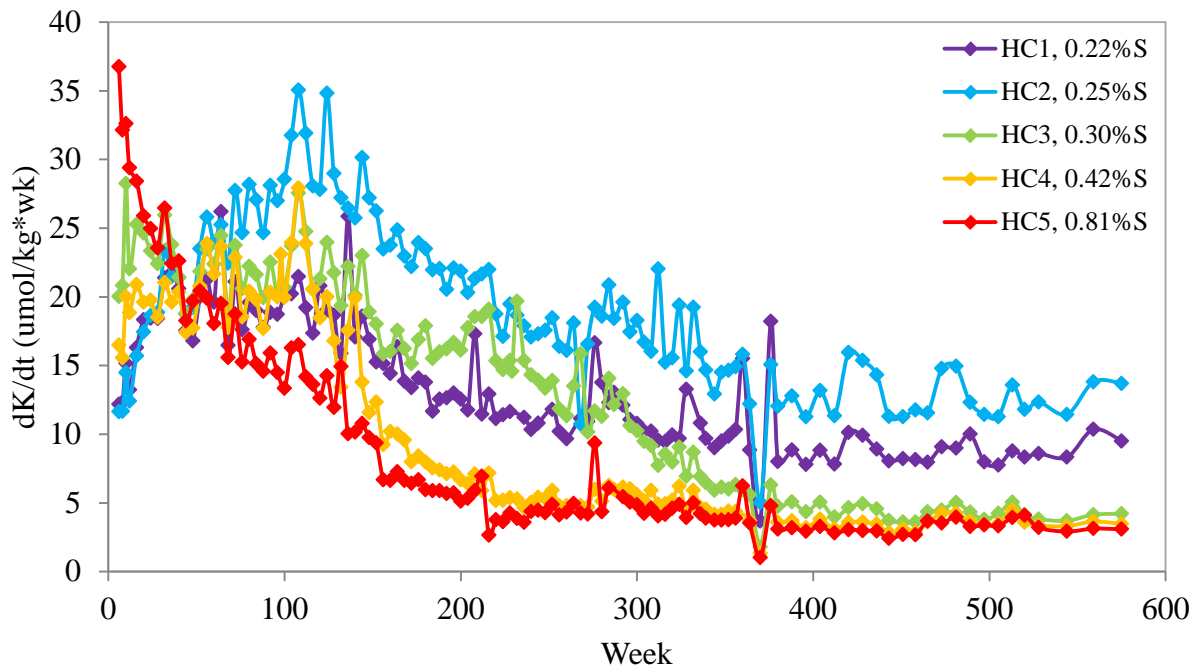


Figure 9. Copper release vs time for DNR VF humidity cells. Weeks 0-5 excluded to improve resolution.

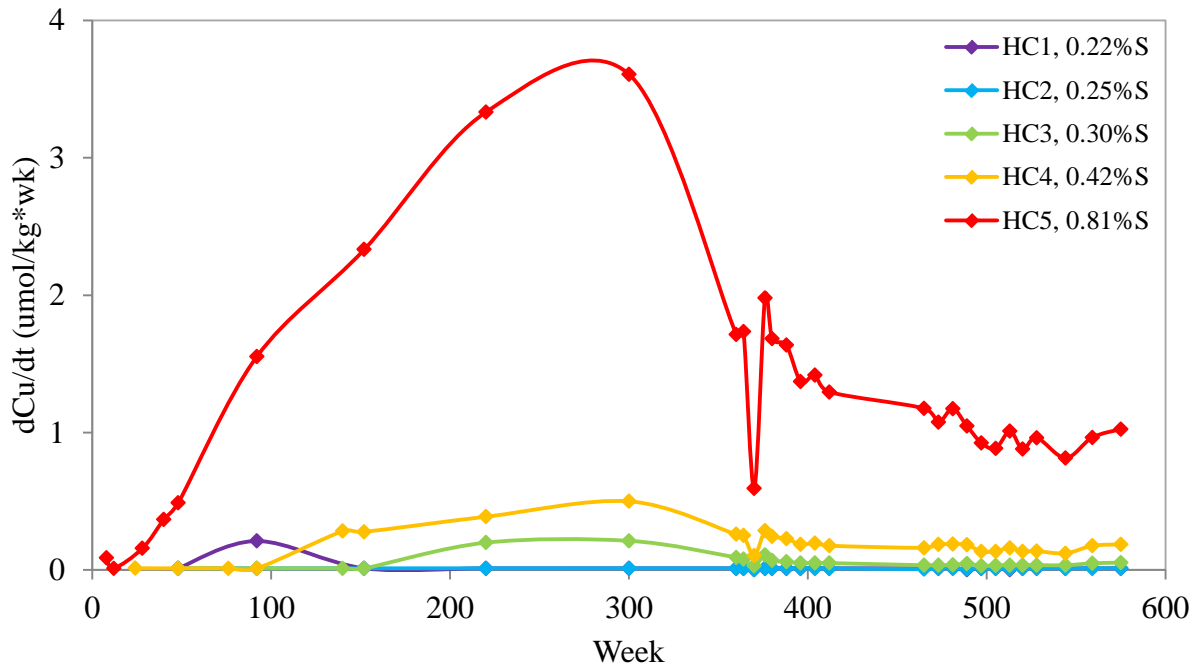


Figure 10. Cobalt release vs time for DNR VF humidity cells. Weeks 0-5 excluded to improve resolution.

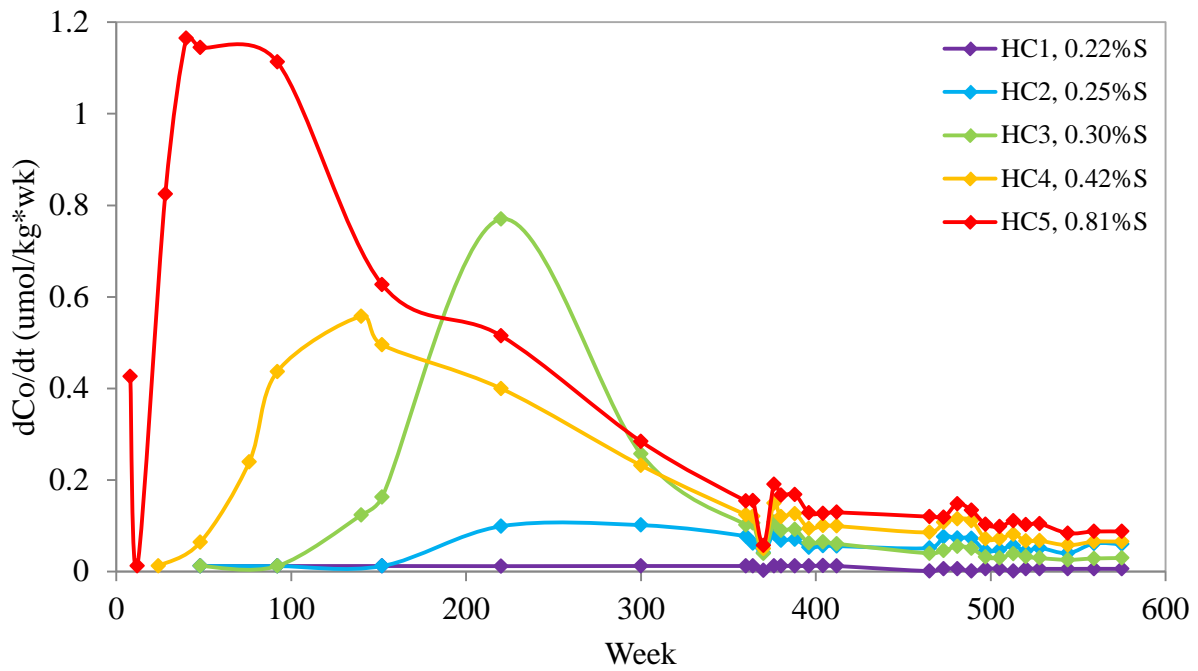


Figure 11. Nickel release vs time for DNR VF humidity cells. Weeks 0-5 excluded to improve resolution. Samples were analyzed for nickel from weeks 465-580.

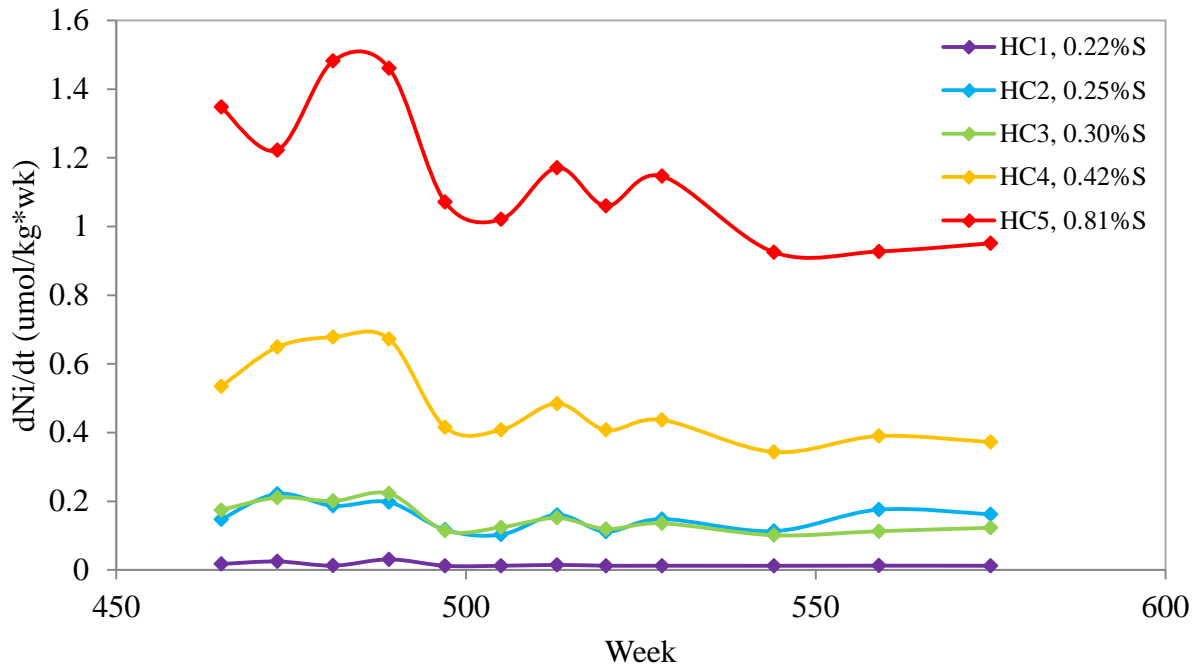


Figure 12. Zinc release vs time for DNR VF humidity cells. Weeks 0-5 excluded to improve resolution. Samples were analyzed for zinc from weeks 465-580.

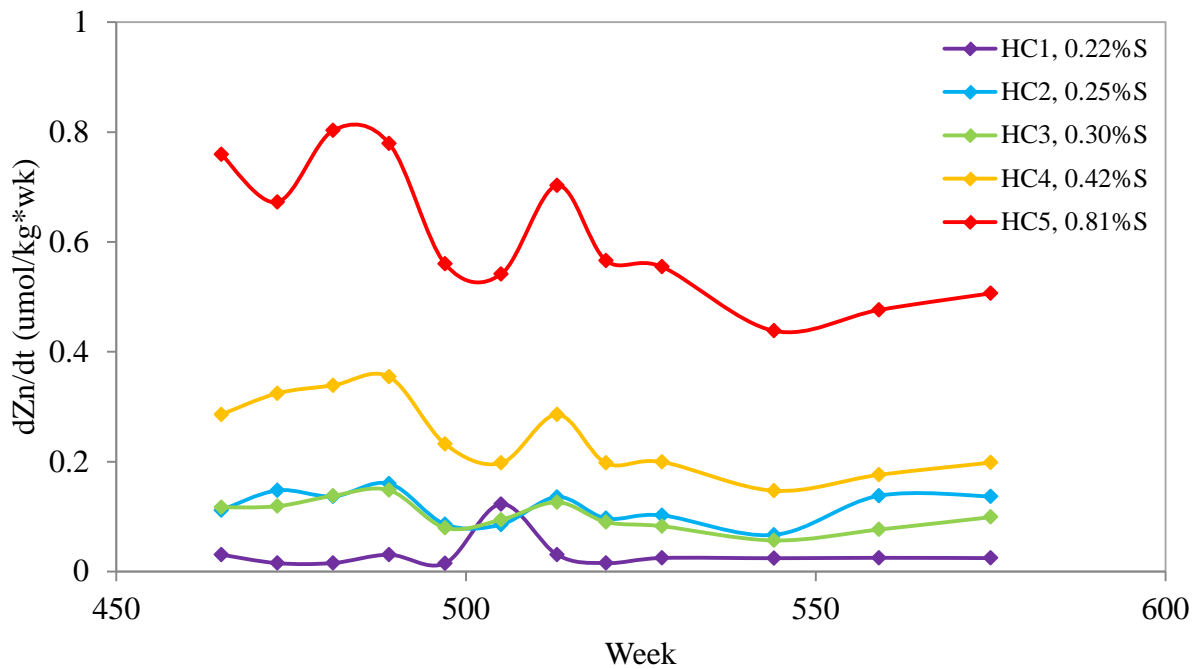


Figure 13. Arsenic release vs time for DNR VF humidity cells. Weeks 0-5 excluded to improve resolution. Values after 100 weeks were all below the detection limit of 0.002 mg/L.

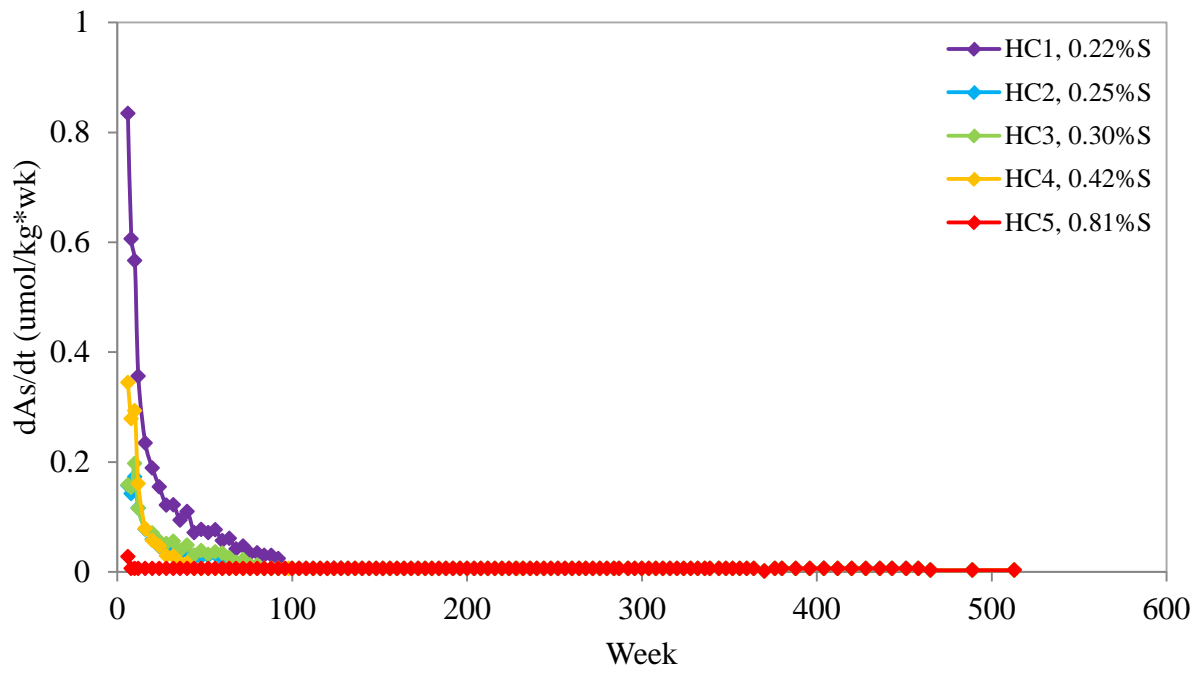




Figure 14. Minimum pH vs. % sulfur for DNR and NSM VF samples through 580 weeks.

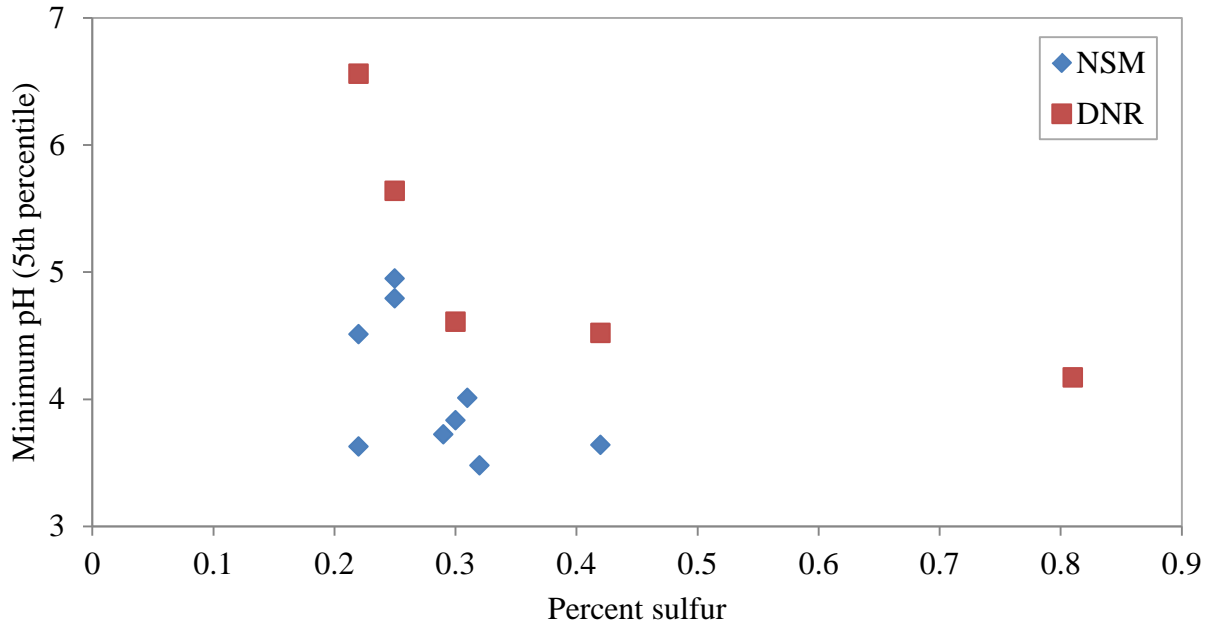


Figure 15. Average sulfate release vs. % sulfur for DNR and NSM VF samples through 580 weeks.

