# Impact of Coal Mine Water on Modern Gas Well Cements

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## Abstract

Approximately 40% of the mines in the Pittsburgh coal seam are abandoned and filled with water (Donovan et al., 2004). Many abandoned coal mines in Northern Appalachia fill with water when mining operations cease. While the discharges from these mines, also known as acid mine drainage, have been researched (Cravotta, 2008), coal mine water has received less attention. When unconventional natural gas wells are drilled in Northern Appalachia in order to access the Marcellus and the Utica formations, the wells pass through coal mines or coal formations adjacent to mines filled with coal mine water. Coal mine water may compromise the sealing integrity of the wellbore cement used to line or plug a well. This study aims to improve our understanding of how waters in flooded coal mines may affect gas well cements.

Experiments were designed to simulate conditions that a gas well cement might encounter when a well is drilled either through or near a coal mine and is exposed to coal mine water. A series of Class H Portland cement cores were prepared and exposed to a lab-generated solution, whose properties were based on median values for bituminous acid mine drainage discharges from previous research (Cravotta, 2008). Batch reaction experiments occurred in static reaction vessels for time periods of 1, 2, 3, and 4 weeks.

Results suggest that the lab-generated solution impacted the porosity, permeability, and matrix mineralogy of the cement. Scanning electron microscopy analysis shows a steady and incremental growth of void space and calcite crystals as well as the development of reaction rims during the 4-week period. Permeability tended to increase with increased exposure to the lab-generated solution. The lab-generated solution and the effluent from each reaction vessel were monitored for pH throughout the experiment and analyzed for cations and anions at its conclusion. Although the pH of each solution stabilized around 12 after one week, elemental concentrations varied significantly over the 4-week period. The results suggest that Ca, $SiO_2$, K, and Na containing minerals within the cement matrix dissolved steadily throughout the experiment, while Cl and SO4 forming minerals precipitated within the cement cores.

## Introduction

One of the primary functions of well casing and well cement is to preserve zonal isolation throughout the length of the wellbore. Previous research has identified failures between well casing and well cement as a primary pathway for vertical fluid migration in unconventional wells in Northern Appalachia (Jackson et al., 2013; Vengosh et al., 2014). An acidic fluid in contact with well cement may chemically degrade well cement (Kutchko et al., 2007; Kutchko et al., 2008). This degradation of well cement could create a pathway for vertical migration along the well annulus as well as expose the well casing to the same acidic fluid.

The water that fills a coal mine after production ceases is often naturally acidic and poses a potential threat to wellbore cement integrity throughout Northern Appalachia. When coal mine water is discharged from a coal formation, the water is often referred to as acid mine drainage (AMD) because oxidation reactions typically make the water more acidic. While previous research has documented the characteristics of acid mine drainage (Cravotta, 2008a; Cravotta, 2008b) and its effects on stream quality (Herlihy et al., 1990; Sams and Beer, 2000), coal mine water has received less attention. Previous research has shown that while coal mine water can evolve from acidic to pH neutral over multiple decades, some coal mine waters continue to have a low pH over the same time frame (Skousen et al., 2006). Studies on coal mine water have also shown that it can travel between adjacent coal mines separated by coal formation pillars and barriers (Perry and Hawkins, 2004; Light and Donovan, 2015), indicating that coal extraction techniques have created artificial horizontal migration pathways through coal layers that have naturally low porosity and permeability values.

Marcellus and Utica unconventional oil and gas wells overlap the same spatial extent as coal mining in Northern Appalachia. Given its often acidic nature and its flow between mines, coal mine water has the potential to interact with unconventional wellbore cements that have been placed through coal mines or coal formations that are adjacent to abandoned mines. This study investigates this potential issue by observing the permeability, porosity, and chemical effects of coal mine water on cement cores.

## Method

Cement samples were prepared using Class H Portland cement (Lafarge, Herndon, VA) with deionized water and a water-to-cement (w/c) ratio of 0.38. Samples were mixed according to API Recommended Practice 10B (API, 1997). This cement slurry was poured into 1" diameter plastic tube molds and cured in a 50°C water bath. After 4 days the cores were removed from the water bath and demolded. The cores were then placed in a plastic container filled with deionized water, where continued to cure.

The cured Portland Class H cement cores were cut into 3" tall sections and exposed to a lab-generated solution that mimicked the median value for bituminous acid mine drainage (AMD) from previous research (Cravotta, 2008b). The cores were exposed for periods of 1, 2, 3, and 4 weeks in static reaction vessels. The static reaction vessels were made of non-reactive, plastic (Teflon) that were not open to the atmosphere. These vessels were placed in a refrigerator set for 12°C (53.6°F) in order to replicate the median temperature of Pennsylvanian bituminous AMD waters (Cravotta, 2008b). A control cement core sample was not exposed to any solution after the curing process in order to serve as a comparison to the experimental samples.

The pH of the experimental solutions were monitored throughout the experiment. After the cement cores were exposed to the lab-generated solution, subsamples of the static reaction vessel effluent were taken and measured for alkalinity, cations (ICP) and anions (IC). Two chemistry controls were prepared by filling one clean, static reaction vessel with deionized water and another clean, static reaction vessel with the lab-generated coal mine water solution.

When a cement core was removed from the static reaction vessel, it was dried in a desiccator for ~48 hours. After it was dry, it was sliced into six different horizontal subsections (Figure 1). Permeability measurements of two of the subsections (1.5" and 2.5") were measured in a constant-flow permeameter, UltraPerm-500 (TEMCO, Inc.), using nitrogen gas as the pore fluid. This device is capable of determining the permeabilities of various media over a range of 0.001 mD to 30,000 mD. The permeability is estimated using Darcy's Law:

$$K=Q\mu l/A\Delta p$$

In this equation, Q ($m^3/s$) is the volumetric flow rate of fluid through the sample; $\mu$ (Pa·s) is fluid dynamic viscosity [in this case nitrogen at atmospheric conditions (0.000017631 Pa·s)]; l (m) is the sample's length; A ($m^2$) is the area of the sample's cross section; $\Delta p$ (Pa) is the pressure difference at the ends of the sample. The standard units of measurement for permeability are $m^2$. Since values of permeability are very small, it is commonly presented in non-SI units known as milli-Darcies ($1mD \approx 9.87\cdot 10\text{-}16\ m^2$). Due to gas slippage, a Klinkenburg correction was applied for "true" or "liquid" permeability measurements.

The other four cement subsections were polished and analyzed using a Scanning Electron Microscope (SEM). The back scatter electron (BSE) detector was used to generate images and observe changes in the size and distribution of minerals and void spaces throughout the cement matrix.

