

CO₂ Sequestration in Unmineable Coal Seams: Potential Environmental Impacts

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ABSTRACT:

An initial investigation into the potential environmental impacts of CO₂ sequestration in unmineable coal seams has been conducted, focusing on changes in the produced water during enhanced coalbed methane (ECBM) production using a CO₂ injection process (CO₂-ECBM). Two coals have been used in this study, the medium volatile bituminous Upper Freeport coal (APCS 1) of the Argonne Premium Coal Samples series, and an as-mined Pittsburgh #8 coal, which is a high volatile bituminous coal. Coal samples were reacted with either synthetic produced water or field collected produced water and gaseous carbon dioxide at 40 °C and 50 bar to evaluate the potential for mobilizing toxic metals during CO₂-ECBM/sequestration. Microscopic and x-ray diffraction analysis of the post-reaction coal samples clearly show evidence of chemical reaction, and chemical analysis of the produced water shows substantial changes in composition. These results suggest that changes to the produced water chemistry and the potential for mobilizing toxic trace elements from coalbeds are important factors to be considered when evaluating deep, unmineable coal seams for CO₂ sequestration.

Keywords: Geological sequestration, CO₂ sequestration, coalbed methane

INTRODUCTION:

Geological sequestration is an immediately available and technologically feasible option for sequestering CO₂. [White, et al. (2003); Bustin and Clarkson (1998)] Among the many geological CO₂ sequestration options currently being studied, CO₂ enhanced oil recovery (EOR) and CO₂ enhanced coalbed methane production (CO₂-ECBM/sequestration) are two of the most promising options. CO₂-ECBM/sequestration is attractive because methane is a valuable commodity and laboratory results suggest that at least two to three molecules of CO₂ can preferentially adsorb onto the coal for each one molecule of CH₄ released. There are regionally large unmineable coal seams capable of accepting large volumes of CO₂ (90 billion metric tones of CO₂ [Reeves (2003)]) directly from power plants without the need for long transport pipelines. Therefore, sequestration of CO₂ into unmineable coal seams is an important strategy for the mitigation of global warming. [DOE/SC/FE-1 (1999); Smith (1999)]

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Coalbed methane is unique in that it is retained in a number of ways including 1) adsorbed molecules within micropores (< 2 nm in diameter); 2) trapped gas within matrix porosity; 3) as a solute in ground water within coal fractures; and 4) infrequently as free gas, i.e. gas in excess of that which can be adsorbed, in the cleats and fractures.[Bustin and Clarkson (1998)] Nearly all coal seams contain some water either from inherent or adjacent aquifer sources.[Byrre and Guthrie (1998)] In order for coalbed methane to be produced from water-saturated coal seams, the pressure exerted by the gas phase has to be equal to that of the water. Normally, water pressure is greater than the gas pressure in the virgin methane reservoir. As water is removed from the cleat system, the pressure in the coal is reduced until the water pressure equals the gas pressure; then, methane gas is desorbed from the coal matrix (i.e. the micropore system) to the adjacent cleats (the macropore system). Usually, large quantities of water have to be extracted from the coalbed before the desorption pressure is reached. Degasification of coal is a two-step process: first, desorption of the gas from the coal matrix, followed by flow of the gas and water through the cleats to the production well.[Gunter, et al. (1997)]

Huge amounts of water (billion barrels/year) are produced during coalbed methane (CBM) and enhanced coalbed methane (ECBM) production.[Davidson, et al. (1995)] Generally, the produced water is brackish water or brine containing substantial amounts of Na^+ , Cl^- , HCO_3^- , and other dissolved solids and organics. On average, for wells in the USA, coalbed CH_4 produces approximately 1.74 cm^3 of water per m^3 of gas.[Davidson, et al. (1995)] The total dissolved solids associated with produced water from CBM wells range from 200 to 170,000 mg/L with values typically less than 30,000 mg/L. Their pH generally ranges between 7 & 8. Typical anions include $\text{CO}_3^{=}$, HCO_3^- , Cl^- , and $\text{SO}_4^{=}$ and cations include Na^+ , K^+ , Ca^{++} , and Mg^{++} in amounts that vary considerably. Trace element concentrations in CBM produced water are generally low and CBM produced water is generally of better quality than waters produced from conventional oil and gas wells.[Rice & Nuccio (2000)]

Burlington Resources performed a large scale CO_2 -ECBM/sequestration field test in the Allison Unit of the San Juan Basin in northern New Mexico.[Reeves, et al. (2002)] The field test showed that water production increased substantially when CO_2 injection was restarted and the CH_4 production was increased by CO_2 injection, and CO_2 was sequestered. However, the physical, chemical, thermodynamic phenomena, and the environmental impact of the produced water occurring during the process remain poorly understood.[White, et al. (2003)]