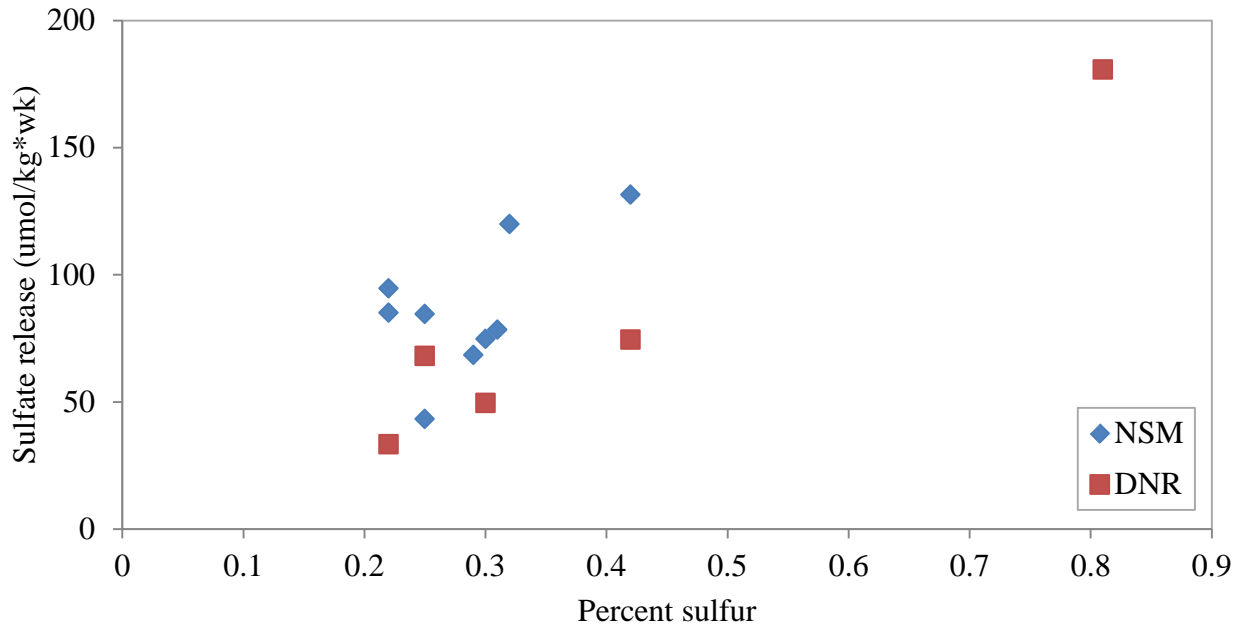


Figure 16. Sulfate release vs time for NSM VF samples from different rock types with ~0.3 %S. Weeks 0-5 excluded to improve resolution.

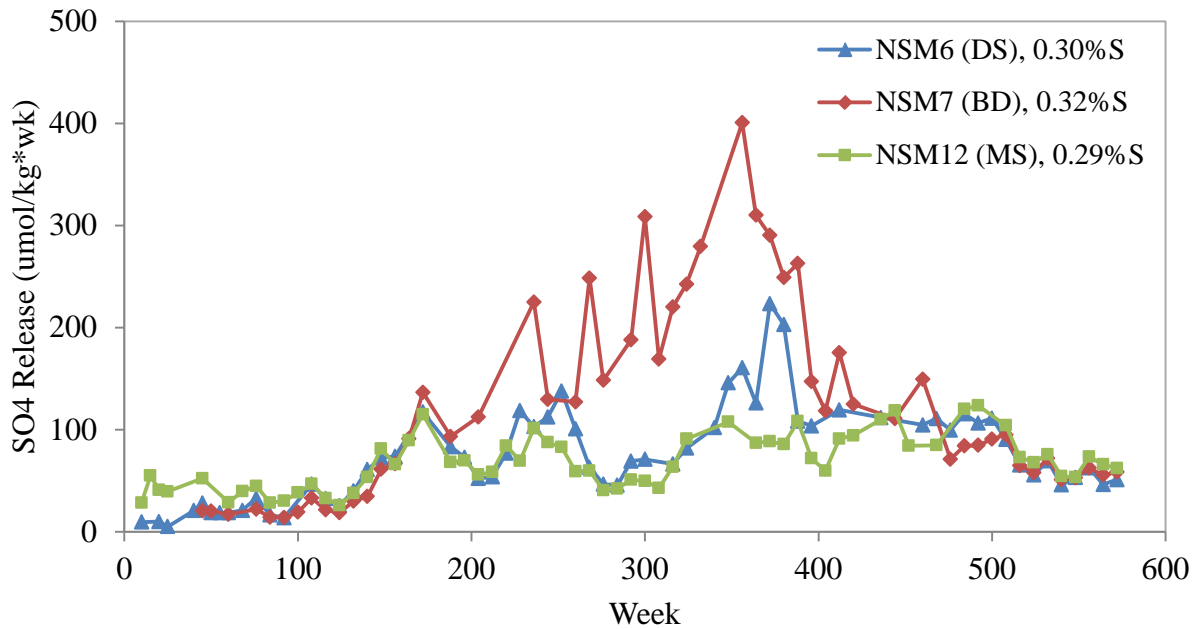


Figure 17. Drainage pH vs time for NSM VF samples from different rock types with ~0.3 %S. Weeks 0-5 excluded to improve resolution.

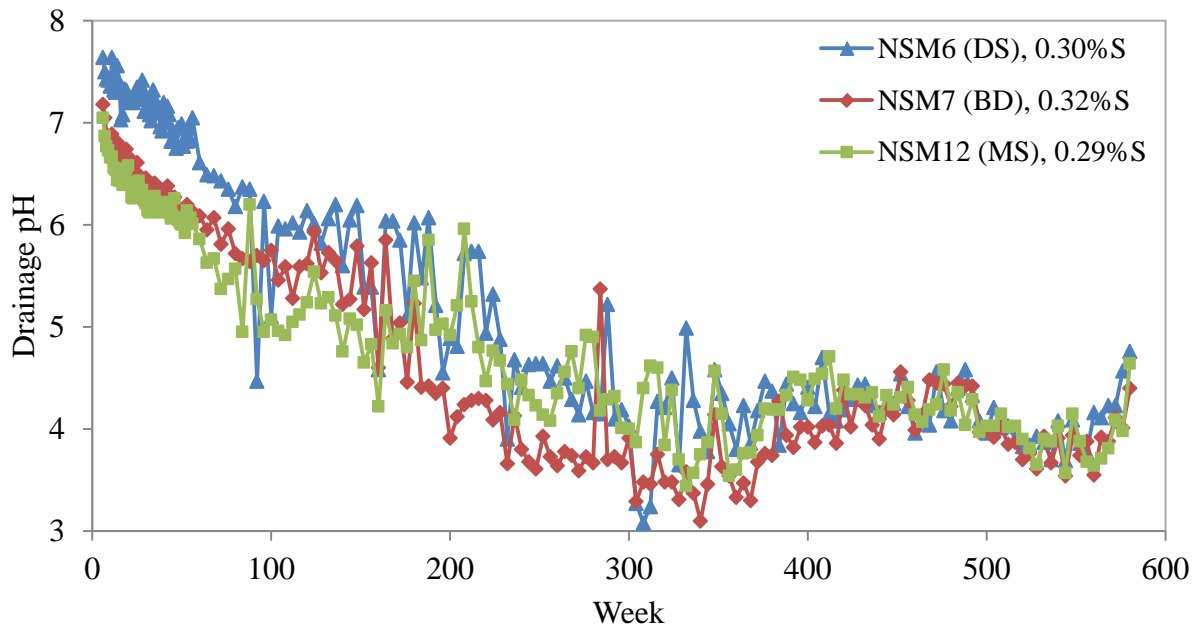


Figure 18. Drainage pH vs time for DNR and NSM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

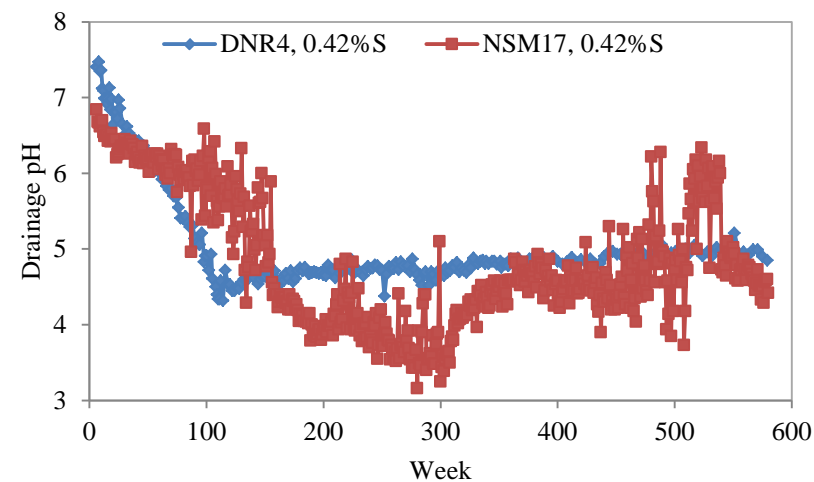
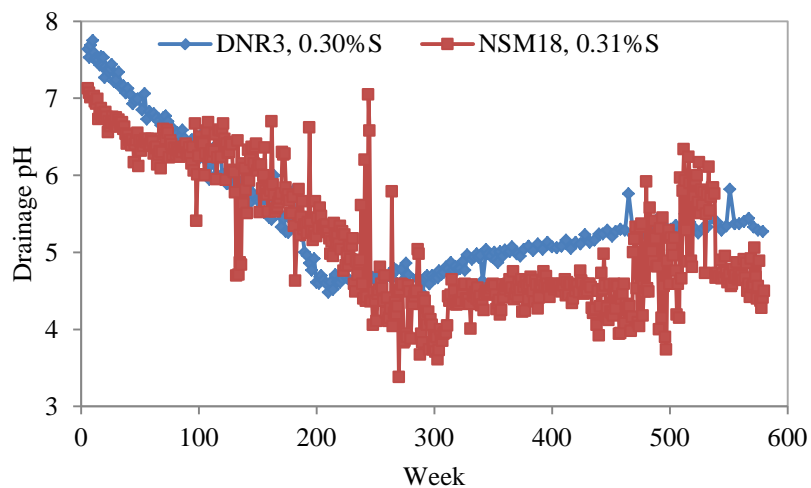
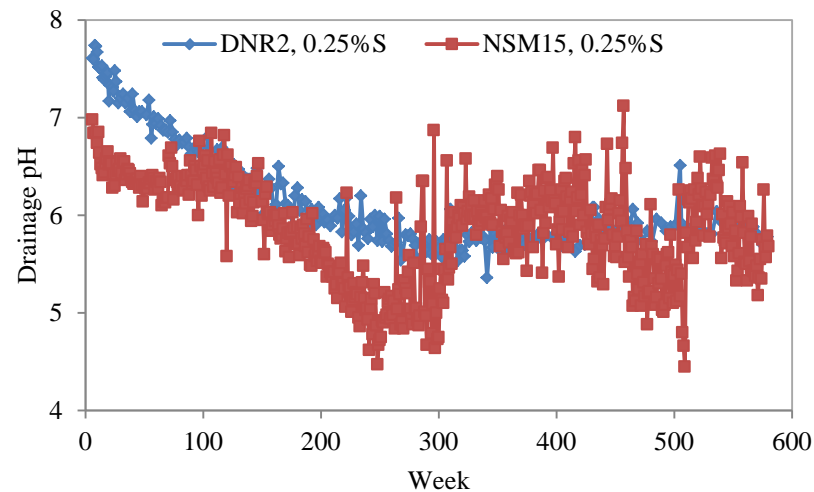
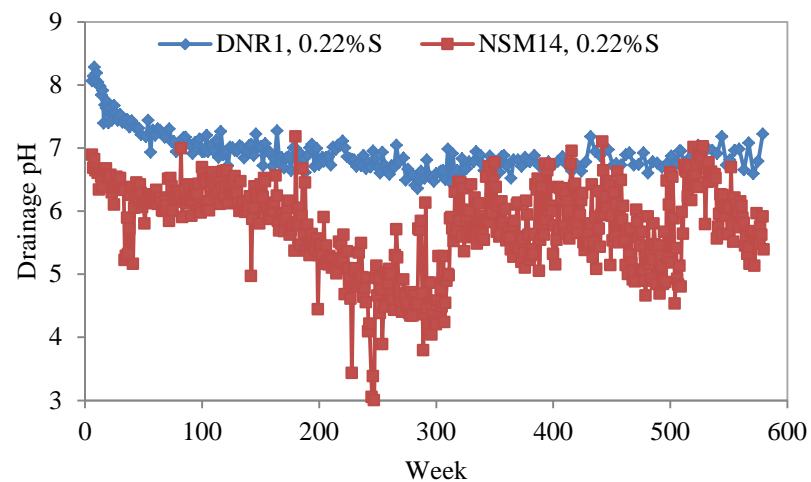


Figure 19. Sulfate release vs time for DNR and NSM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

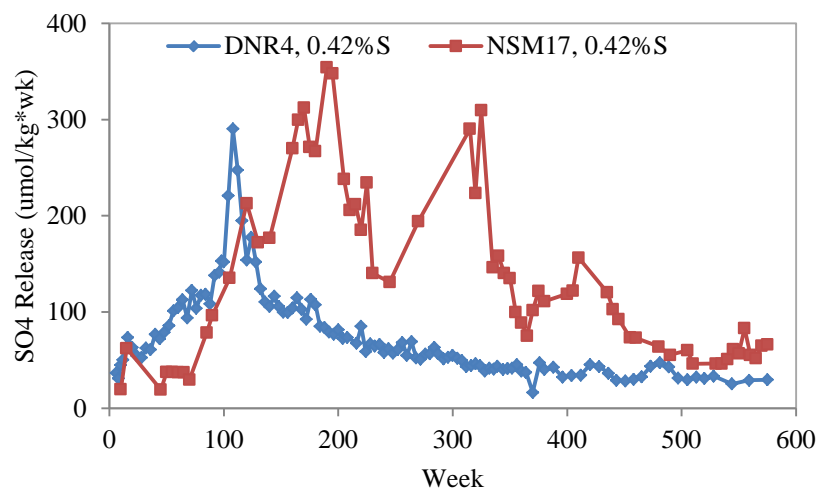
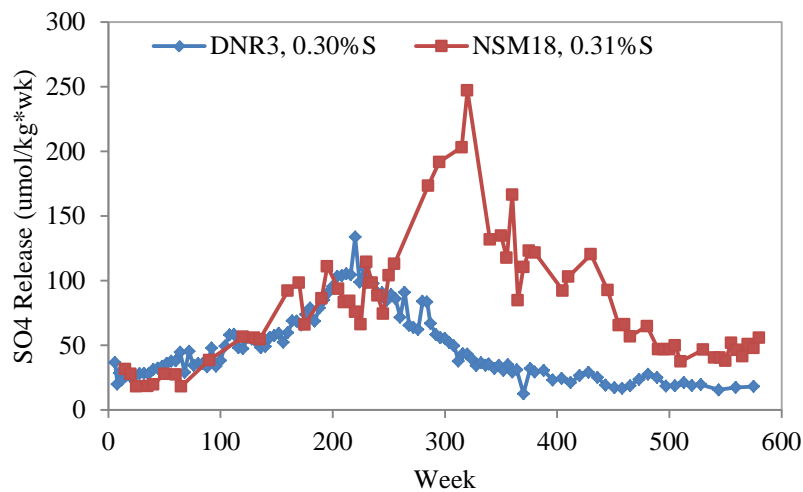
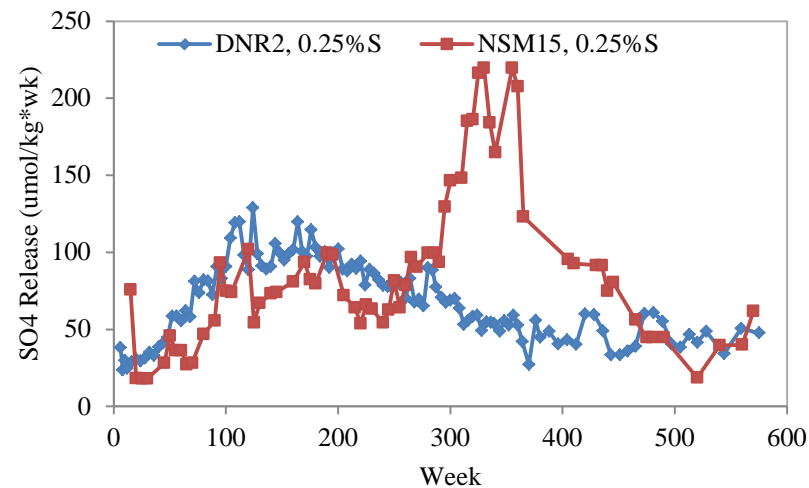
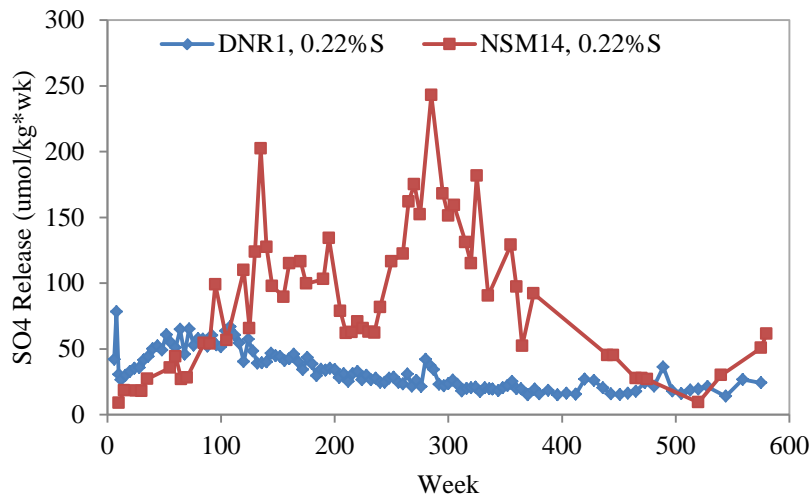


Figure 20. Calcium release vs time for DNR and NSM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