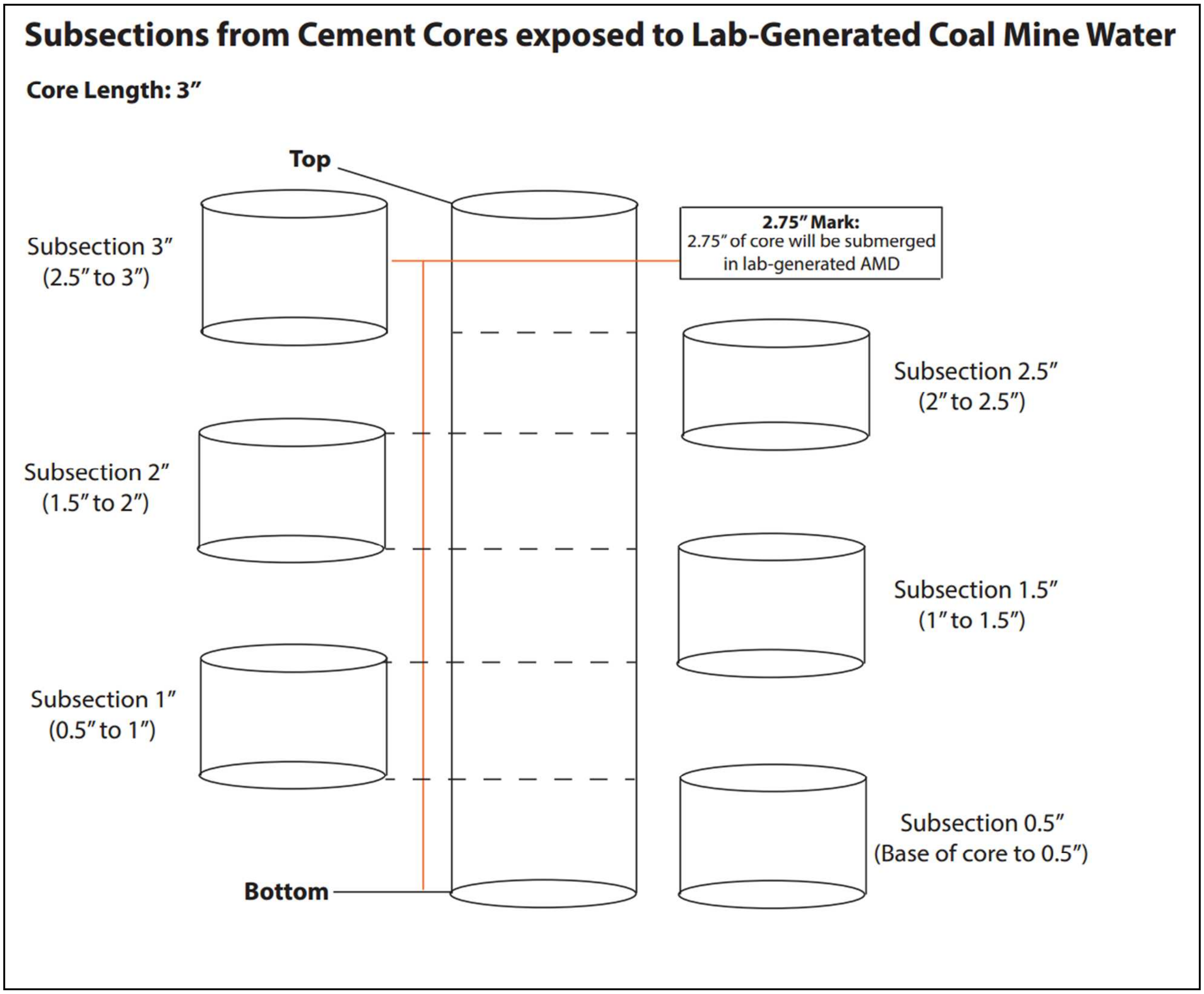


Figure 1. Schematic illustrating the division of 3" cement cores into six different horizontal subsections. Four of the subsections were analyzed using an Environmental Scanning Electron Microscope (ESEM) and the other two subsections were measured for permeability.

## Results & Discussion

### ESEM Images of Cement Core

The cement subsections that were exposed to the lab-generated coal mine water displayed growth in the overall number and size of calcite crystals (Figure 2). These calcite crystals are particularly apparent close to the rim of each cement core and appear to be part of a reaction rim. The growth of calcite crystals appears to be incremental and increases with increased exposure to the solution. While the control sample contain small calcite crystals (Figure 2A), these crystals grow to form large euhedral crystals during the four week exposure to the coal mine water (Figure 2D). Linear void spaces (cracks) also become more common with increased exposure to the solution. There are often calcite crystals and other precipitate minerals inside these linear void spaces (Figure 2D), suggesting that the minerals precipitated after the formation of the void. If the minerals did in fact form after the void space was created, this would suggest that increased exposure to the lab-generated coal mine water results in an increase in connected void spaces.