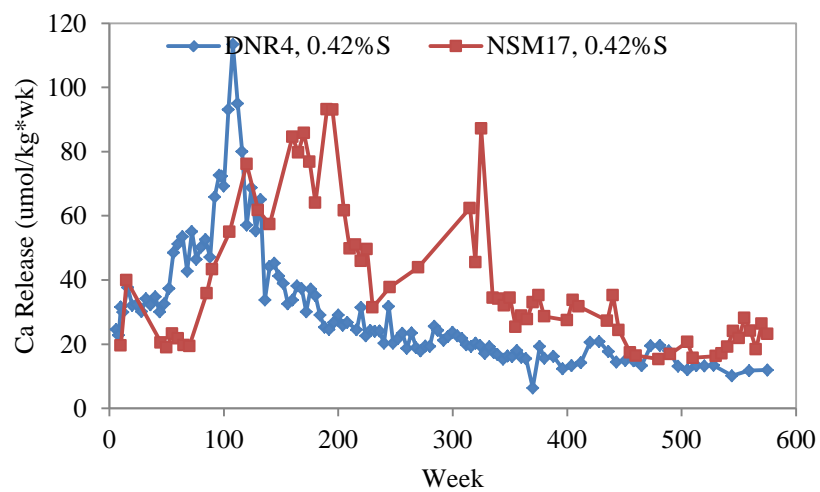
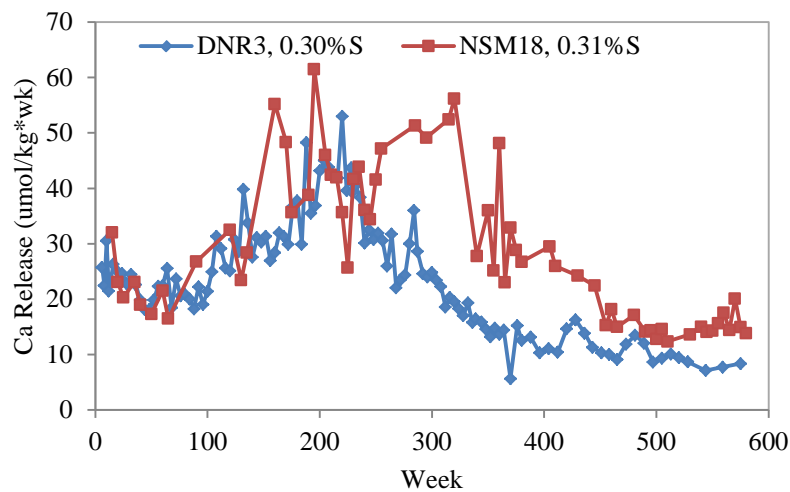
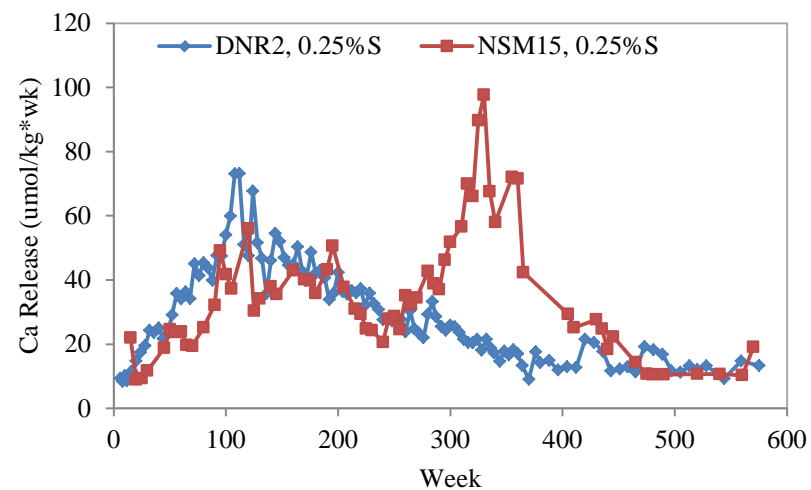
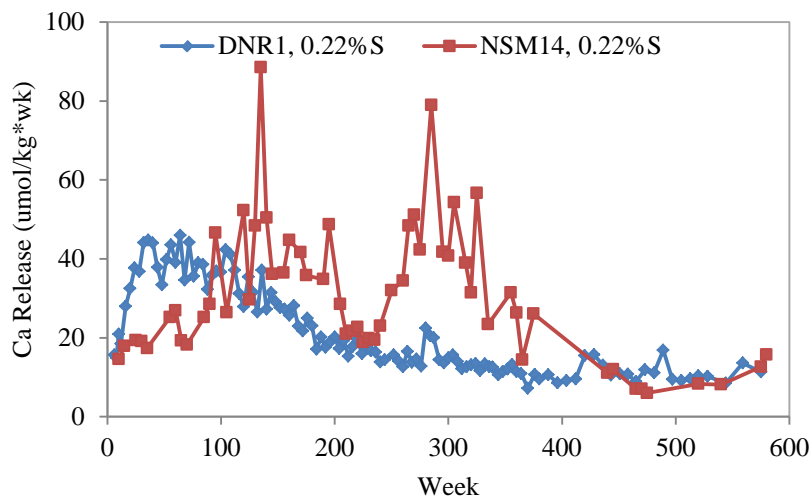


Figure 21. Magnesium release vs time for DNR and NSM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

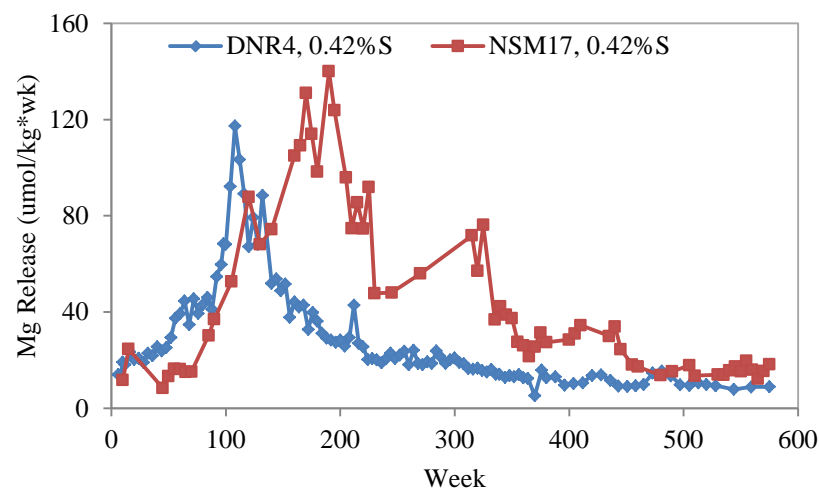
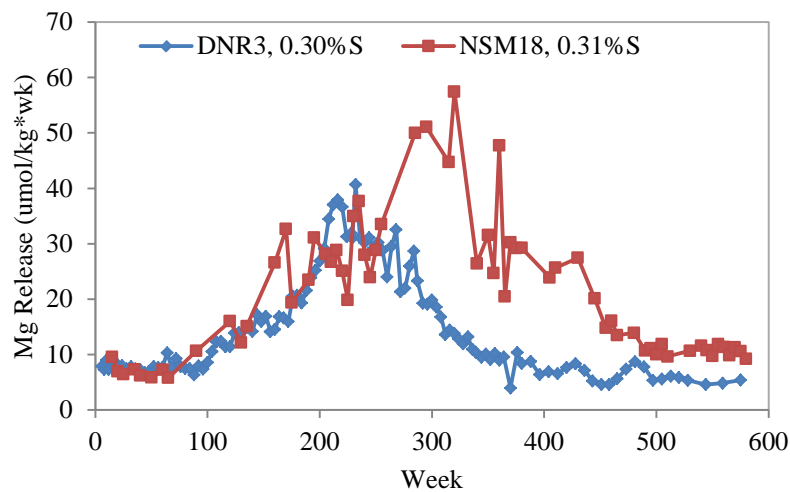
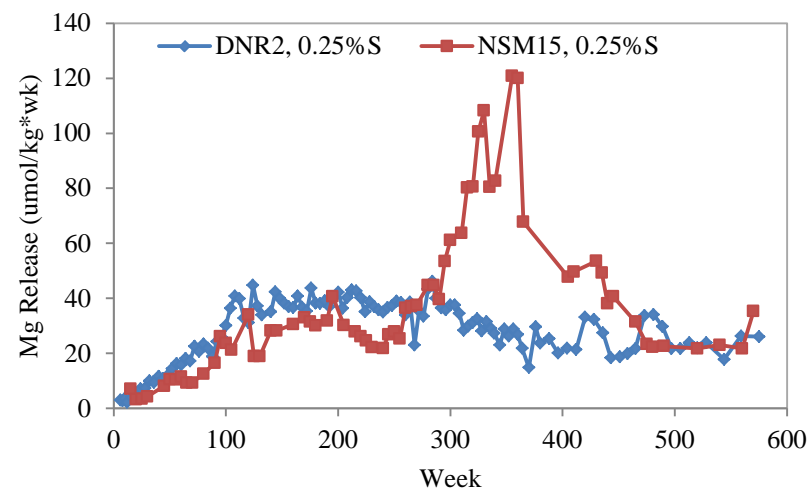
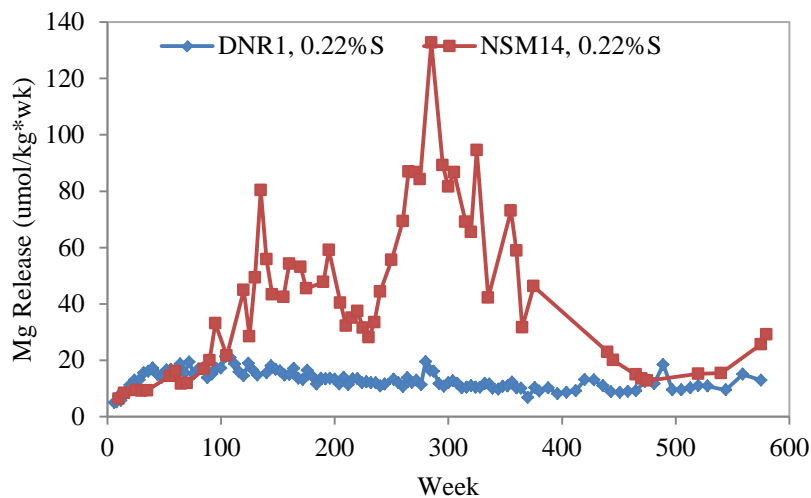


Figure 22. Sodium release vs time for DNR and NSM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

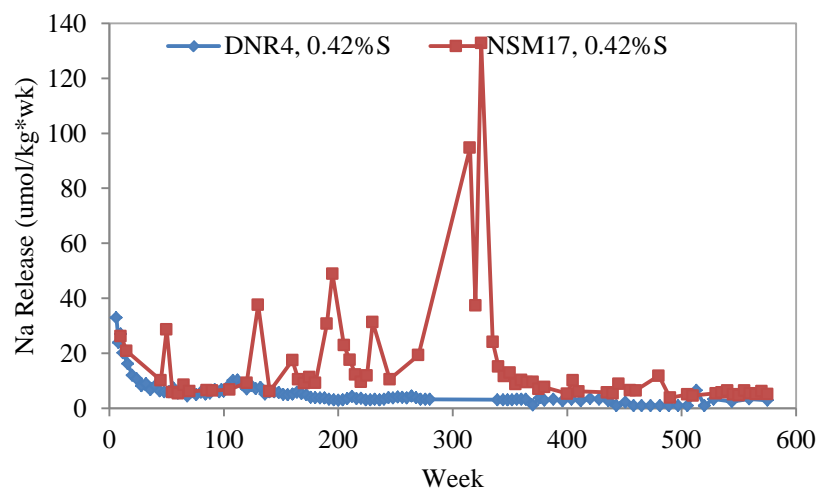
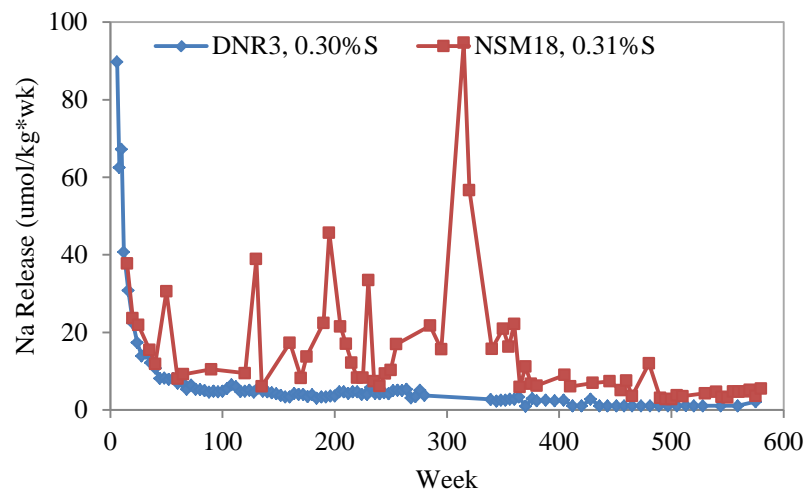
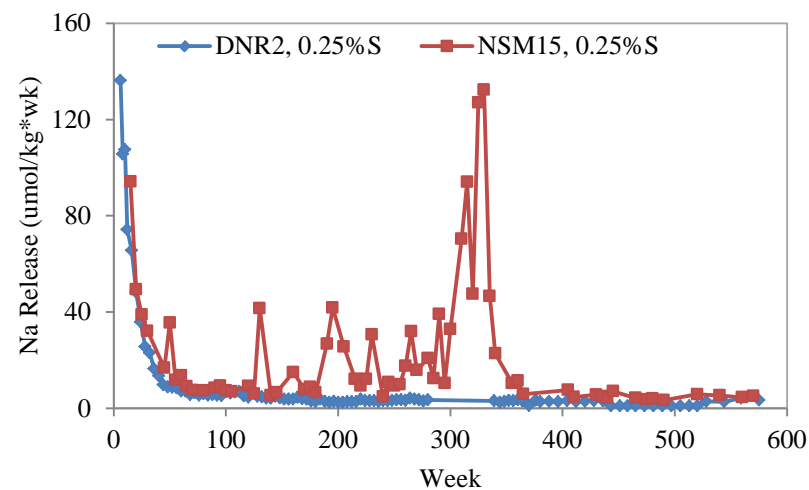
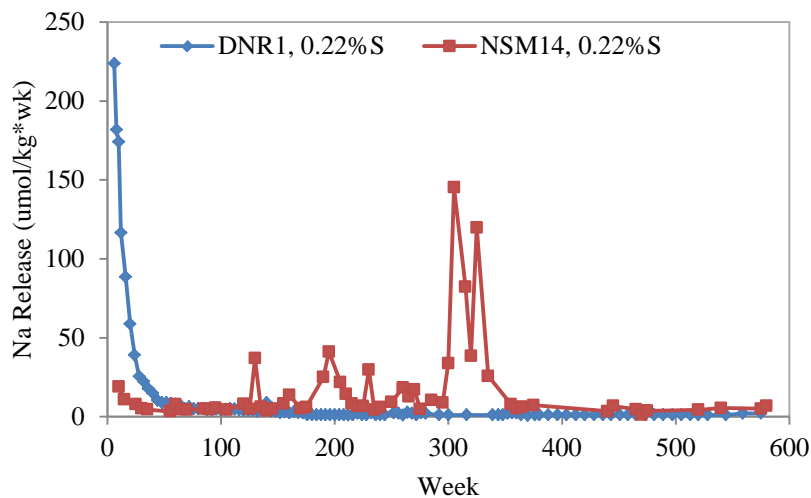


Figure 23. Potassium release vs time for DNR and NSM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

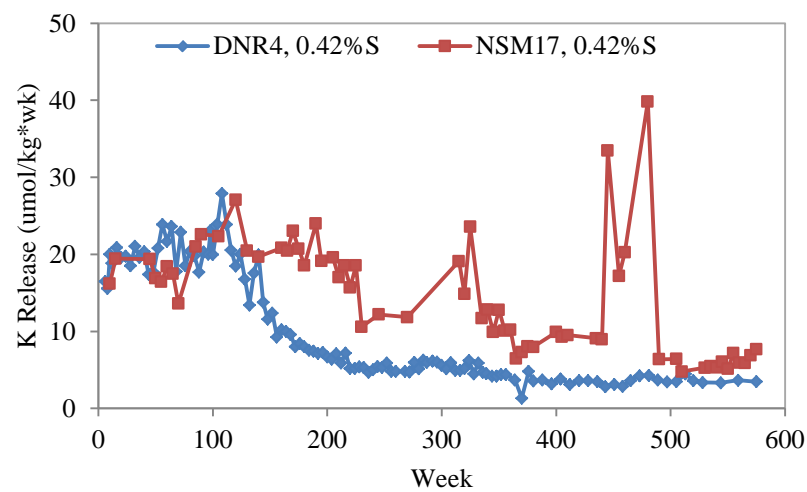
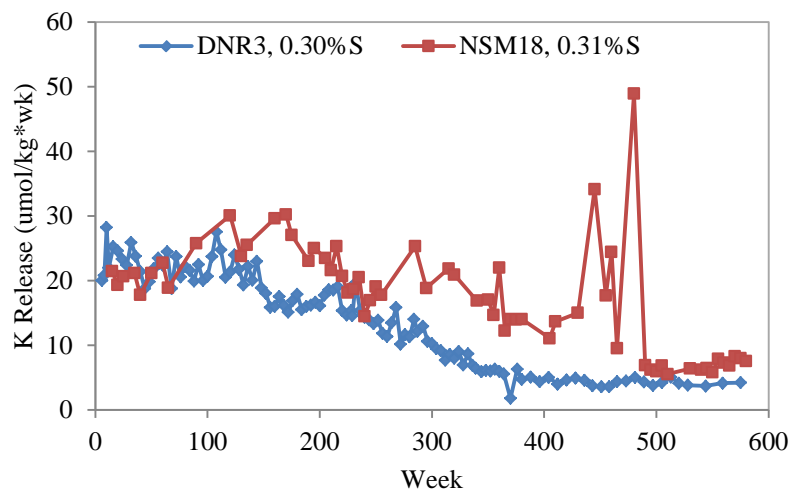
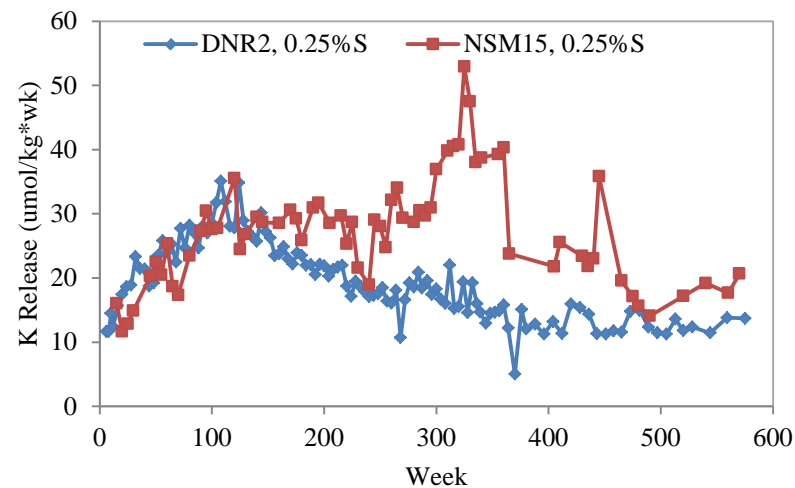
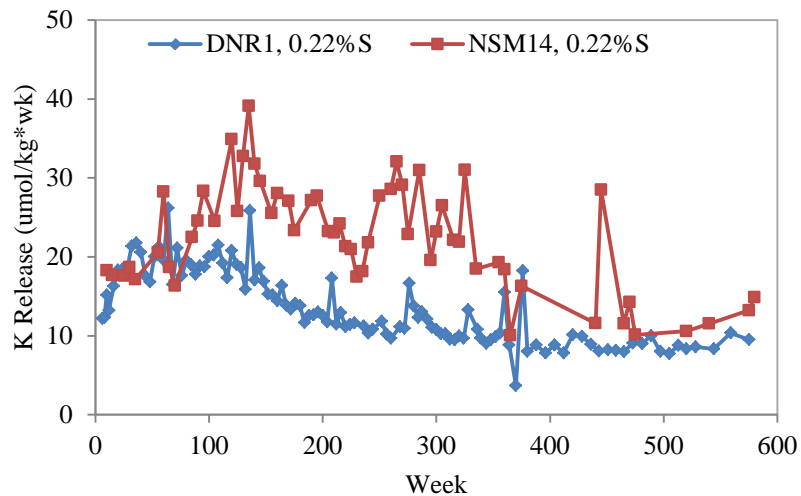




Figure 24. Copper release vs time for DNR and NSM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