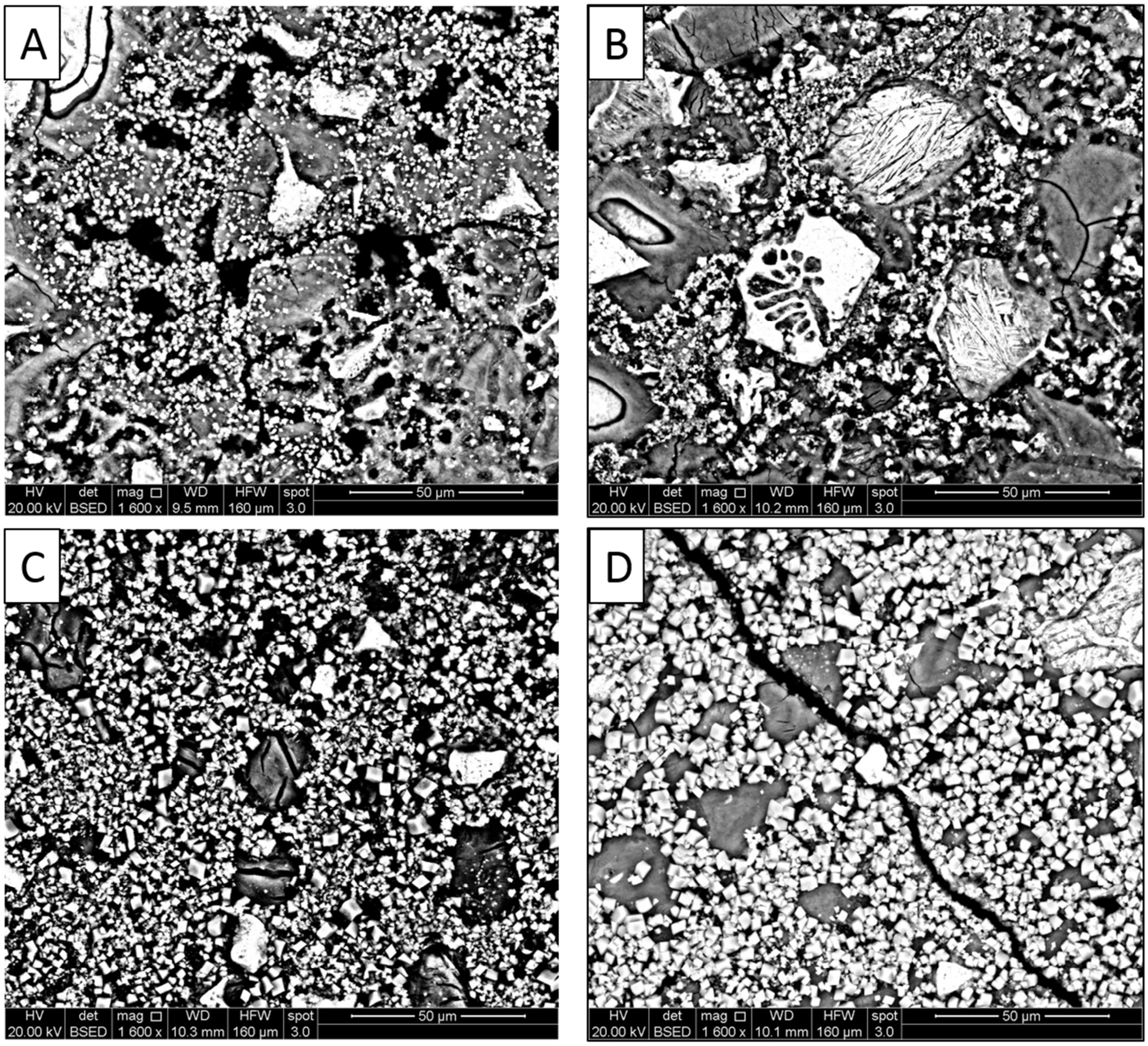


Figure 2. SEM-BSE images of the effects of lab-generated coal mine water on the rims of cements cores at 1600x magnification. These images are from the top of the cement cores (3” subsections). From upper left, (A) the unexposed control sample, (B) the one week exposure, (C) the two week exposure, and (D) the four week exposure.

While calcite crystal growth is more common in the cores’ rims, an increase in the visible pore space is also observed in the interior of the exposed cement cores (Figure 3). The control sample exhibited a minimal number of visible pore spaces at 400x, but exposed cement cores displayed an increasing number of visible pore spaces with increased exposure to the coal mine water solution. Components of the cement matrix, including the lighter gray calcium hydroxide [$Ca(OH)_2$] and the darker gray calcium-silicate-hydrate (C-S-H), appear to decrease after each week of exposure (Figure 3A-D). In addition, it is apparent from the SEM images that the large, unhydrated cement grains have been decalcified. This degradation of calcium hydroxide and the unhydrated cement grains in these samples is similar to that seen in cement samples exposed to $CO_2$-saturated brines at 50°C and 30.3 MPa (Kutchko et al., 2007; Kutchko et al., 2008). This previous work proposed that the $CO_2$ would lower the pH of $CO_2$-saturated brines and that this low pH brine-water would dissolve calcium hydroxide inside the cement. A similar reaction may be occurring with the low-pH coal mine water, which could leach calcium from calcium hydroxide in a similar manner. In this experiment, it is possible that the leached calcium from the calcium hydroxide then formed the euhedral calcite ($CaCO_3$) crystals seen growing in the exposed samples (Figure 2B-D).

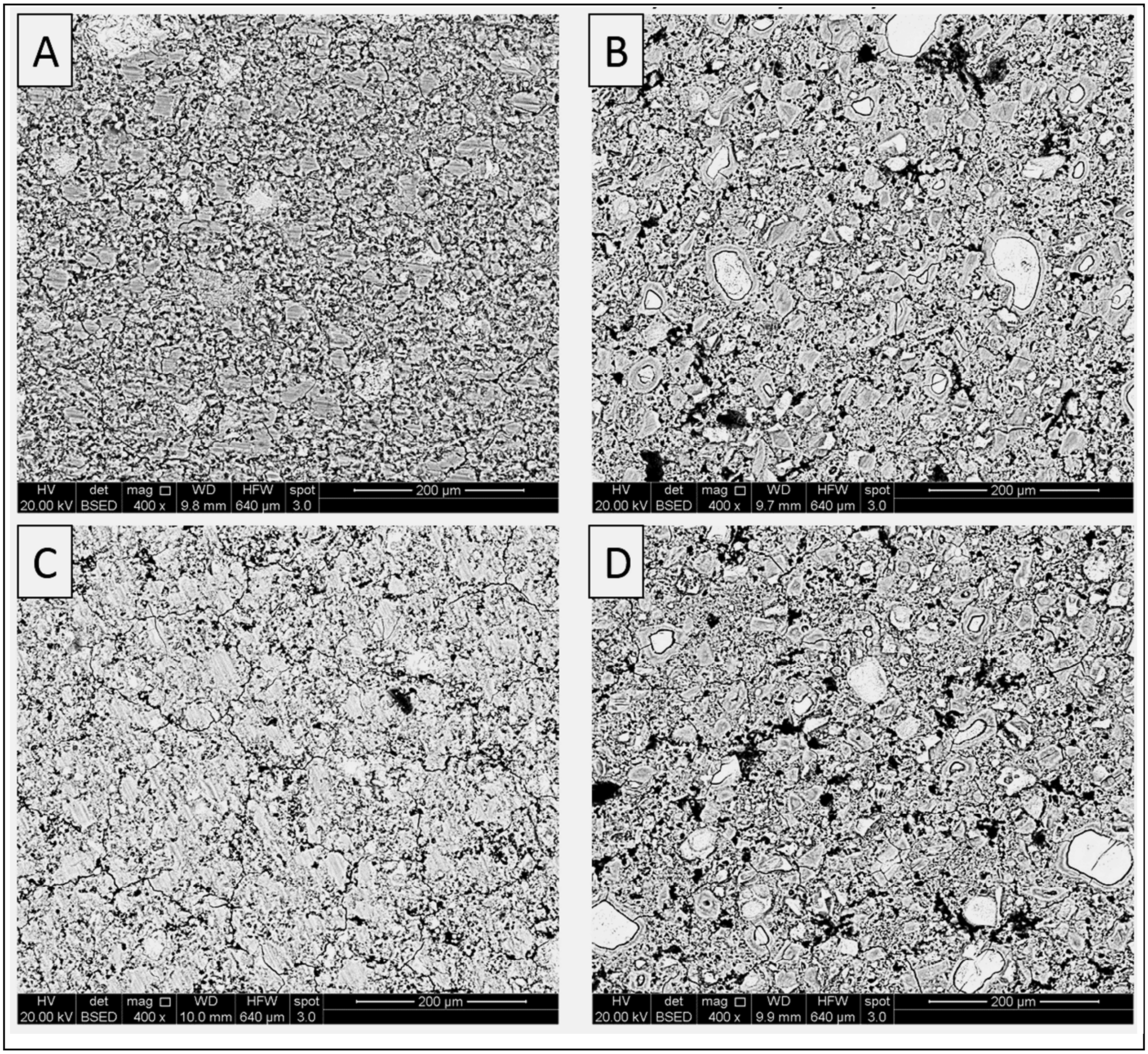


Figure 3. SEM-BSE images of the effects of lab-generated coal mine water solution on the interior of cements cores at 400x magnification. These images are from the 1" subsections, which are close to the base of the cement cores. From upper left, (A) the unexposed control sample, (B) the one week exposure, (C) the two week exposure, and (D) the three week exposure.

## Permeability Measurements of Cement Core

Permeability measurements were made on two different vertical subsections (1.5" and 2.5") for each exposure period (Table 1). The control cement core, which was not exposed to the coal mine water solution, had a measured permeability of 0.0077 millidarcies (mD).

For the 1.5" cement core section, the measured permeability increases linearly (Figure 4, $R^2 = 0.911$) with increased exposure time to the coal mine water. Every exposure period had a measured permeability that was higher than the previous exposure period and also higher than the control sample. This relationship suggests that the coal mine water solution may cause an increase in cement pore-connectivity.

Higher up on the cement core, at the 2.5” subsection, the measured permeability values had more variability. The permeability measurements of the 1-week exposure (0.0046 mD) and the 3-week exposure (0.76 mD) were lower than the control sample (Figure 4). These values suggest that the coal mine water solution may cause a significant decrease in pore-connectivity after the first week. This decrease may have been caused by a series of dissolution-precipitation reactions occurring within the core. A possible scenario is that the solution is dissolving calcium hydroxide [$Ca(OH)_2$] from the cement matrix. Leaching of calcium from calcium hydroxide has been shown to increase macroporosity in cement pastes (Carde and François, 1999). These leached calcium ions could potentially precipitate in the form of calcite ($CaCO_3$) crystals, which were observed at the reaction rims (Figure 2).

These permeability values for the 2.5” subsections display variability and suggest that the chemical reactions inside the cement core are not simply dissolution reactions. These values also suggest a chemical gradient in the solution that causes different reactions at different locations in the core. In this scenario, cement may experience a decrease in permeability in certain parts of the core after initial exposure due to the vertical chemical gradient of the coal mine water.

Despite this variability in permeability over time and spatial location within the core, the permeability value for the 4-week exposure at 2.5” (0.0136 mD) is significantly higher than the control (0.0077 mD) and higher than the 4-week exposure at 1.5” (0.0129 mD). Permeability values still display a linear relationship ($R^2$ =8274) at the 2.5” section of the cement core. Although this is a limited sample set, with a sample size of four, the overall trend suggests that precipitation reactions were followed by dissolution reactions for the 2.5” core subsections.

Overall, permeability values in cement cores tended to increase with longer exposure time to a lab-generated coal mine water solution, suggesting that coal mine water may increase pore connectivity in gas-well cement over time. This finding corroborates the SEM observations that indicated that the formation of large pores and cracks were enhancing the pore-connectivity of the exposed cement cores.

Table 1. Permeability (mD) results for Class H Portland cement core subsection. The control sample was not exposed to the coal mine water solution. The vertical location of the core subsection is indicated in inches.

| Sample | Permeability (mD) |
|---|---|
| Control | 0.0077 |
| 1 Week Exposure-1.5" | 0.0099 |
| 2 Week Exposure-1.5" | 0.0101 |
| 3 Week Exposure-1.5" | 0.0113 |
| 4 Week Exposure-1.5" | 0.0129 |
| 1 Week Exposure-2.5" | 0.0046 |
| 2 Week Exposure-2.5" | 0.0082 |
| 3 Week Exposure-2.5" | 0.0076 |
| 4 Week Exposure-2.5" | 0.0136 |