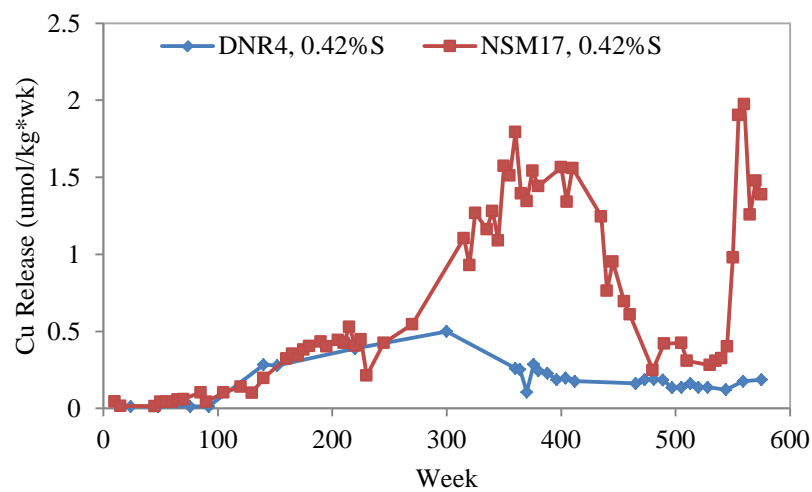
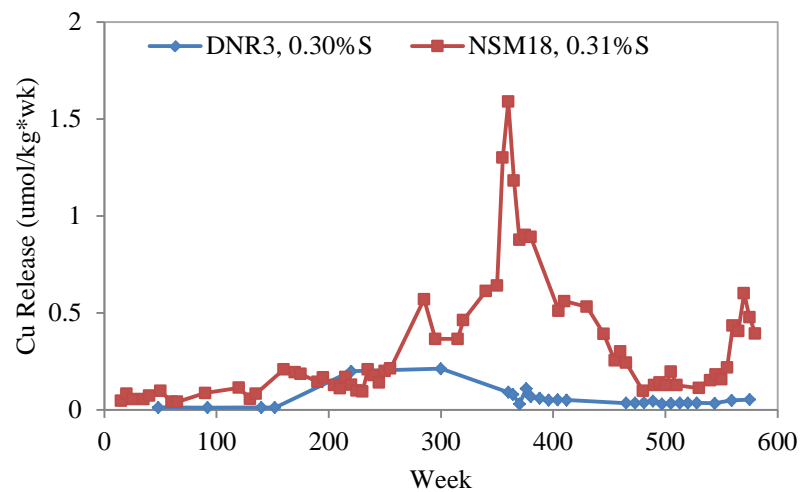
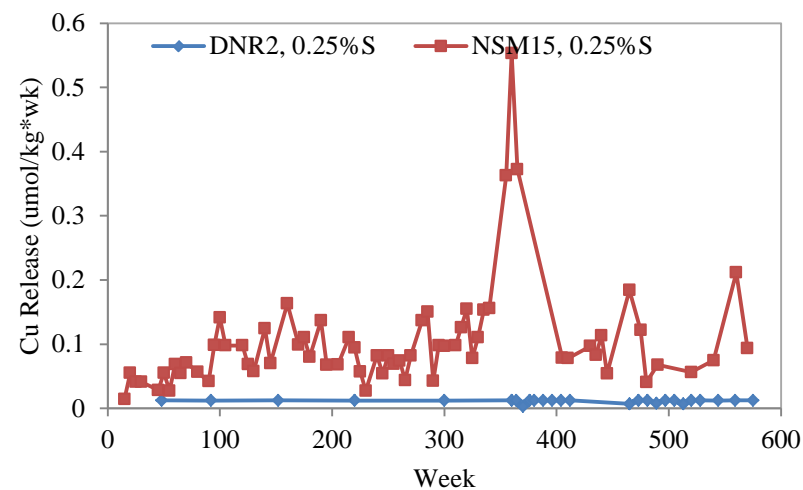
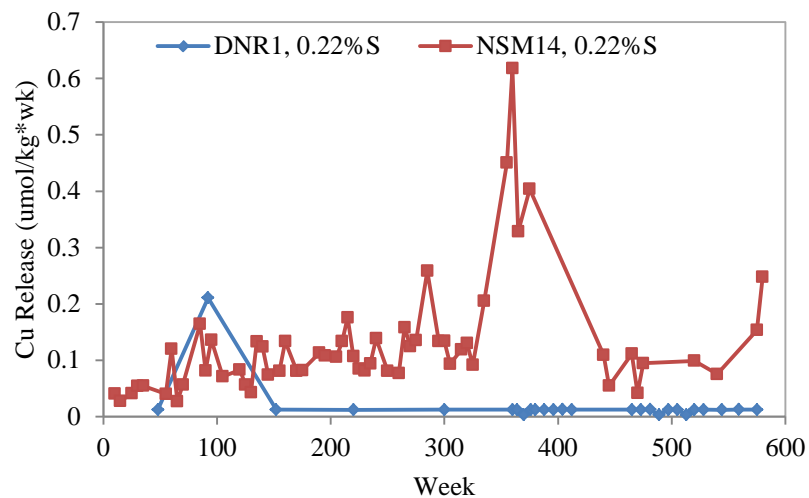


Figure 25. Cobalt release vs time for DNR and NSM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

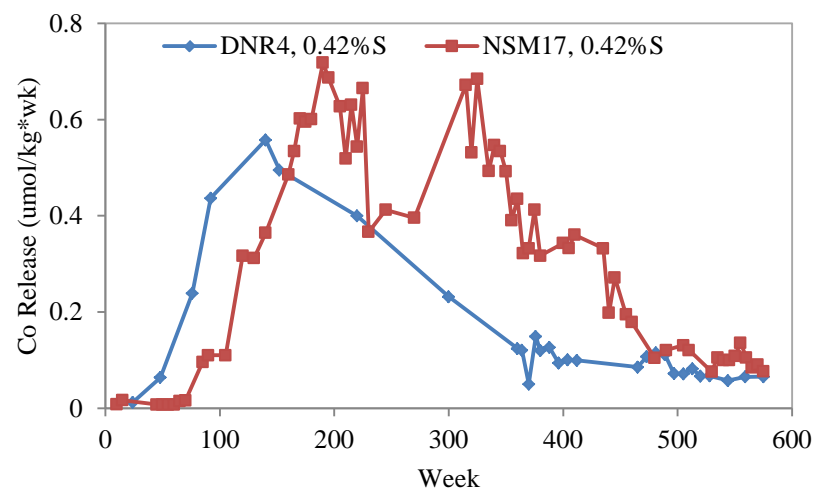
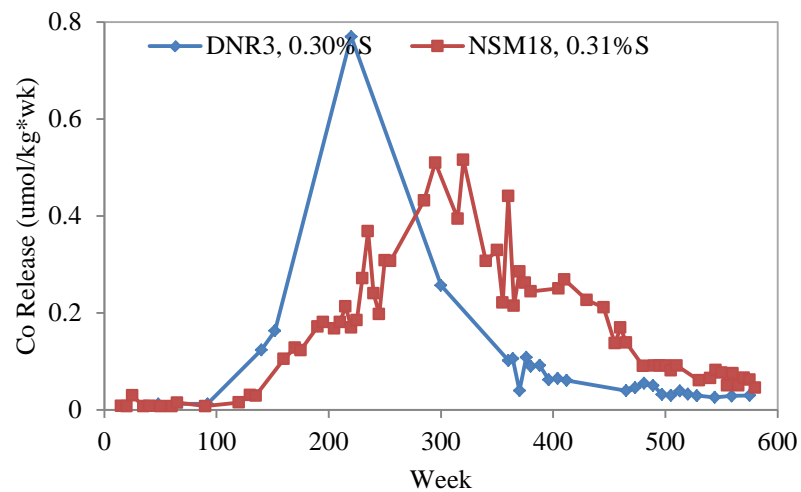
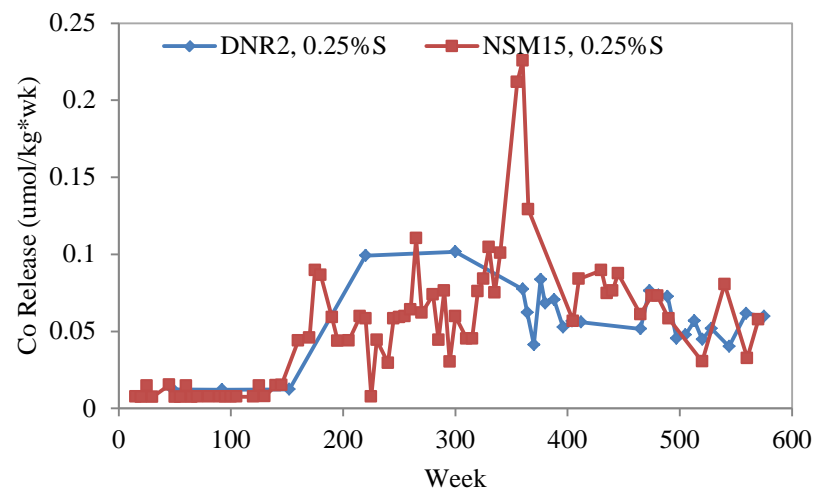
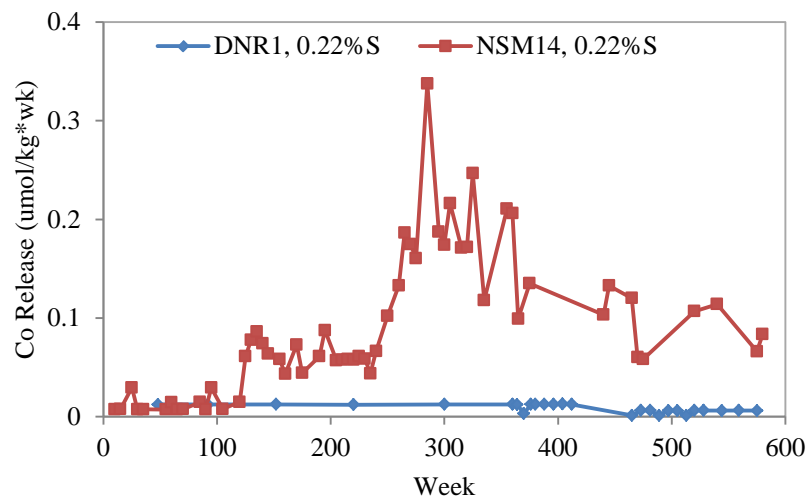


Figure 26. Arsenic release vs time for DNR and NSM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

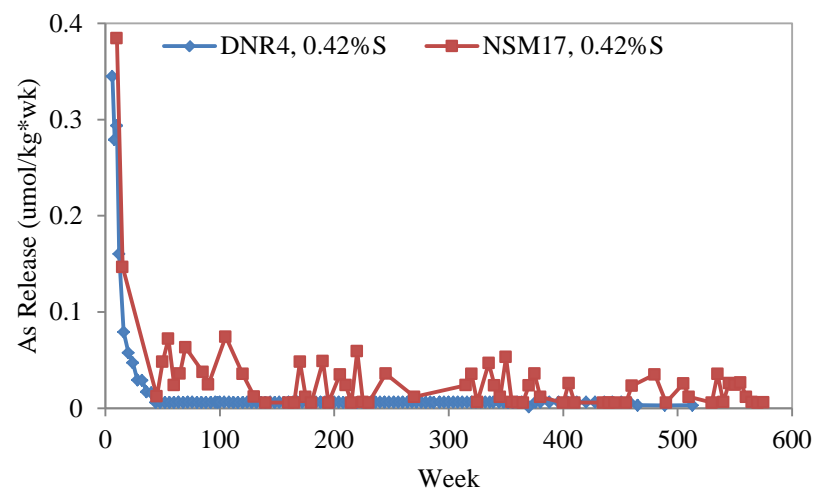
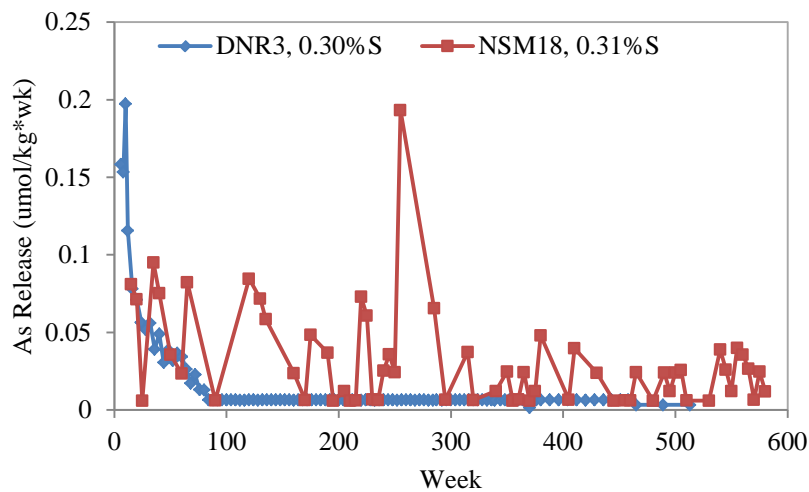
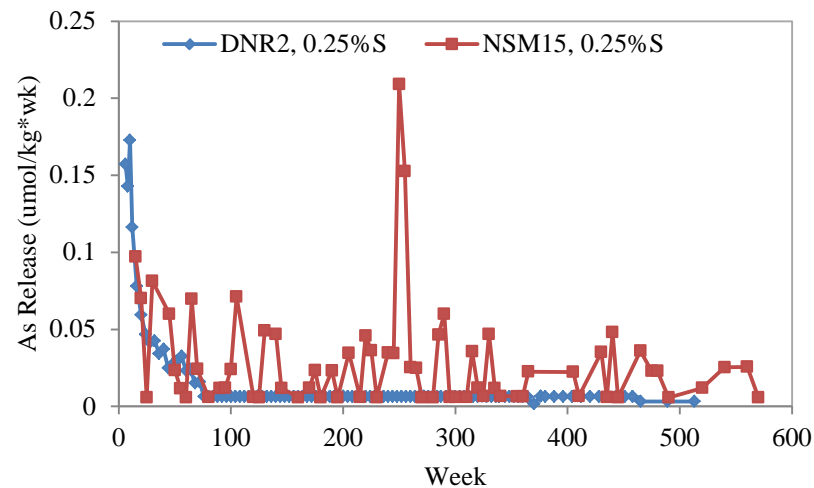
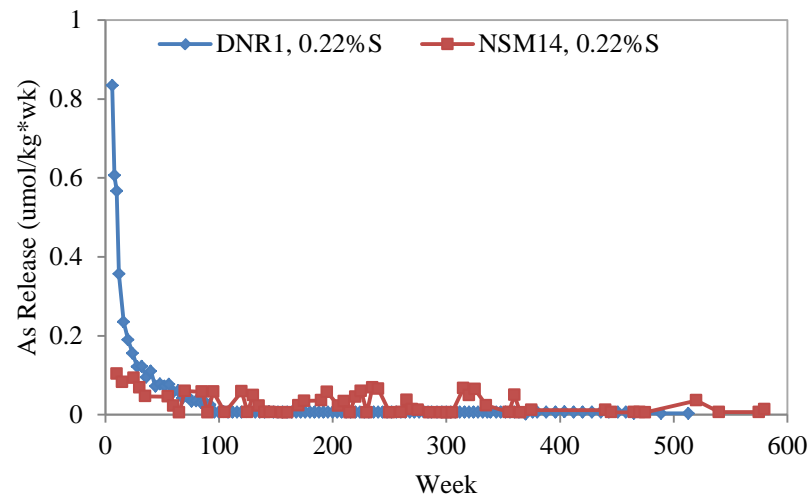


Figure 27. Drainage pH vs time for DNR and PM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

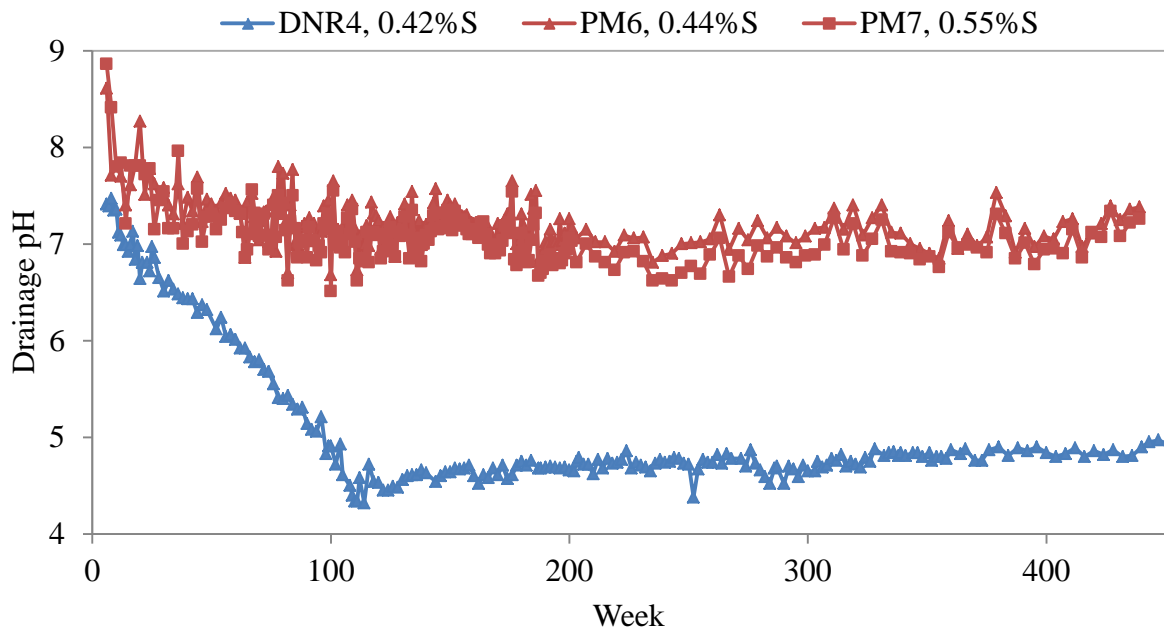
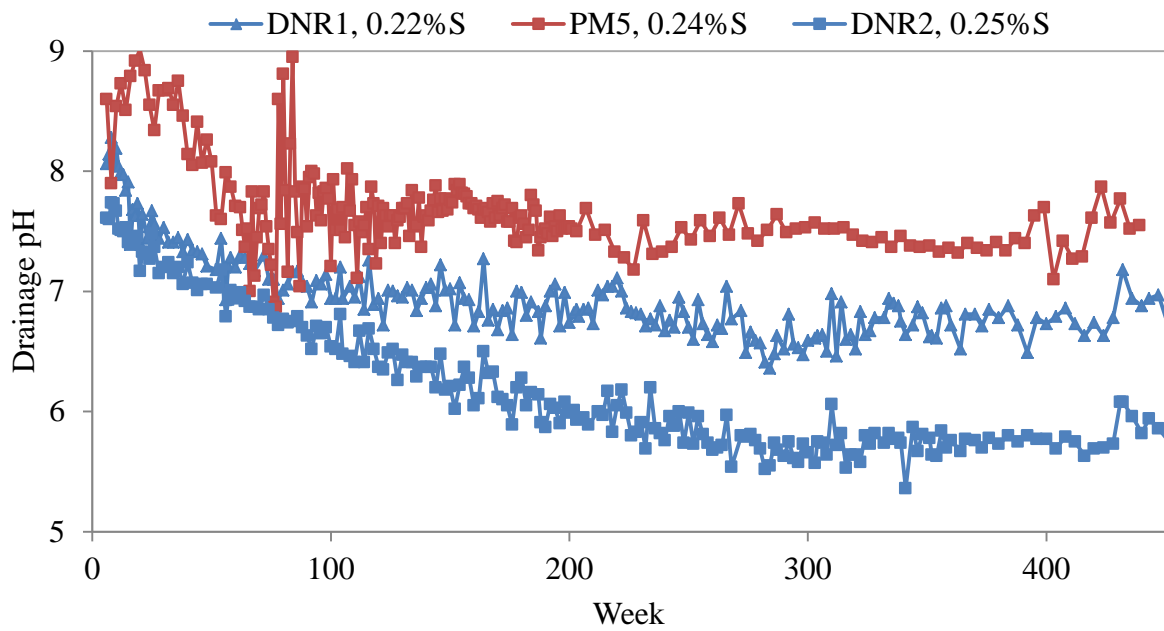