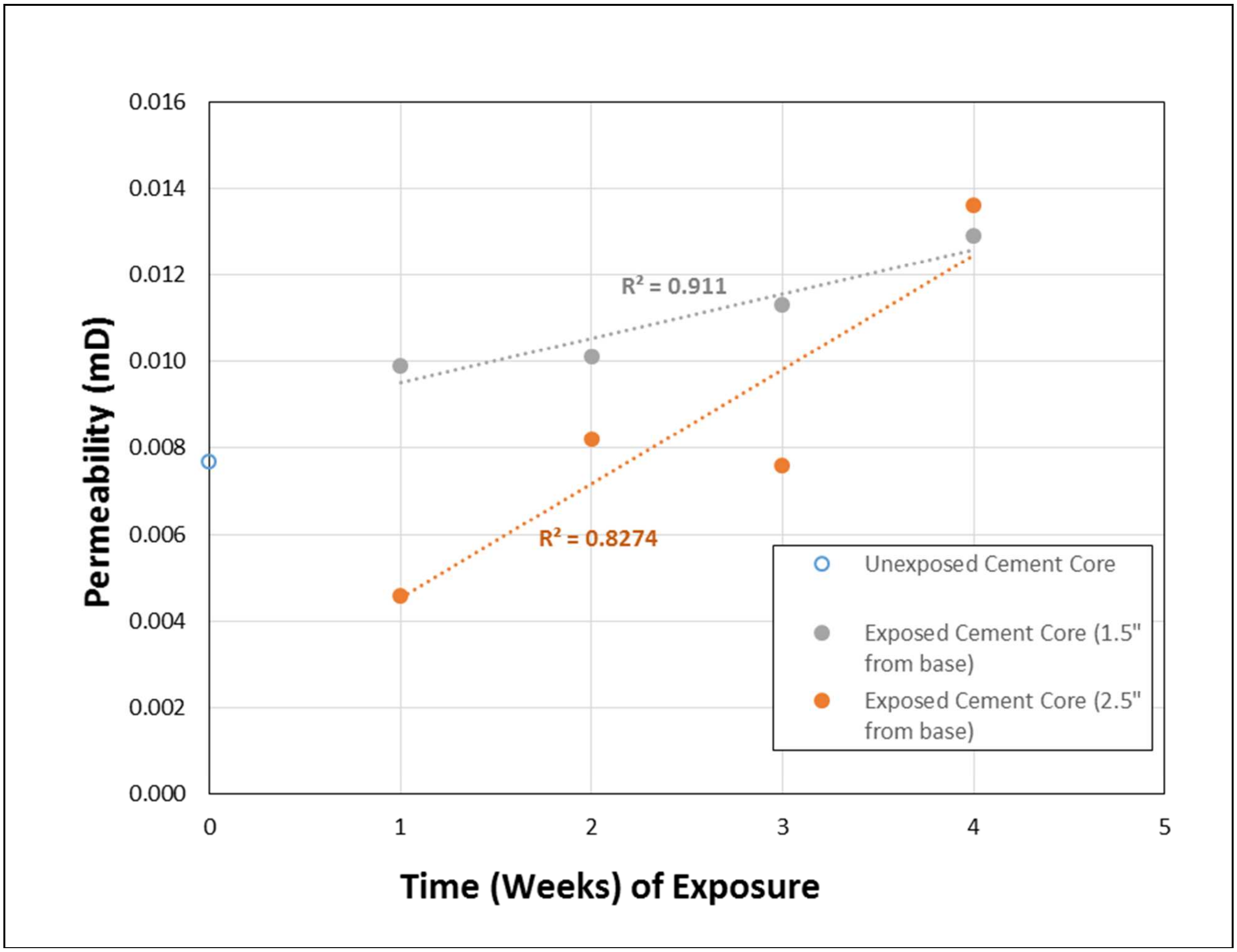


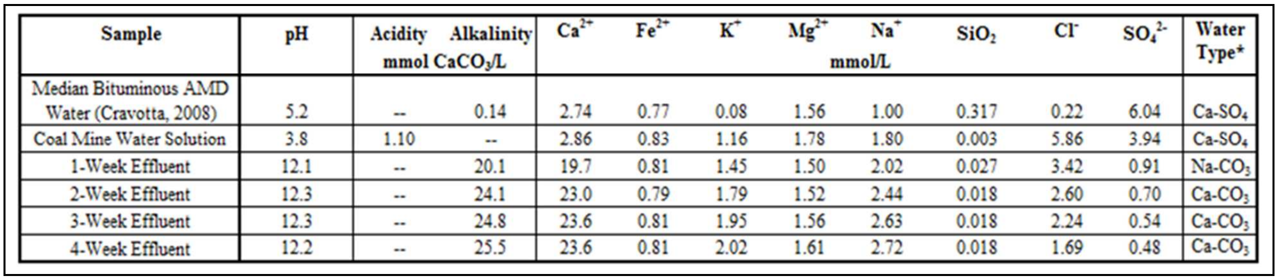
Figure 4. Permeability (mD) measurements of the Portland Class H cement cores plotted versus the amount of time each core was exposed to the lab-generated coal mine water.

### Chemistry Data from Coal Mine Water Solution and Static Reaction Vessel Effluents

The coal mine water solution and the effluents from the static reaction vessels were measured for acidity and alkalinity, pH, and dissolved species (Table 2). This data is displayed in a Piper diagram (Figure 5). The coal mine water generated in the lab is similar to median bituminous AMD water from previous research (Cravotta, 2008b). Both the coal mine water and the median bituminous AMD water have similar concentrations of Ca and Mg and both are classified as Ca-$SO_4$ waters. Despite these similarities, the coal mine water solution used in these experiments has significantly lower sulfate concentrations and a lower pH than the median bituminous AMD water. All of the measured values for the coal mine water, except for dissolved $SiO_2$, are within the observed values of bituminous coal waters (Cravotta, 2008b), suggesting that the coal mine water solution is a representative solution for these experiments. The lower levels of dissolved $SiO_2$ are taken into account later in this section.

All of the effluent waters plot in the same locations on the Piper diagram (Figure 5). The one-week effluent is classified as classified as a Na-$CO_3$ water while the remaining effluent samples are Ca-$CO_3$ samples. This suggests that after a brief increase in dissolved Na, the waters were dominated by dissolved Ca. This evolution of the waters from Ca-$SO_4$ (coal mine water solution) to Na-$CO_3$ (one-week effluent) to Ca-$CO_3$ (remaining effluent samples) suggests that the dominant cation varied temporarily, while there was a shift in the dominant dissolved anion. The rise in the presence of carbonate is apparent through the rise in alkalinity, measured as mmol $CaCO_3$/L (Table 2). The coal mine water has a measured acidity, while every effluent has a higher alkalinity value after each week of exposure to the cement core. This steady rise in alkalinity suggests that the coal mine water is continuing to react with the cement core even after four weeks.

Table 2. Measurements of chemical parameters including pH, acidity and alkalinity, and dissolved species for experimental solutions. Data from previous research (Cravotta, 2008) is included as a comparison for the coal mine water solution used in this study. *Water type was calculated using Geochemists Workbench 10.0.4.



| Sample | pH | Acidity | Alkalinity | $Ca^{2+}$ | $Fe^{2+}$ | $K^{+}$ | $Mg^{2+}$ | $Na^{+}$ | $SiO_2$ | $Cl^{-}$ | $SO_4^{2-}$ | Water Type* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | mmol $CaCO_3$/L |  | mmol/L |  |  |  |  |  |  |  |  |
| Median Bituminous AMD Water (Cravotta, 2008) | 5.2 | -- | 0.14 | 2.74 | 0.77 | 0.08 | 1.56 | 1.00 | 0.317 | 0.22 | 6.04 | Ca-$SO_4$ |
| Coal Mine Water Solution | 3.8 | 1.10 | -- | 2.86 | 0.83 | 1.16 | 1.78 | 1.80 | 0.003 | 5.86 | 3.94 | Ca-$SO_4$ |
| 1-Week Effluent | 12.1 | -- | 20.1 | 19.7 | 0.81 | 1.45 | 1.50 | 2.02 | 0.027 | 3.42 | 0.91 | Na-$CO_3$ |
| 2-Week Effluent | 12.3 | -- | 24.1 | 23.0 | 0.79 | 1.79 | 1.52 | 2.44 | 0.018 | 2.60 | 0.70 | Ca-$CO_3$ |
| 3-Week Effluent | 12.3 | -- | 24.8 | 23.6 | 0.81 | 1.95 | 1.56 | 2.63 | 0.018 | 2.24 | 0.54 | Ca-$CO_3$ |
| 4-Week Effluent | 12.2 | -- | 25.5 | 23.6 | 0.81 | 2.02 | 1.61 | 2.72 | 0.018 | 1.69 | 0.48 | Ca-$CO_3$ |