Figure 28. Sulfate release vs time for DNR and PM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

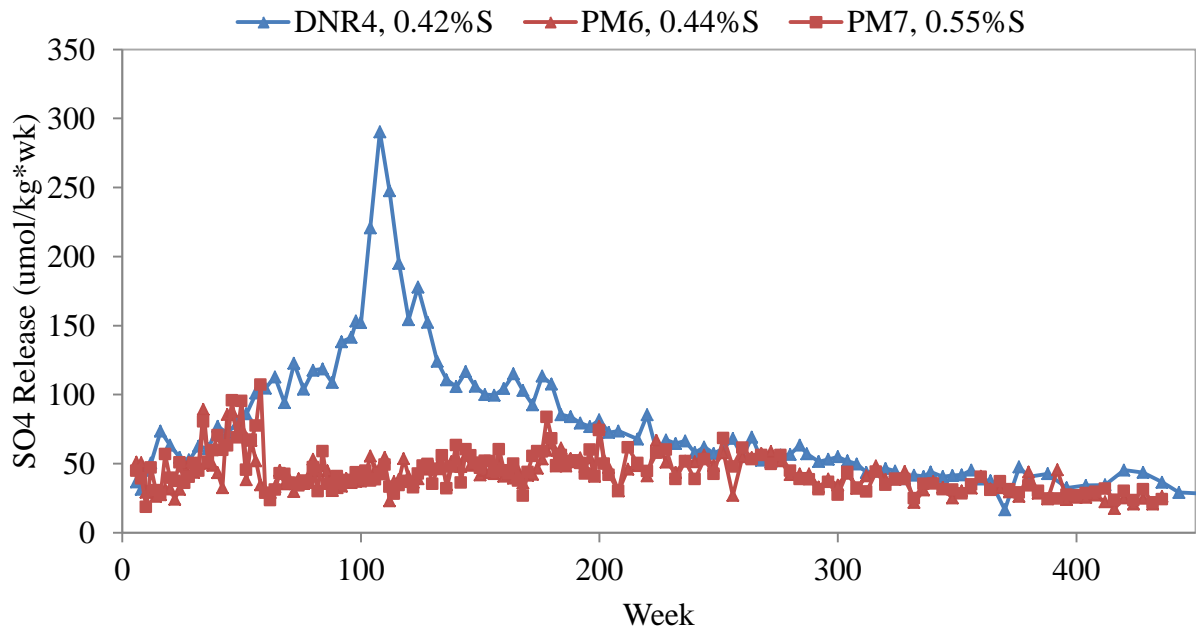
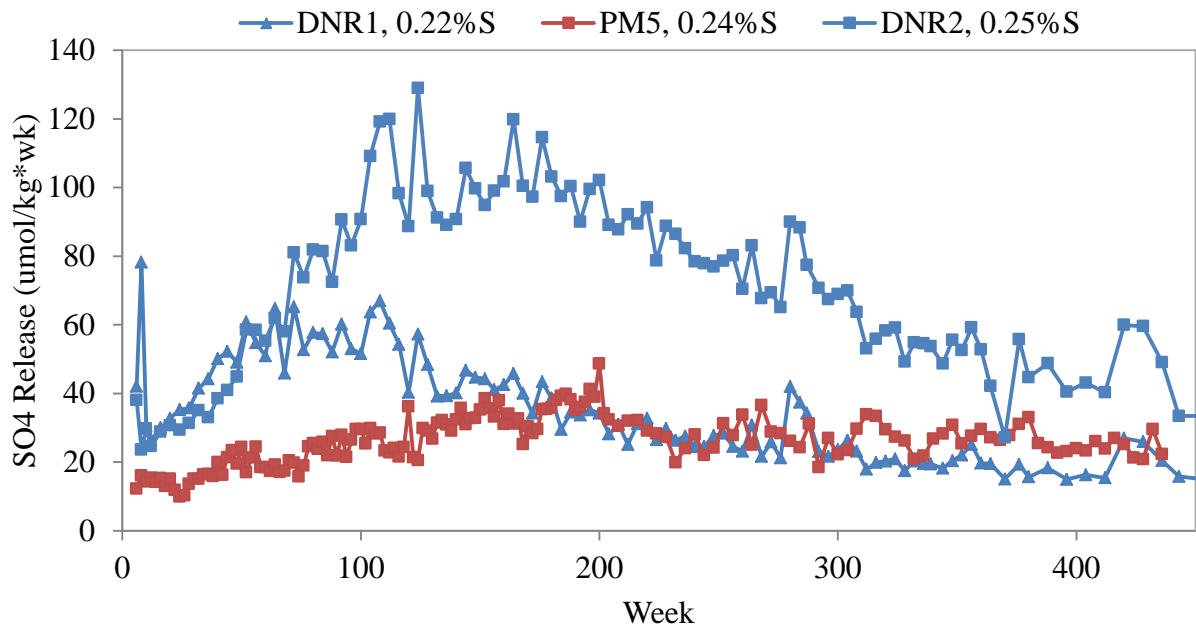


Figure 29. Calcium release vs time for DNR and PM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

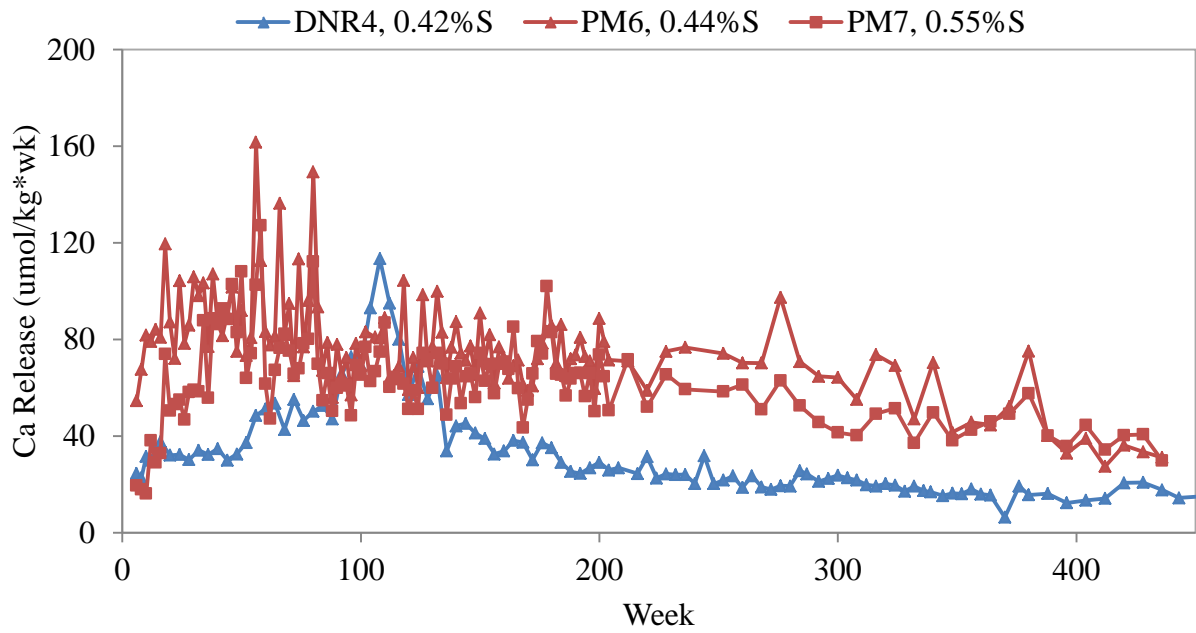
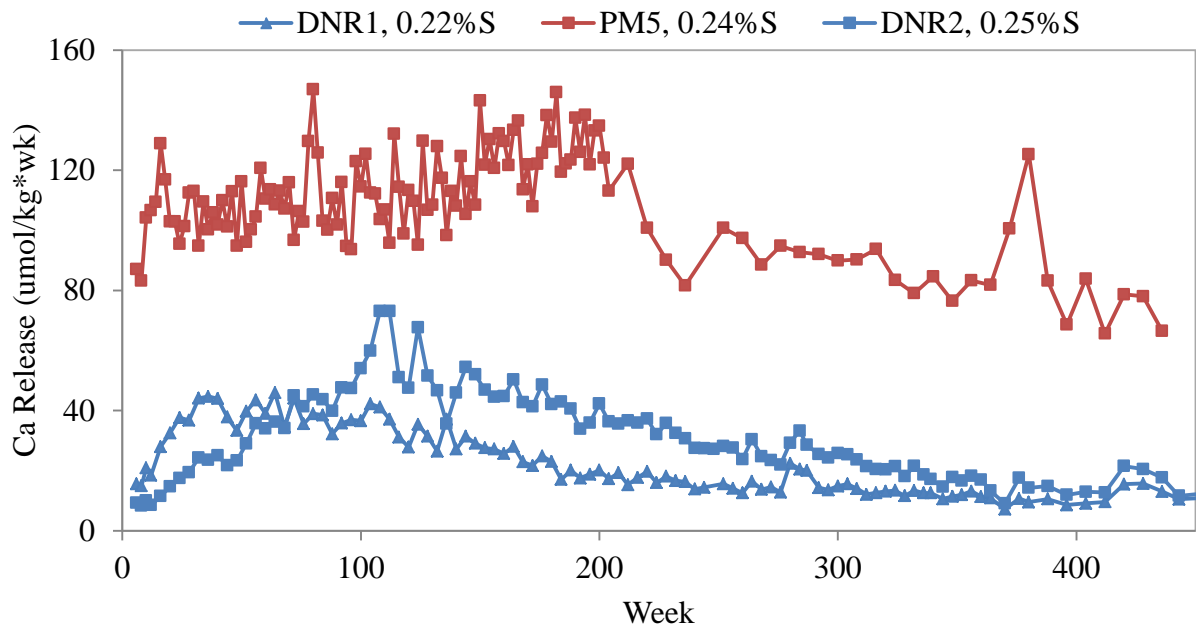


Figure 30. Magnesium release vs time for DNR and PM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

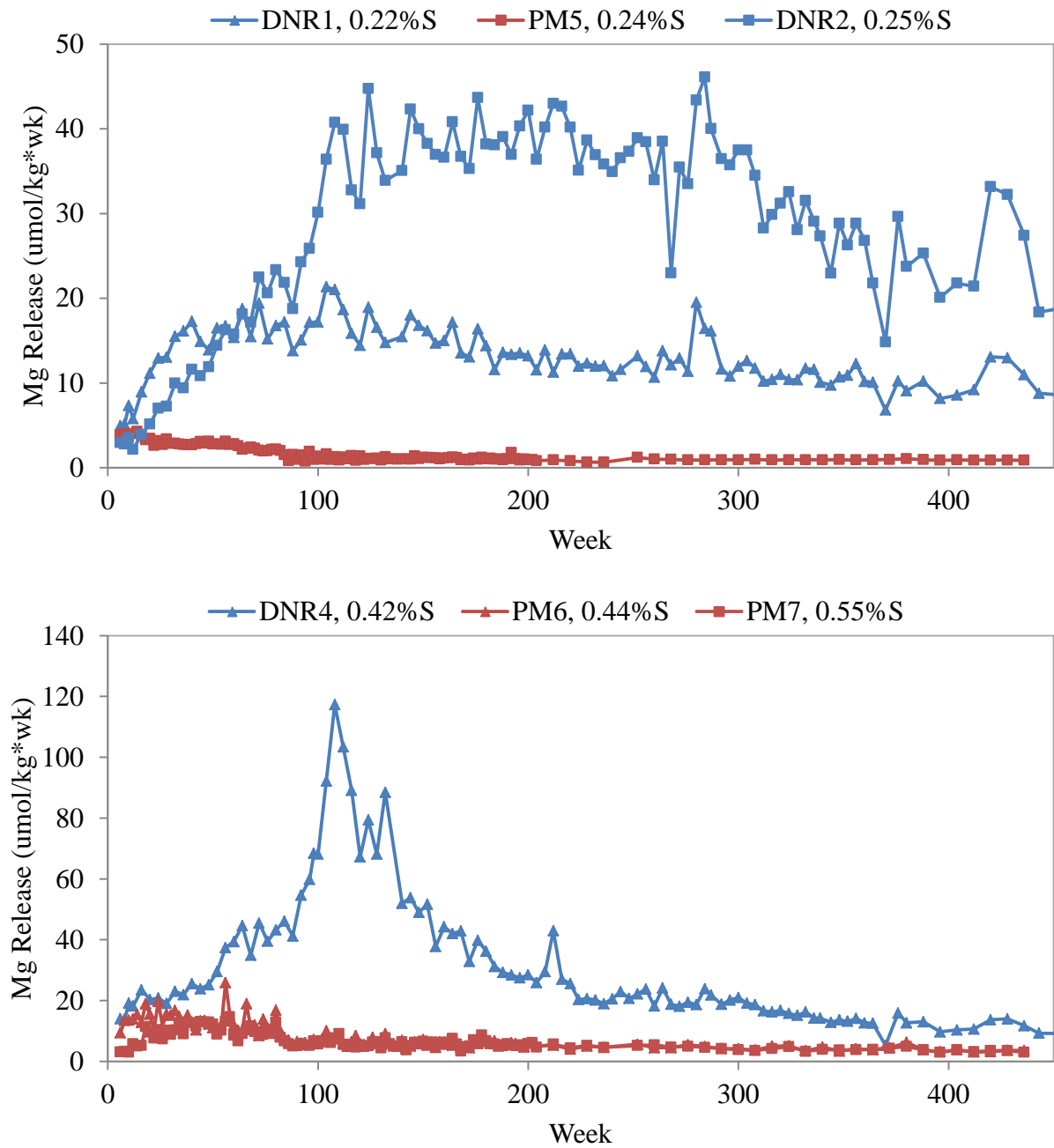


Figure 31. Sodium release vs time for DNR and PM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

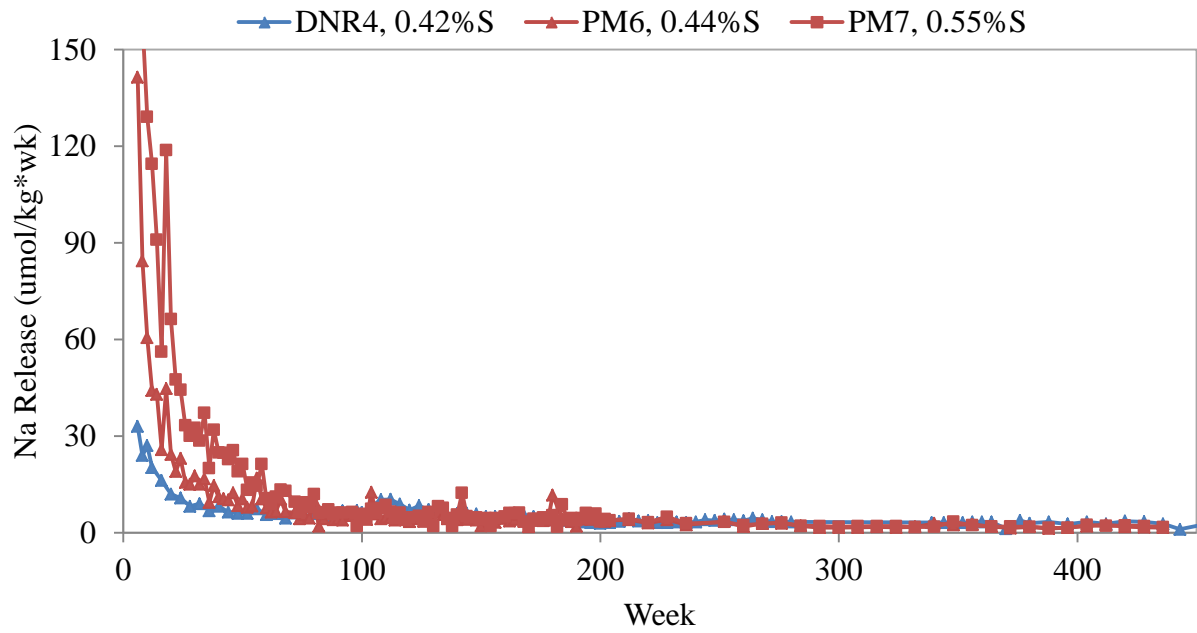
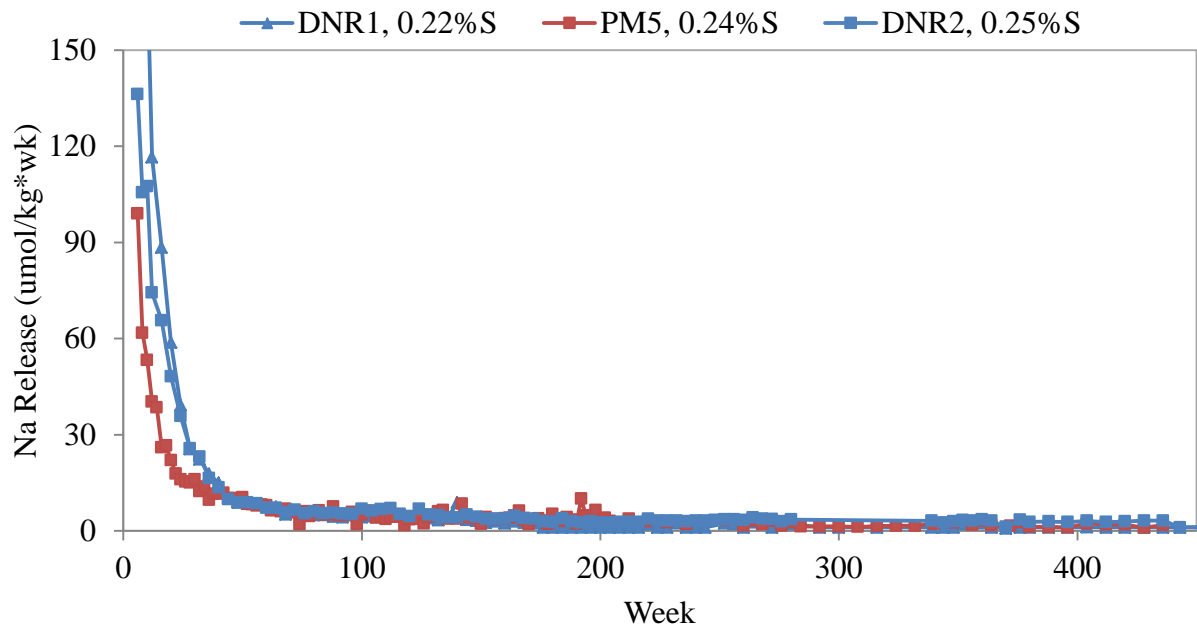




Figure 32. Potassium release vs time for DNR and PM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

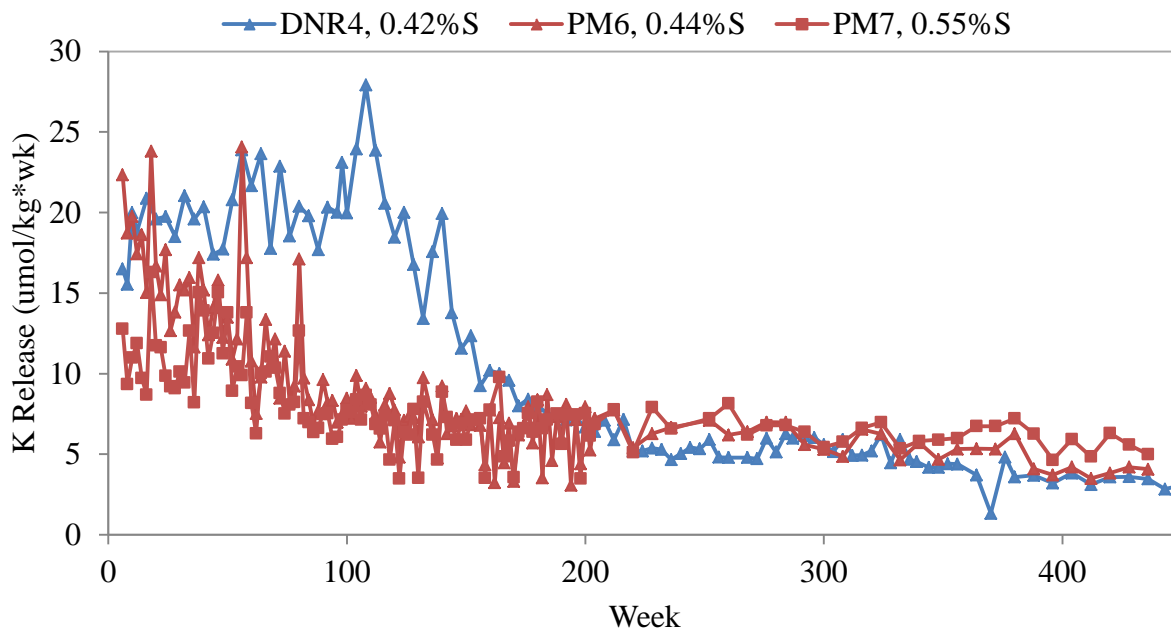
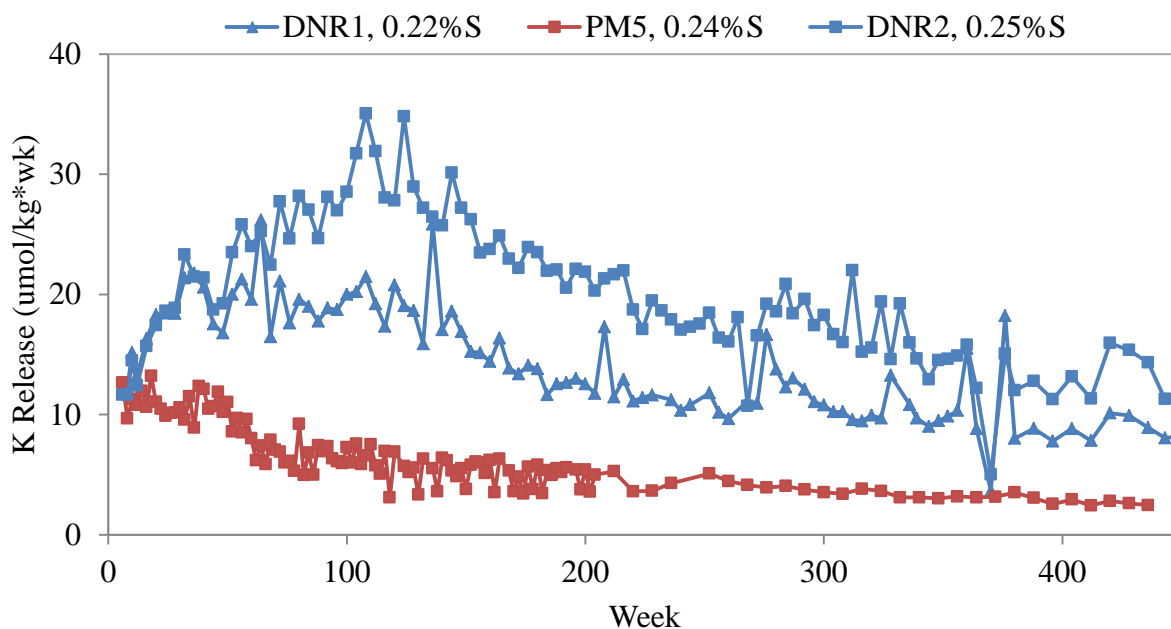


Figure 33. Copper release vs time for DNR and PM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

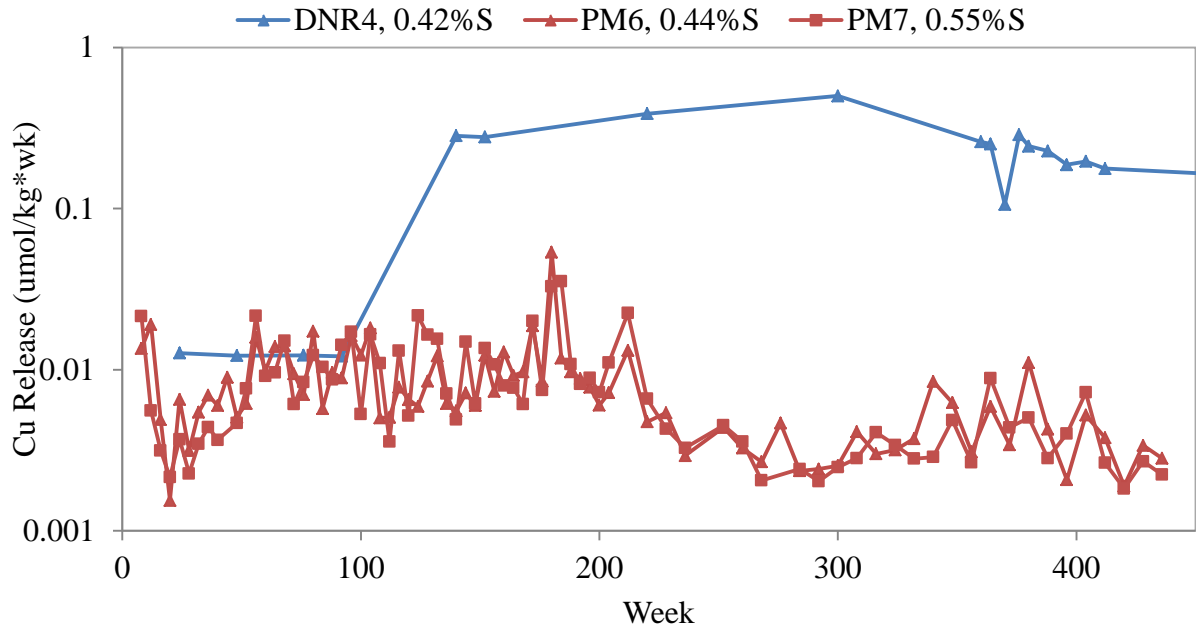
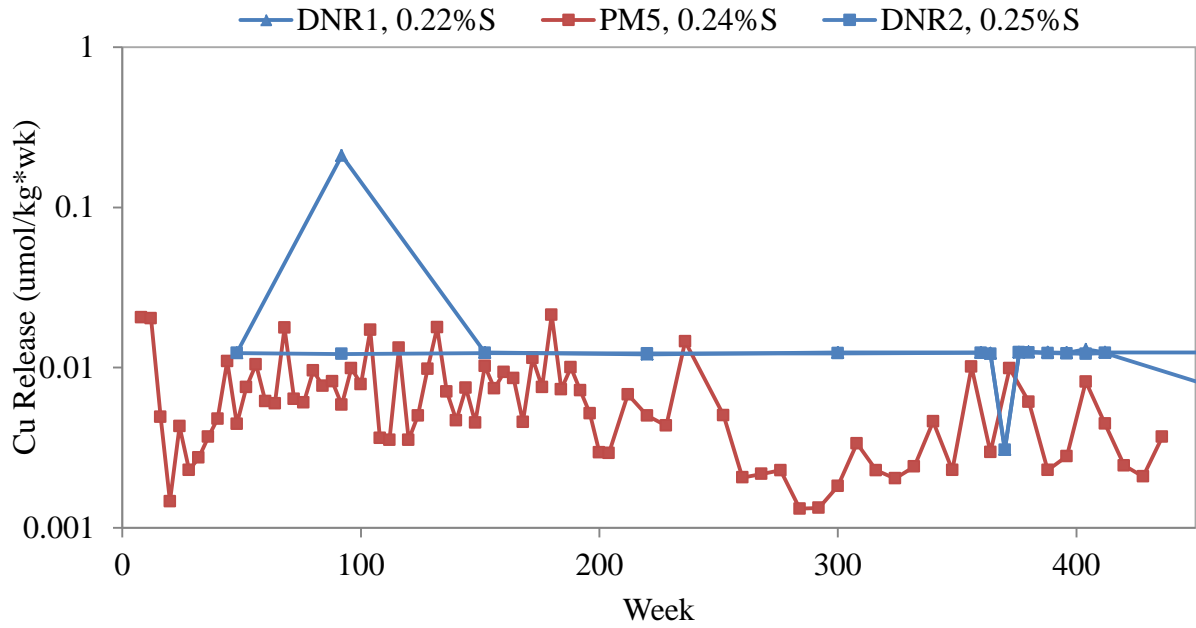


Figure 34. Cobalt release vs time for DNR and PM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

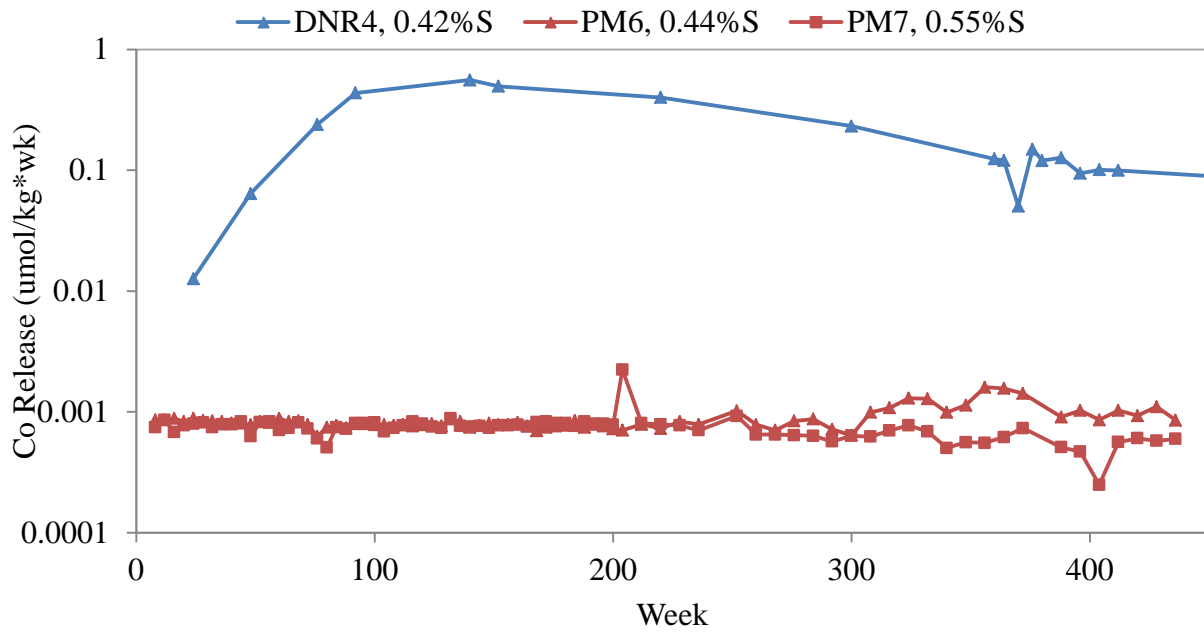
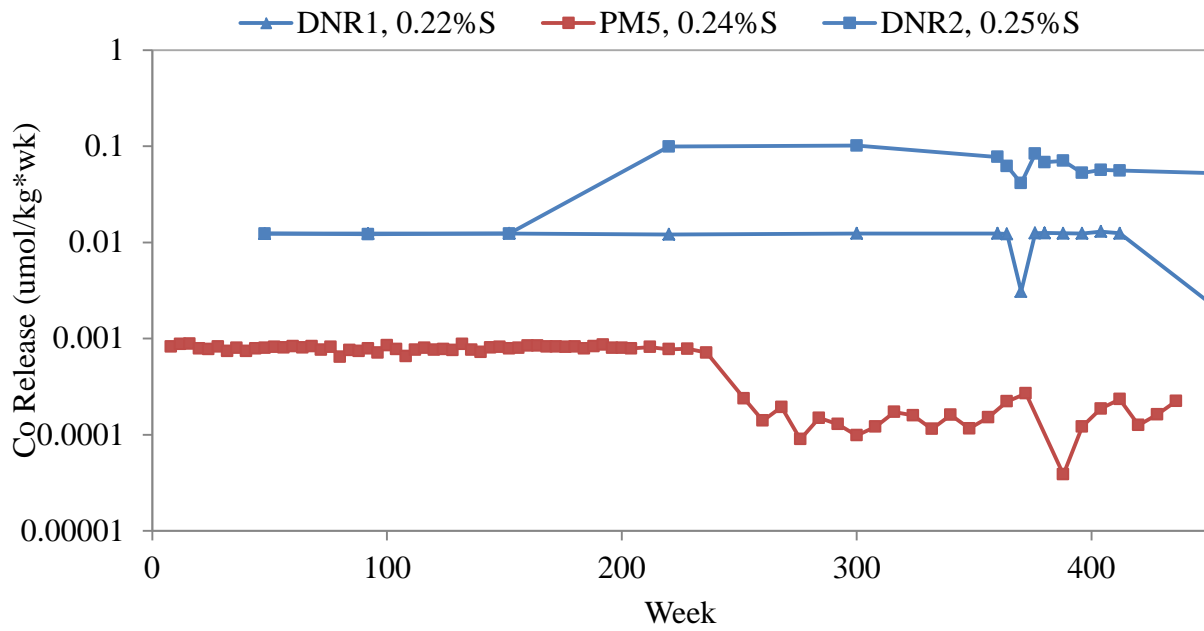


Figure 35. Arsenic release vs time for DNR and PM VF humidity cells, comparing samples with similar sulfur content. Weeks 0-5 excluded to improve resolution.

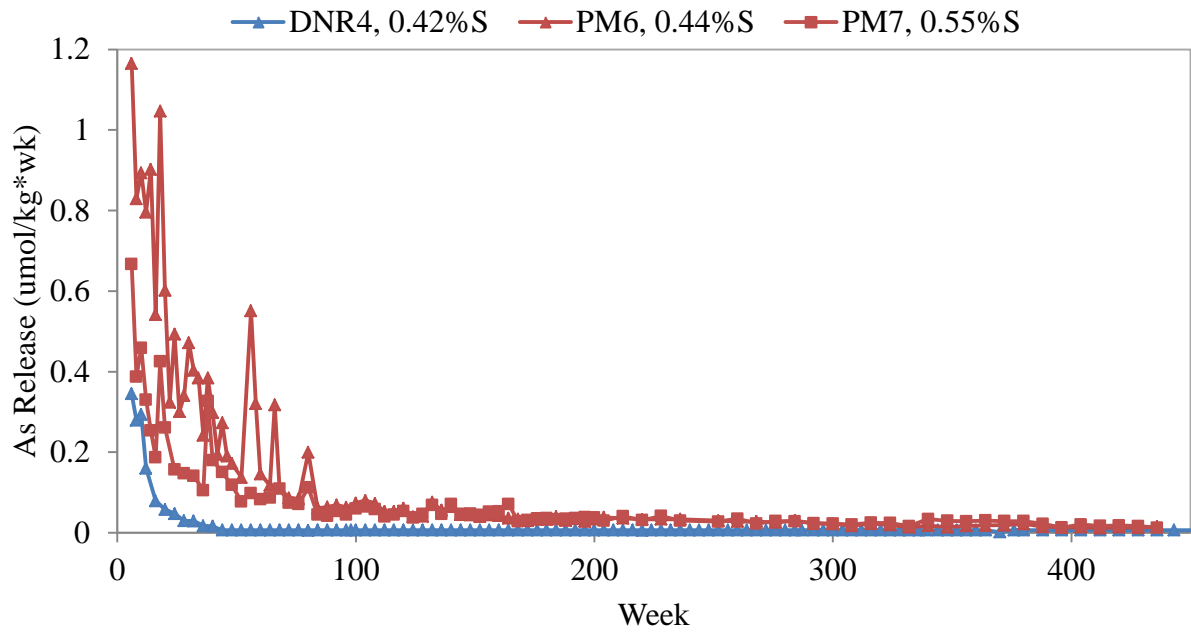
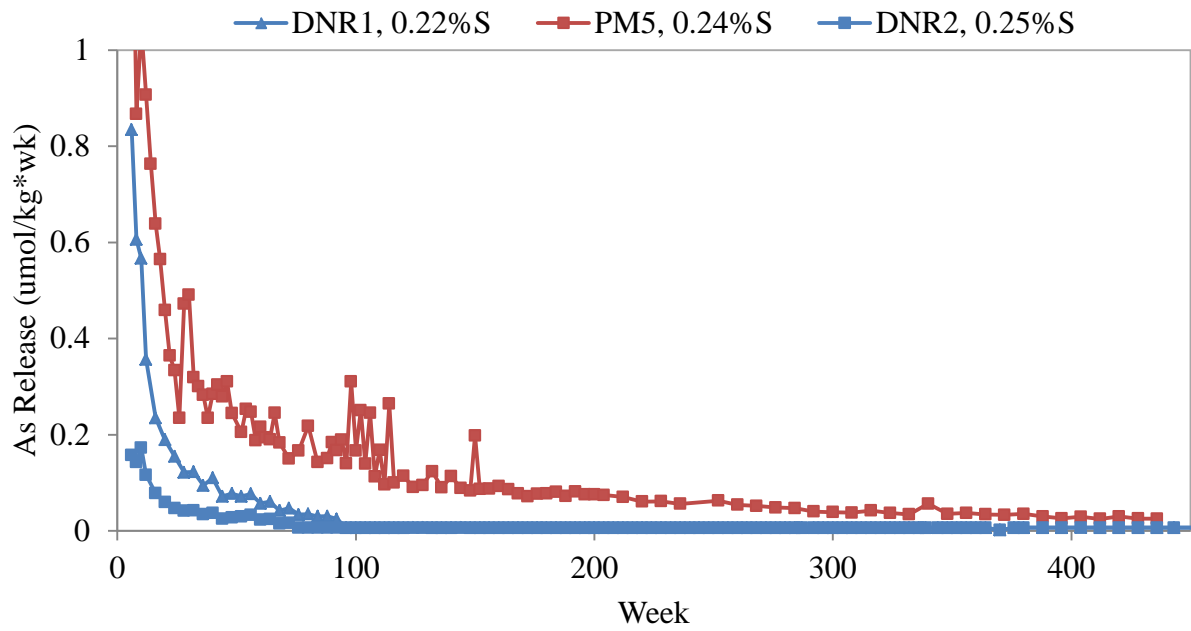


Figure 36. Minimum pH vs. % sulfur for DNR VF and DCWR samples through 400 weeks. Blue = VF, Red = DCWR.