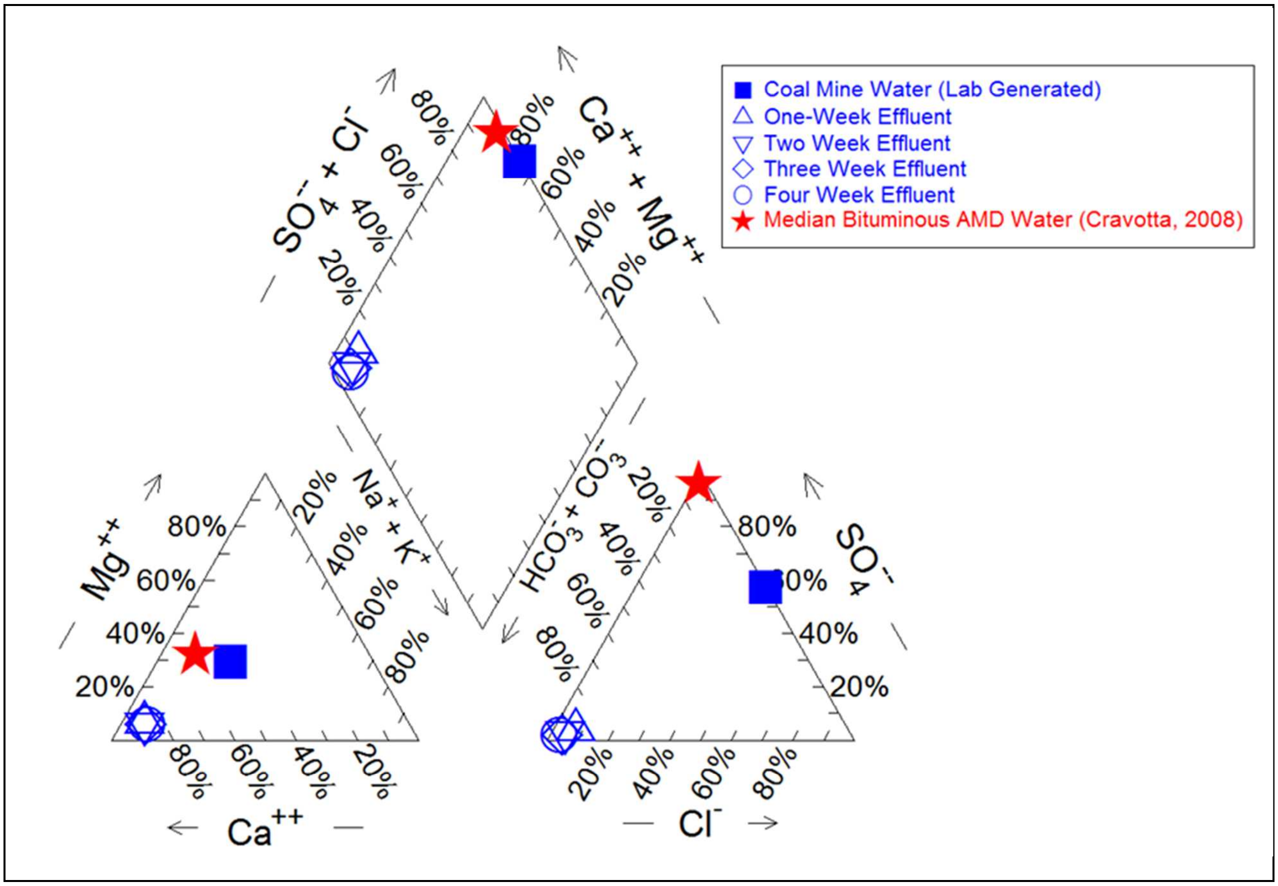


Figure 5. Piper diagram of the solutions involved in this experiment created using Geochemists Workbench 10.0.4. The starting solution was a lab-generated solution that was designed to replicate coal mine water and was based on measurements of bituminous acid mine drainage water from previous research (Cravotta, 2008).

The pH of the coal mine water (3.72) rose to levels around 12 in the 1-week effluent sample and stayed there throughout the experiment (Figure 6). The reactions between the acidic coal mine water and the cement cores are likely to be related to the pH of the coal mine water. Although the pH is basic and relatively stable, a pH below 12.5 has the potential to leach Ca from cement paste (Gaitero et al., 2008). Calcium levels rise from the coal mine water solution (2.86 mmol/L) to the 3-week effluent (23.6 mmol/L), which represents a ~725% increase in dissolved calcium. This result suggests that the coal mine water was aggressively leaching calcium from the cement core during the first three weeks of the experiment.

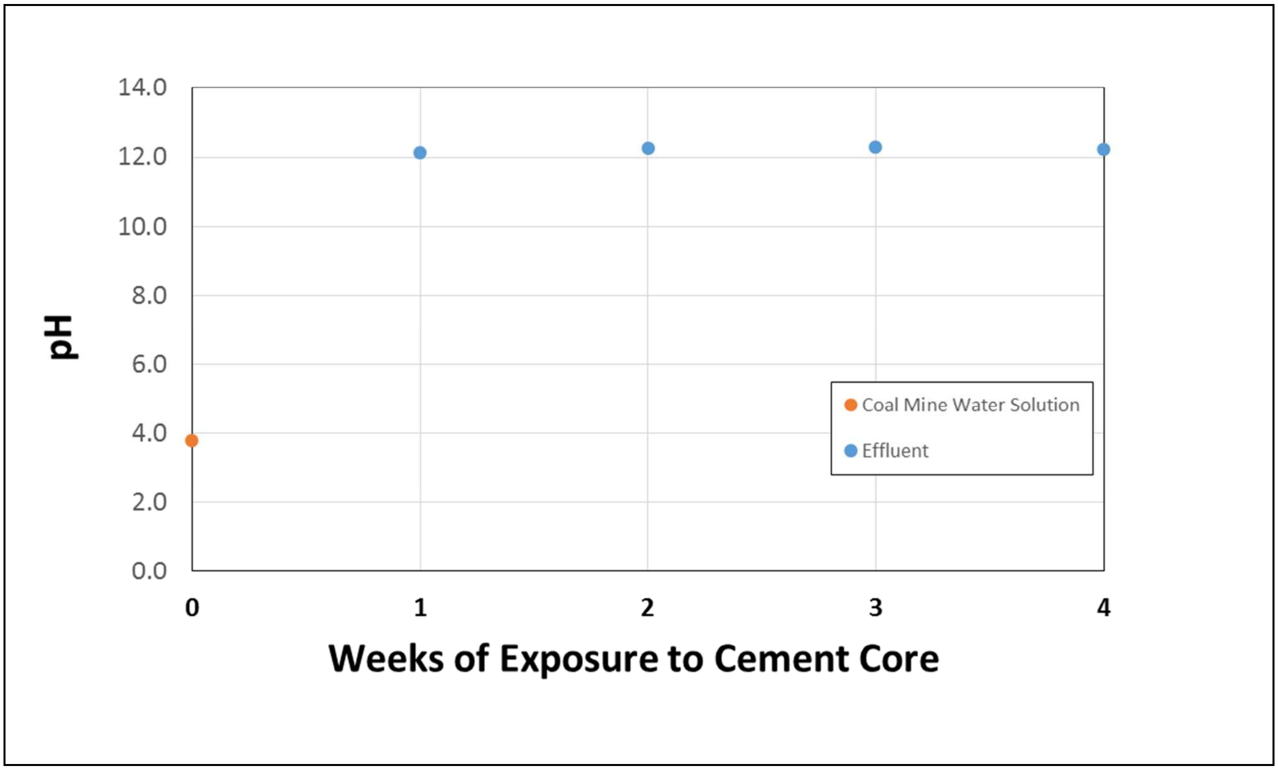


Figure 6. The pH of the coal mine water solution and the effluent from the static reaction vessels.

Dissolved calcium levels remain stable between the 3-week and 4-week effluent (Figure 7A), suggesting that the solution may start to approach equilibrium with the cement core after three weeks of exposure. Calcium leaching has been shown to decrease the strength and increase the porosity of cement pastes (Carde and François, 1999). SEM observations suggested the possibility of calcium leaching and this chemical evidence corroborates those findings and indicates that Ca-leaching is a possible mechanism for the measured permeability increases.

Of the species measured, dissolved calcium and silica dioxide concentrations in the effluent water displayed the biggest changes relative to the coal mine water solution. Dissolved silica dioxide displayed a significant increase (+934%) from a low background concentration (0.003 mmol/L) in the coal mine water solution to a high concentration (0.027 mmol/L) in the 1-week effluent (Table 2). The concentrations were identical in the 2, 3, and 4-week effluents (0.018 mmol/L). These changes in concentration (Figure 7B) suggest that the coal mine water dissolved silica dioxide in the cement core during the first week of exposure and that after the first week, silica dioxide briefly precipitated out of the coal mine water solution. After this brief precipitation phase, reactions between the coal mine water and the cement core were negligible.

Despite the significant increase in dissolved silica dioxide, the overall silica dioxide concentrations were two orders of magnitude lower than any other species (Table 2), suggesting that any reactions related to silica dioxide were minor. In addition, these results suggest that the low dissolved silica dioxide content of the coal mine water, which was lower than any measured bituminous AMD waters (Cravotta, 2008b), did not result in enhanced dissolution or precipitation reactions with the cement core.

Dissolved potassium and sodium experienced concentration increases relative to the coal mine water (Figure 7C, D). The concentrations for potassium and sodium increase during each exposure period and result in net increases for the 4-week effluent (74% and 52%) relative to the coal mine water solution. These steady and consistent increases suggest that the coal mine water was leaching potassium and sodium from the cement core. Dissolved iron and magnesium display an initial decrease followed by a rise in concentration (Figure 7E, F). Both iron and magnesium have low net decreases (-2% and -9.5%, relatively) when compared to the coal mine water solution. Given the low overall net change, it is possible that these concentration fluctuations are due to reactions within the water itself instead of reactions with the cement core.