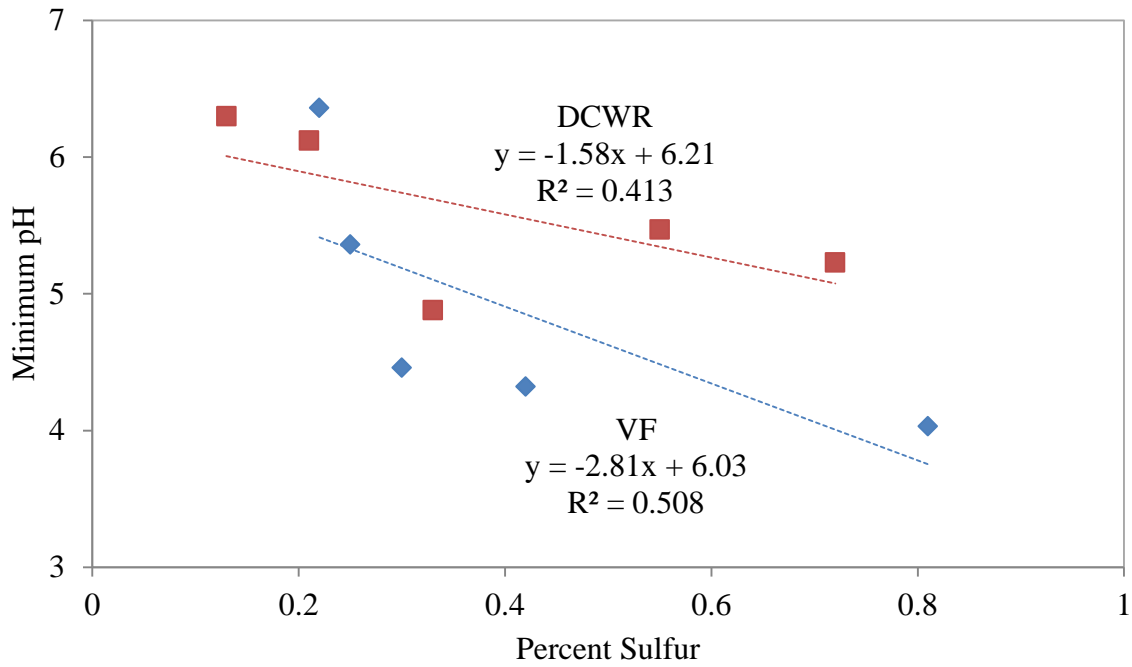


Figure 37. Average sulfate release vs. % sulfur for DNR VF and DCWR samples through 400 weeks. Blue = VF, Red = DCWR.

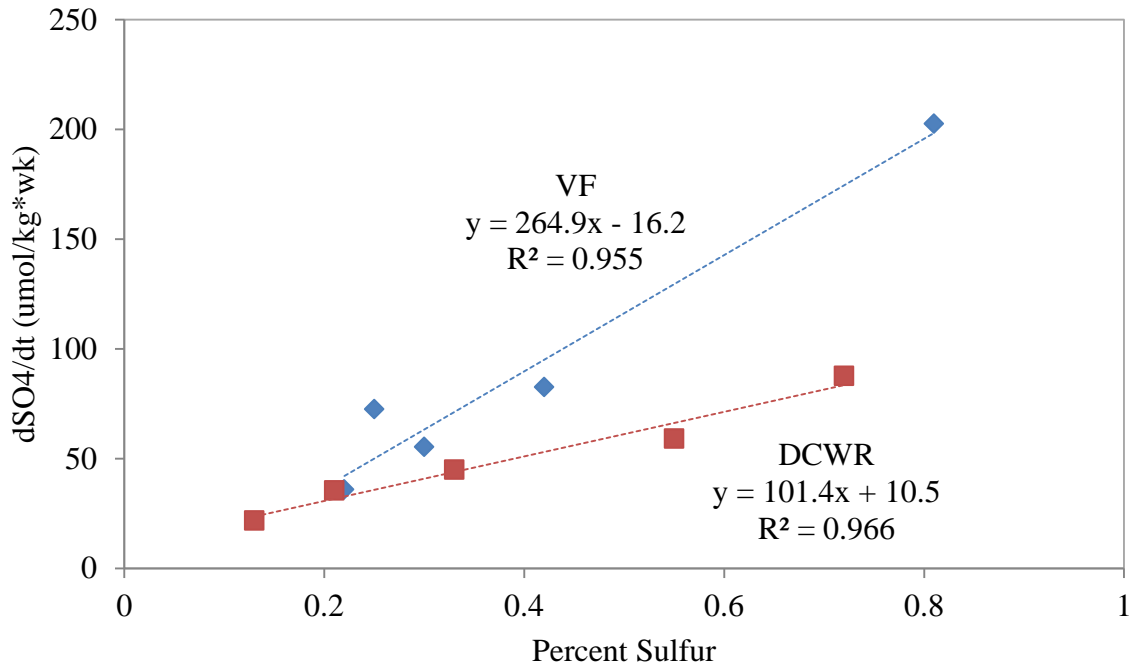


Figure 38. Average calcium release vs. % sulfur for DNR VF and DCWR samples through 400 weeks. Blue = VF, Red = DCWR.

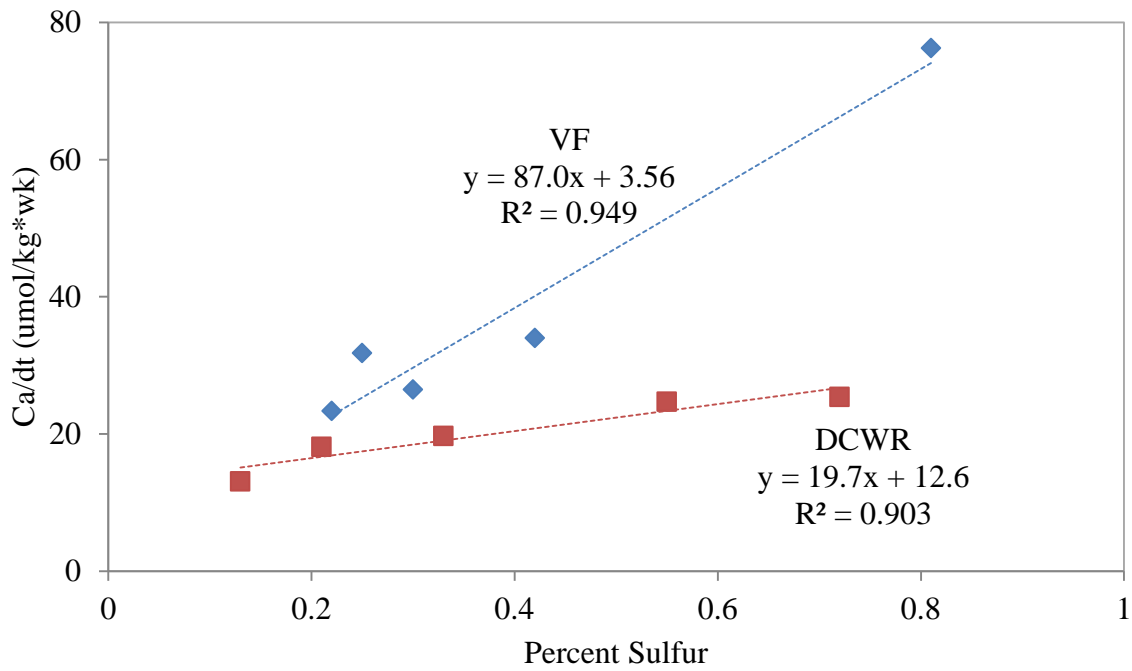


Figure 39. Average magnesium release vs. % sulfur for DNR VF and DCWR samples through 400 weeks. Blue = VF, Red = DCWR.

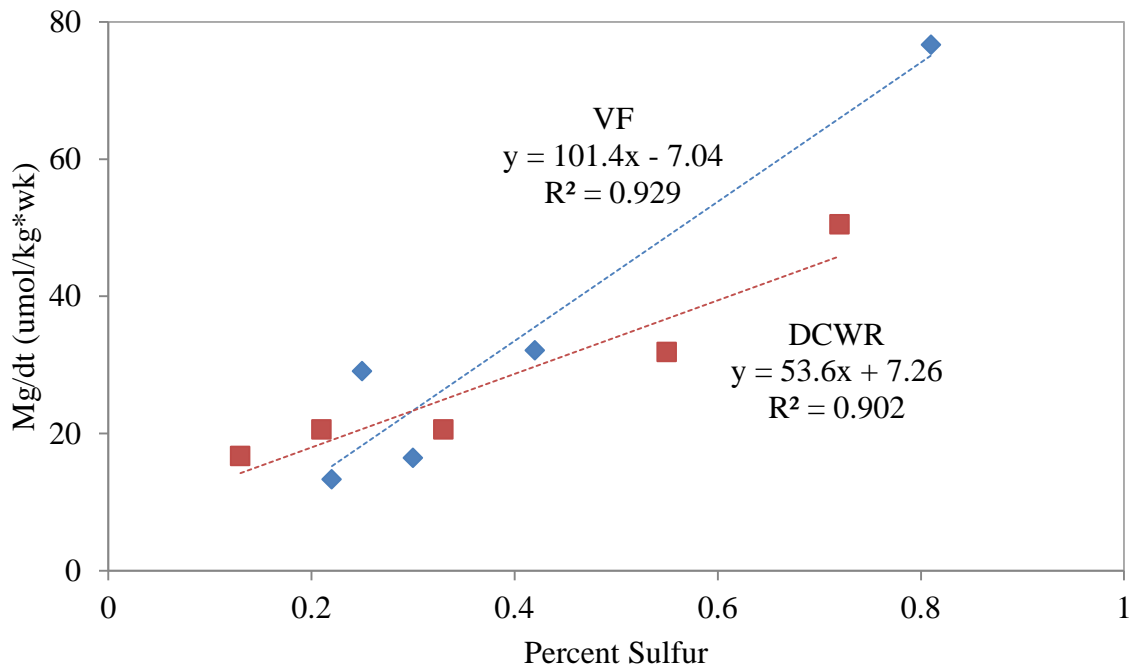


Figure 40. Average sodium release vs. % sulfur for DNR VF and DCWR samples through 400 weeks. Blue = VF, Red = DCWR.

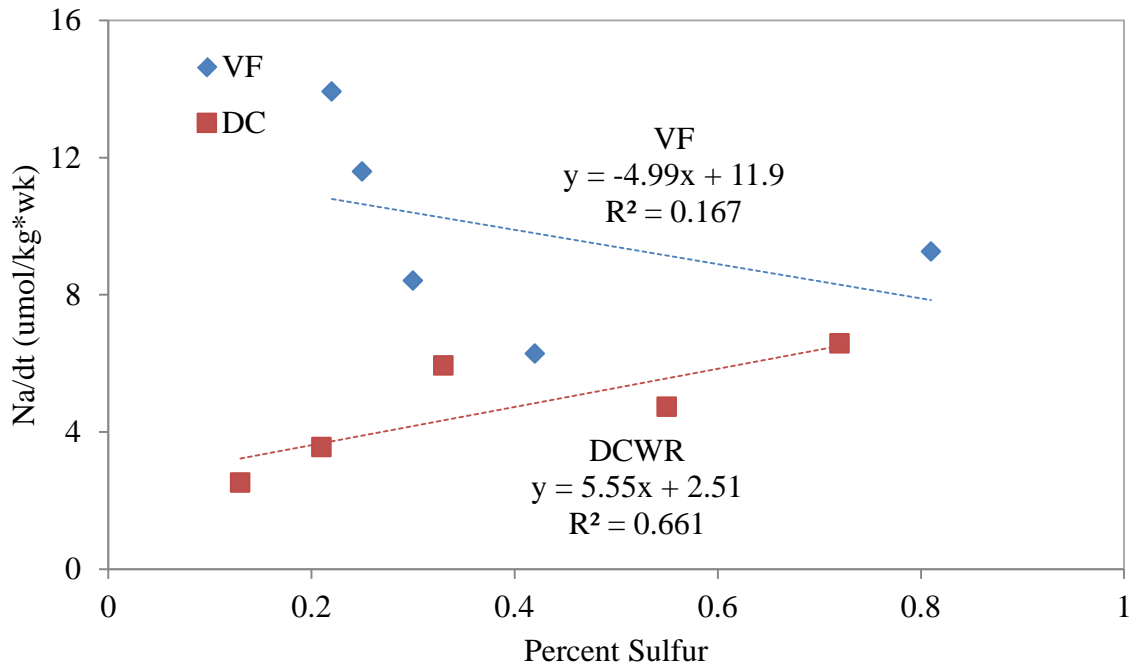


Figure 41. Average potassium release vs. % sulfur for DNR VF and DCWR samples through 400 weeks. Blue = VF, Red = DCWR.

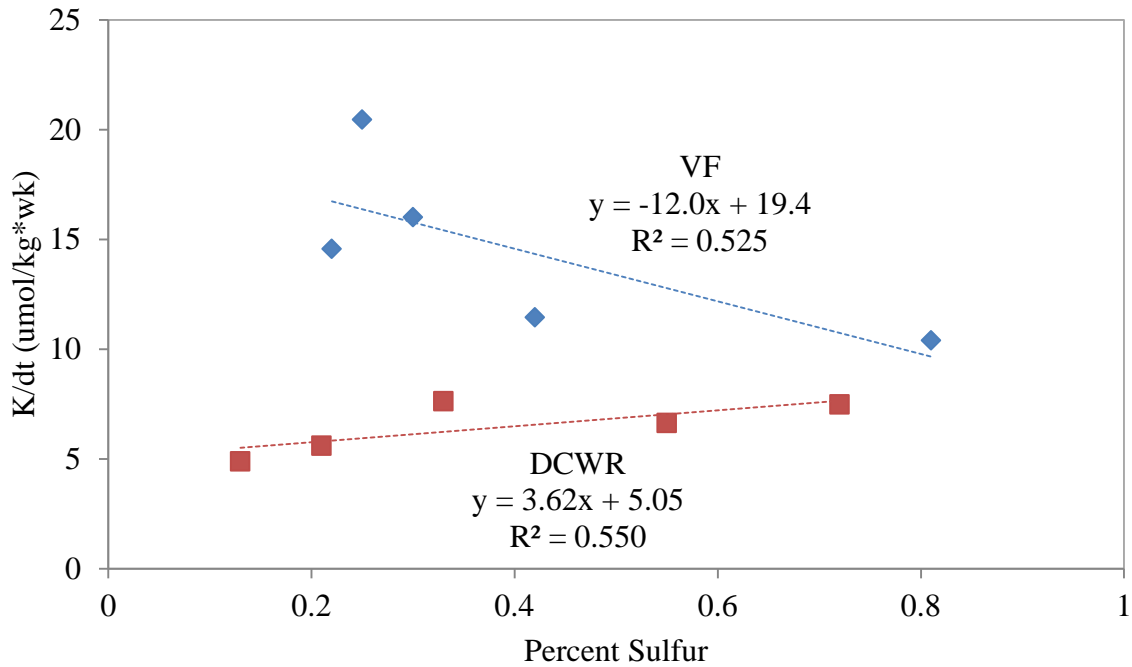


Figure 42. Average copper release vs. % sulfur for DNR VF and DCWR samples through 400 weeks. Blue = VF, Red = DCWR.

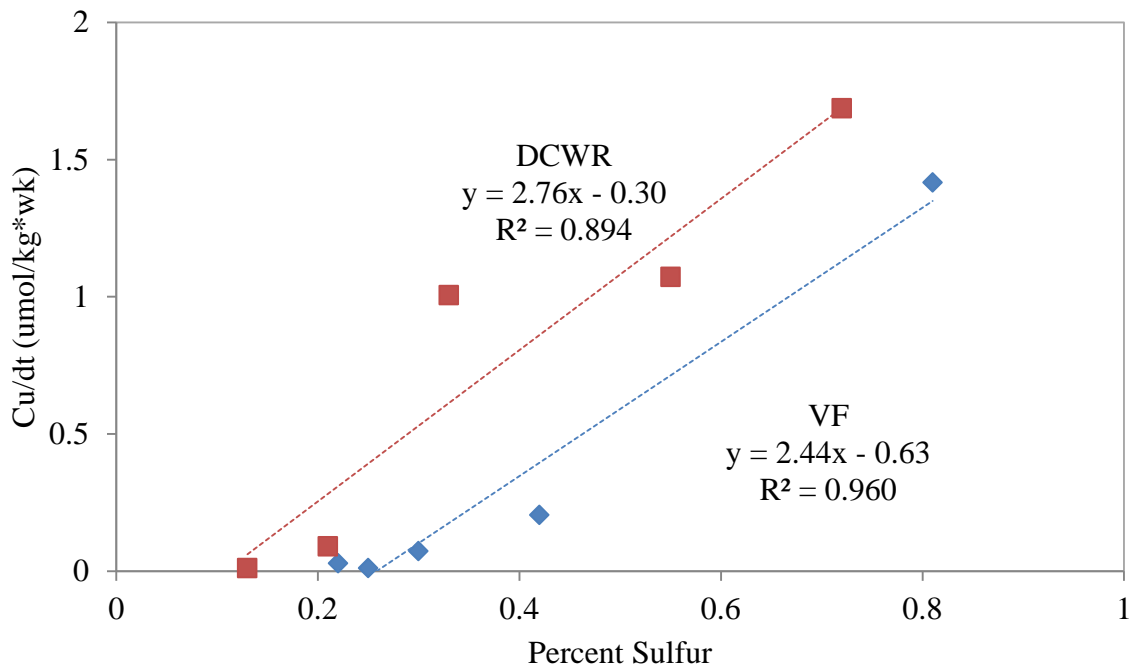


Figure 43. Average cobalt release vs. % sulfur for DNR VF and DCWR samples through 400 weeks. Blue = VF, Red = DCWR.