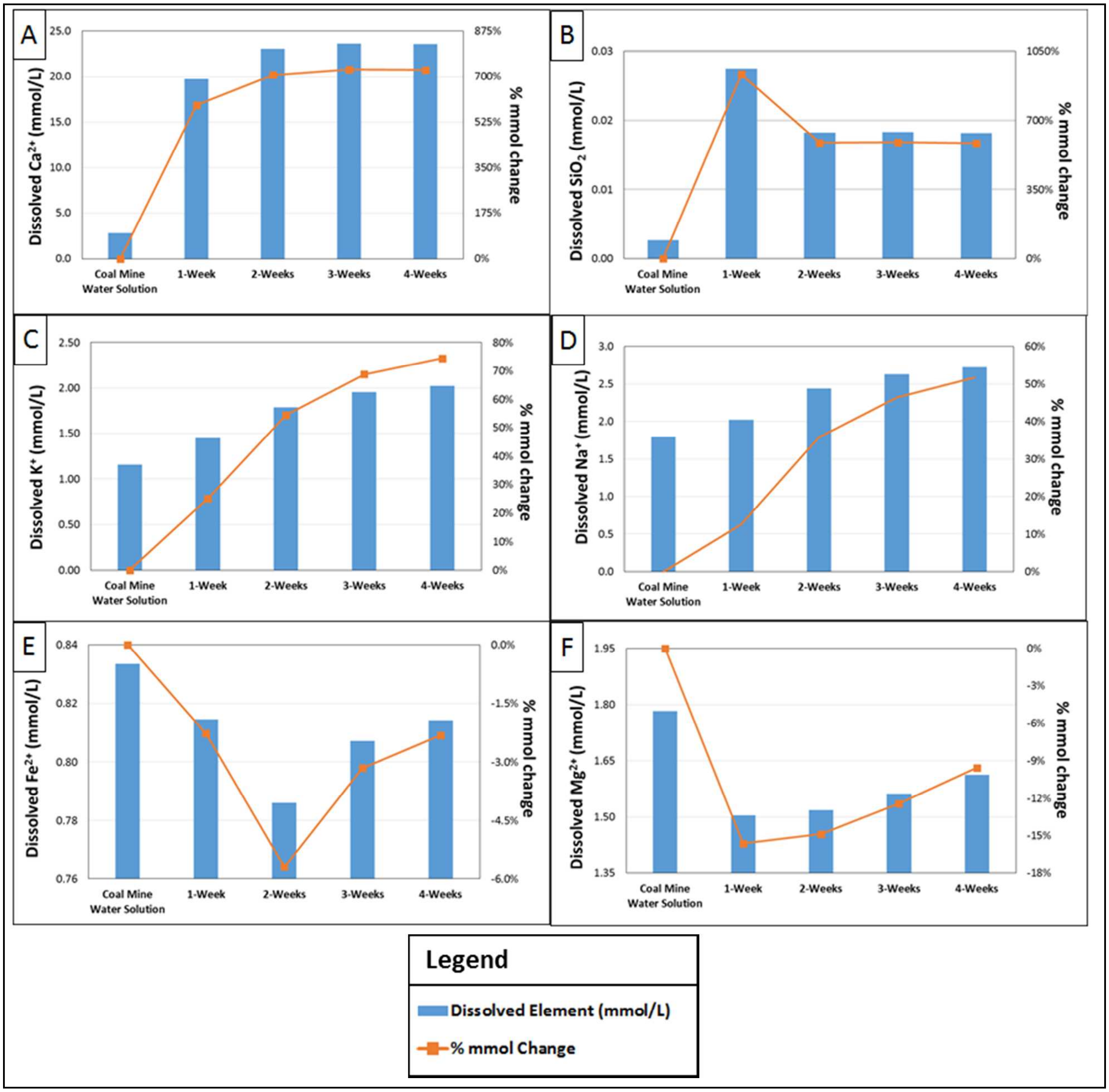


Figure 7. Dissolved cation and silica-dioxide concentrations of the starting solution and the effluents from the static reaction vessels. The concentration (mmol/L) and the percent change relative to the coal mine water solution are plotted for dissolved constituents including (A) calcium, (B) silica-dioxide, (C) potassium, (D) sodium, (E) iron, and (F) magnesium

The measured anions, chloride and sulfate, display the largest net decreases among measured species (Table 1, Figure 8A, B). Chloride concentrations decline steadily in the 1, 2, 3, and 4-week effluents, resulting in a large net decrease (-71%). Sulfate concentrations also display consistently lower concentrations and a large net decrease (-88%) from the starting solution (3.94 mmol/L) to the 4-week effluent (0.48 mmol/L). The sulfate concentrations display small changes between the later samples, suggesting that reactions between the coal mine water and the cement core involving sulfate are becoming less common. Overall, these declining concentrations suggest that chloride and sulfate ions from the coal mine water may be forming different precipitates in and around the cement core.

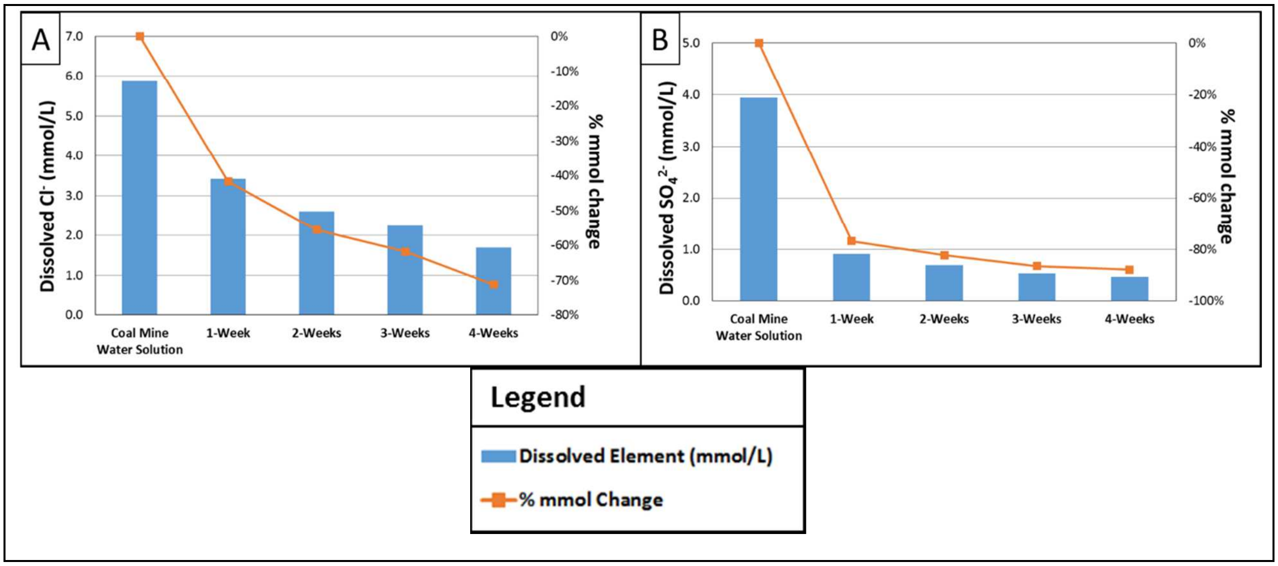


Figure 8. Dissolved anion concentrations of the coal mine water solution and the effluent from the static reaction vessels. The concentration (mmol/L) is plotted along with the percent change relative to the coal mine water solution for (A) chloride and (B) sulfate.

## Conclusions

A lab-generated coal mine water affected the permeability, porosity, and mineralogy, porosity of Class H Portland cements over a four week exposure period. Permeability measurements tended to increase over the exposure period, suggesting that the coal mine water was enhancing pore-connectivity. These permeability measurements, coupled with SEM observations of increased void space and cracks in the cement cores exposed to the coal mine water solution, suggest that coal mine water could create small-scale vertical pathways along wellbore cement over the course of four weeks.

Chemistry data suggest that there are several species involved in dissolution-precipitation reactions between the coal mine water and the cement core, including calcium, potassium, sodium, chloride, and sulfate. The reactions involving calcium are dominant. SEM images and solution chemistry data indicate that increased exposure to coal mine water resulted in pH driven calcium leaching from the unhydrated cement grains as well as from the $Ca(OH)_2$ and the C-S-H phase of the cement matrix. Cement permeability measurements increased with increased exposure to coal mine water and are likely related to the dissolution of these cement components.

Dissolution reactions are also coupled with precipitation reactions inside the cement core, as the leached calcium ions tend to form calcite crystals near the rim of the cement core. These calcite crystals at the rim sit in a matrix of decalcified, amorphous silica gel. With prolonged exposure, it is possible that this reaction will continue toward the center of the cement core at an undetermined rate. The continuation of this reaction could cause the cement to lose its structural integrity, as calcium leaching has been shown to decrease cement strength.

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