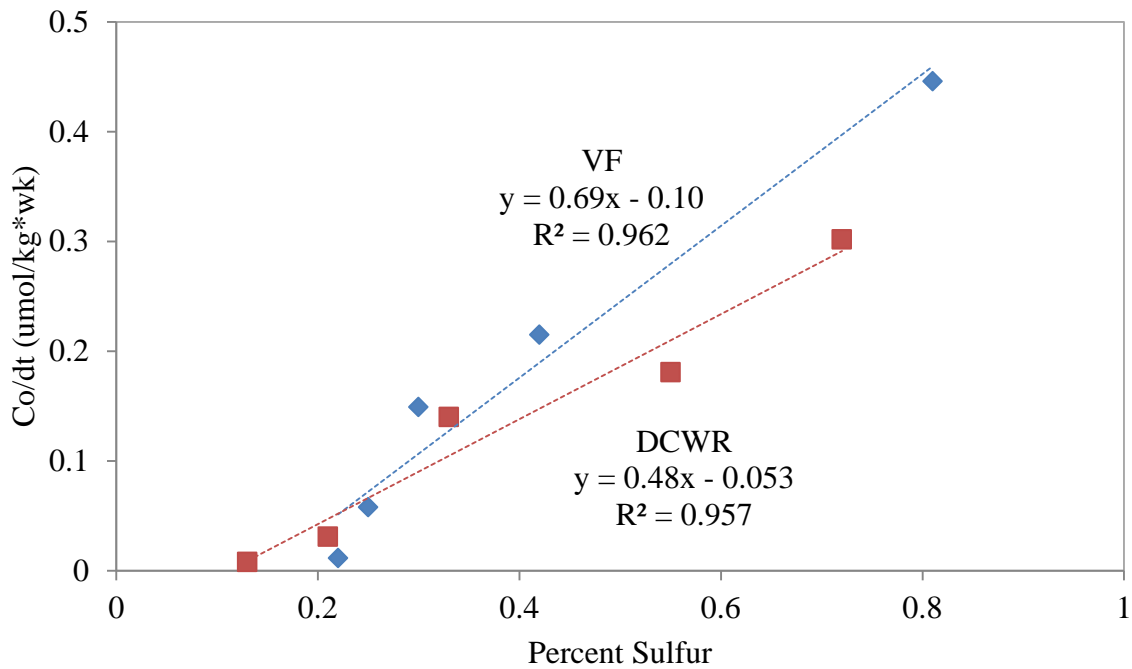




Figure 44. Drainage pH vs time for DCWR humidity cells. Weeks 0-5 excluded to improve resolution.

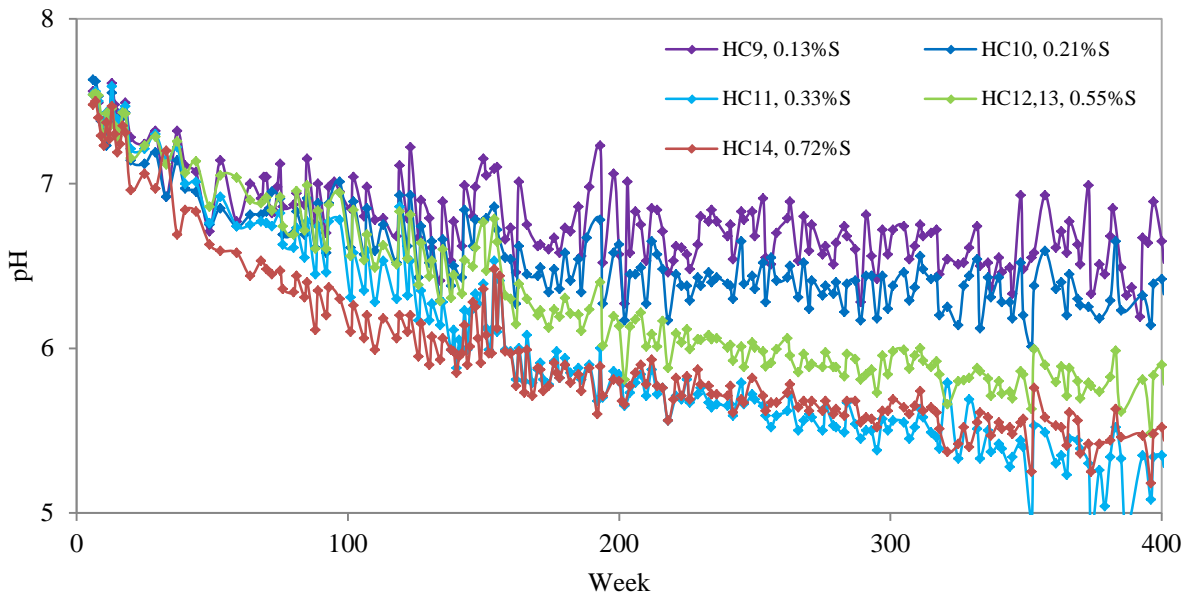


Figure 45. Sulfate release vs time for DCWR humidity cells. Weeks 0-5 excluded to improve resolution.

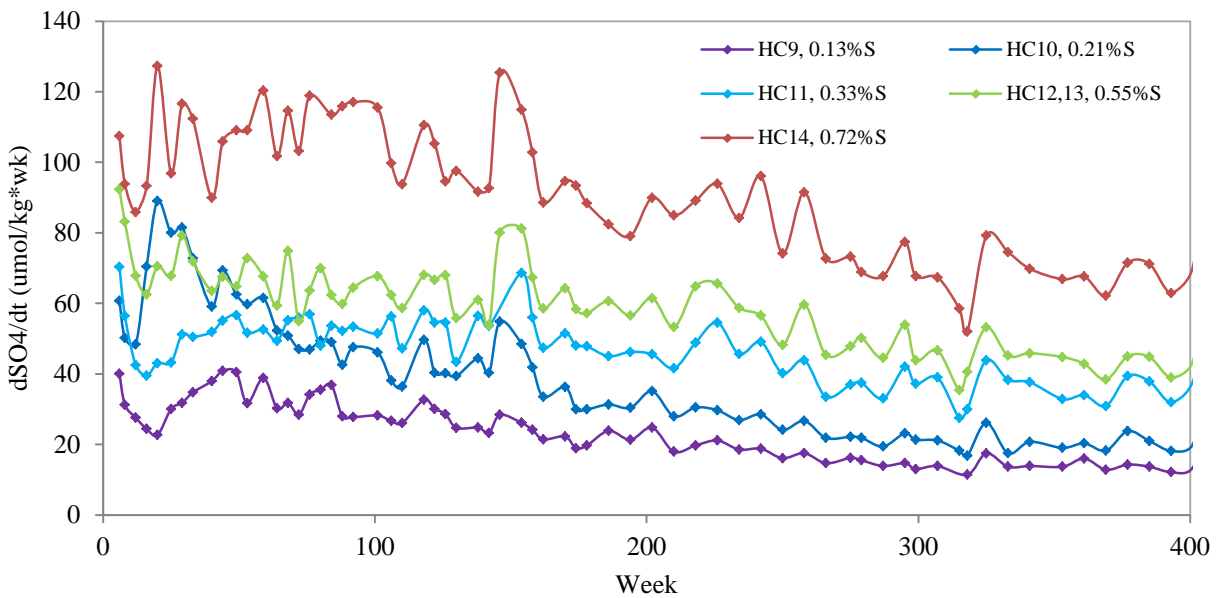


Figure 46. Calcium release vs time for DCWR humidity cells. Weeks 0-5 excluded to improve resolution.

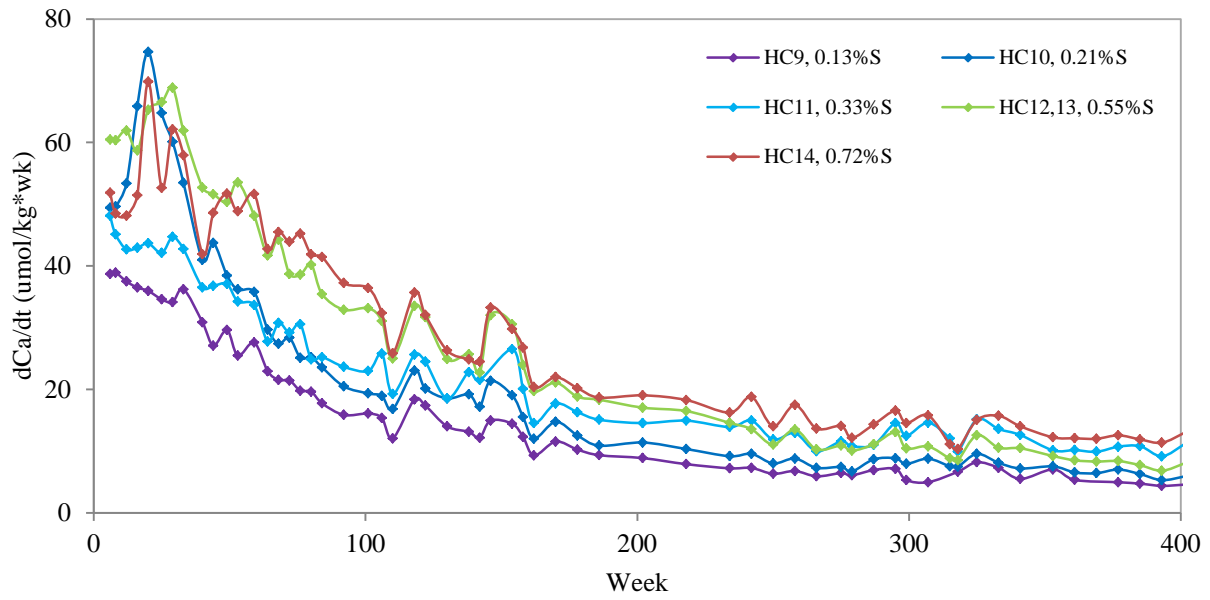


Figure 47. Magnesium release vs time for DCWR humidity cells. Weeks 0-5 excluded to improve resolution.

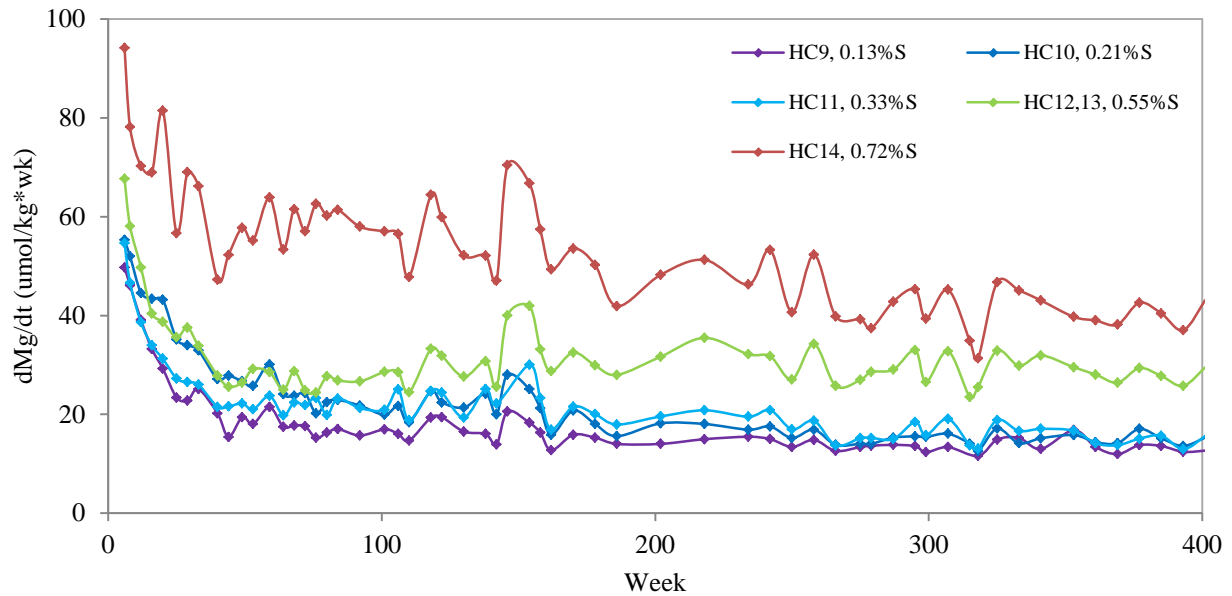


Figure 48. Sodium vs time for DCWR humidity cells. Weeks 0-5 excluded to improve resolution.

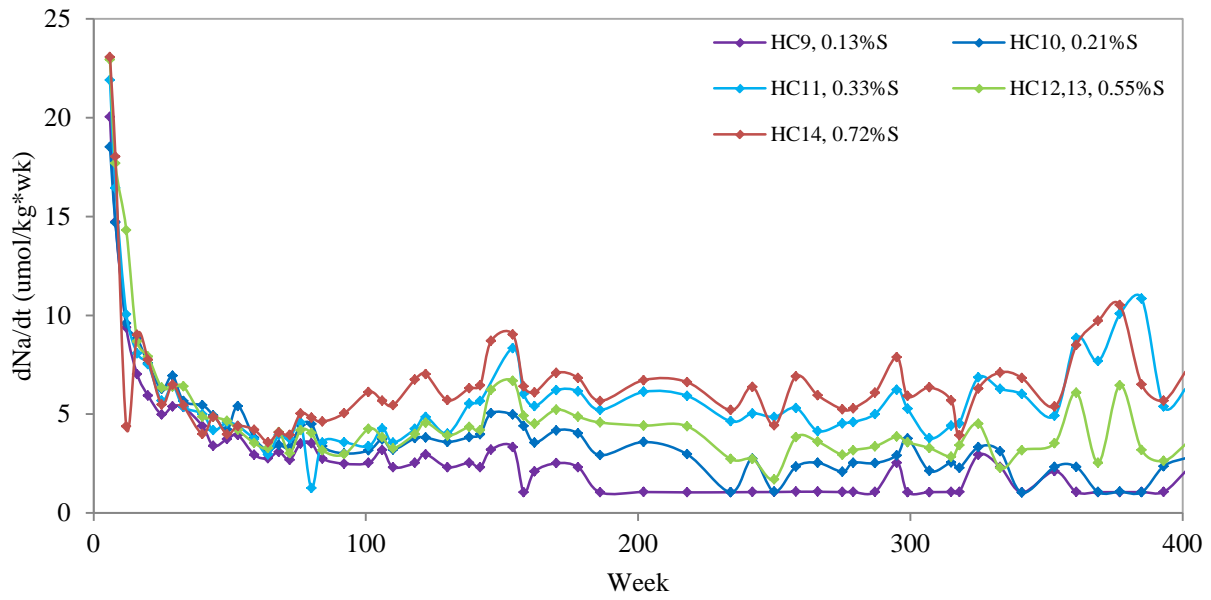


Figure 49. Potassium release vs time for DCWR humidity cells. Weeks 0-5 excluded to improve resolution.

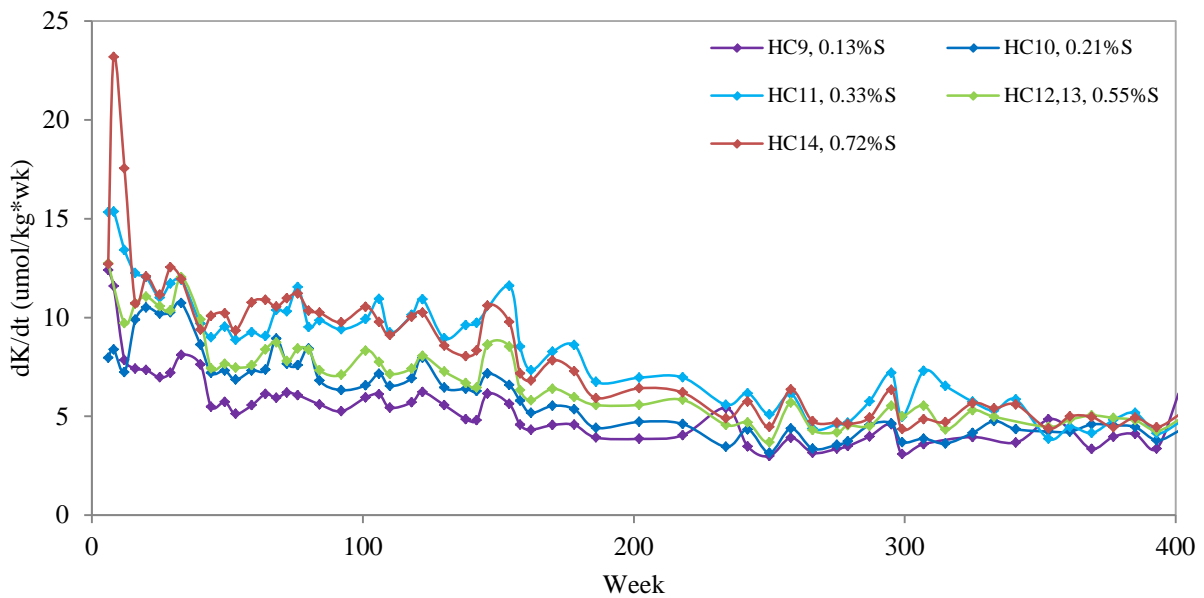


Figure 50. Copper release vs time for DCWR humidity cells. Weeks 0-5 excluded to improve resolution.

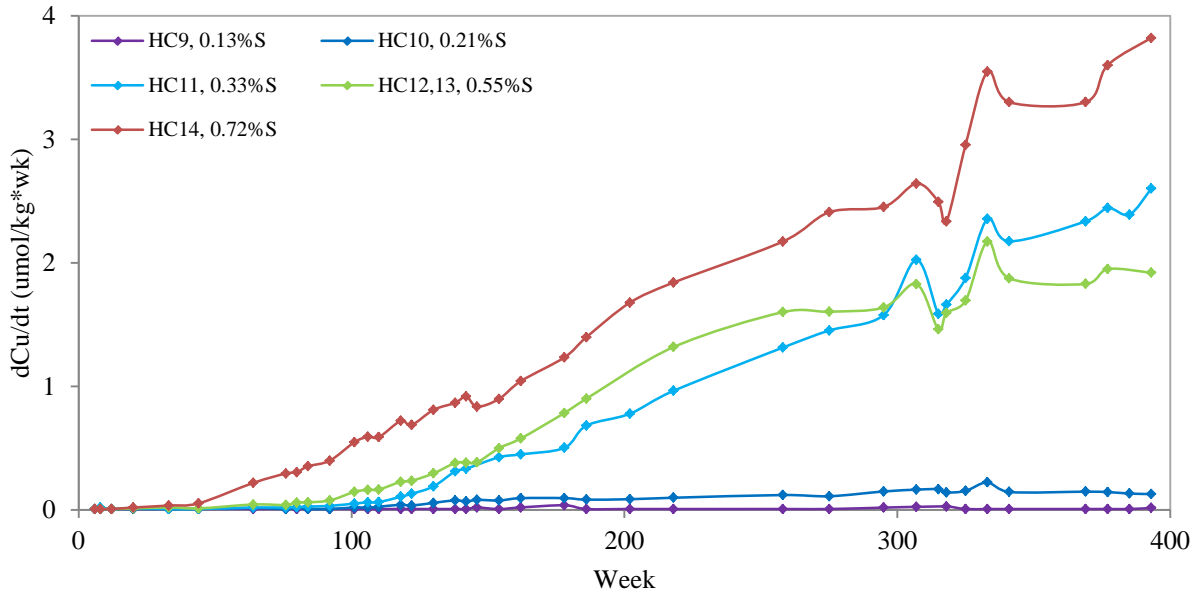


Figure 51. Cobalt release vs time for DCWR humidity cells. Weeks 0-5 excluded to improve resolution.