White and coworkers (2003) summarized three types of chemical changes that have been proposed to occur during a CO_2 -ECBM process: extraction of small molecules trapped within the macromolecular network by the flowing CO_2 , dissolution of associated minerals, and extraction of calcium and magnesium from the coal. Kolak and Burruss (2004) studied the effect of coal rank on the potential environmental impacts of CO_2 sequestration in deep coal beds, and experimentally demonstrated the potential of supercritical CO_2 for mobilizing hydrocarbons from the coalbed at 40°C and 100 bar. It is well known that high-pressure CO_2 and water can have a profound effect on the mineral matter present in coal; various minerals present in coal, such as alkaline earth metal aluminosilicates and carbonate minerals (calcite, dolomite, etc.), are soluble in acidic aqueous solution. Hayashi and coworkers (1991) reported the removal of Ca and Mg from several low-rank coals by batch extraction with CO_2 and showed that Ca extraction depends on the amount of water present.

During CO₂-ECBM, it is likely that the water content of the coal will initially decrease with time. The coal will most probably be dewatered before CO₂ injection, removing some of the bulk water in the cleat system. After CO₂ injection begins, the remaining water in the cleat system and the water present in the pores will likely be further reduced. Depending on the depth of the coal seam, the pressure-temperature conditions in deep coal beds may be above the critical temperature and pressure of CO₂. It has been reported that supercritical CO₂ can remove 83-96% of the moisture content from coal samples in a relatively short period of time.[Iwai, et al. (1998)]

Current treatment of produced water varies depending on its chemical composition and the intended water use. Surface discharge, impoundment, shallow reinjection, and active treatment with reverse osmosis with subsequent trucking and deep disposal of the residual are the four common ways used for disposal of produced water in the Powder River Basin coalbed methane field.[DOE/NETL-2003/1184] The amount of CBM water produced is dependent on the stage of production. It usually decreases as the production period increases. The ratio of CBM water to methane (MBbl/day to MMcf/day) can be between 1.75 to 2.88.[DOE/NETL-2003/1184] Produced water from CBM recovery is usually disposed of by reinjection into another formation or surface disposal, depending upon the water quality. Surface discharge is possible, in part, because the concentration of hazardous trace elements in CBM produced water is generally less than the drinking water standards. The water quality affects the treatment and disposal options. Re-injection into depleted gas reservoirs is widely applied in the San Juan basin, while in the Black Warrior basin surface discharge is commonly used. However, before produced water can be discharged it must be treated. The exact treatment is dependent upon the produced water quality and the local environmental regulations.[White, et al. (2005)] For mines located near fresh water bodies or other vulnerable areas, surface water disposal may not be environmentally acceptable. One possible concern for future CO₂-ECBM/sequestration sites is that changes to the composition of the produced water caused by CO₂ injection may preclude use of existing treatment techniques.

Under the conditions of CO₂-ECBM/sequestration, substantial additional carbonic acid and bicarbonate ion are expected to form in the formation water. This acidic water/brine will dissolve/react with part of the mineral matter in the coal, and these dissolved minerals will likely be transported through the coal seam and eventually recovered in the produced water. As the water content decreases, the amount of Ca and Mg removed will decrease. If water migrates back into the seam, then Ca and Mg removal could increase due to displacement of Ca and Mg from carboxylic acids, especially in low rank coal. The rate and extent of these processes are unknown, but they can be expected to result in changes in composition in the produced water.[White, et al. (2005)] Supercritical CO₂ and acidic, carbonated water may also affect the concentration of dissolved organics in the water. This is in contrast to typical waters from current CBM recovery wells that generally have much lower concentrations of dissolved organics than water recovered from natural gas wells.[White, et al. (2005)] One potential concern is that these produced waters from CO₂-ECBM/sequestration sites may contain increased levels of hazardous trace metals relative to current produced water due to the increased acidity and altered solvent properties caused by high pressure CO₂. Jaffe and Wang (2003, 2004) have shown that if leaking CO₂ reaches shallow drinking water aquifers, it could result in harmful effects on water quality by dissolution of trace metals: specifically, these authors simulated effects of CO₂-induced pH changes on lead mobilization from galena. To experimentally evaluate the potential environmental impacts of CO₂ sequestration in coal seams, an exploratory study of the extraction of metals from coal by CO₂ and synthetic produced water was conducted and is described in this paper.

EXPERIMENTAL:

Two coal samples were used in this study, the Upper Freeport coal (APCS 1) of the Argonne Premium Coal Samples series, and an as-mined Pittsburgh seam coal collected from Bruceton, PA. Detailed analyses of the coal itself were not performed for these preliminary tests: however, characterizations of Pittsburgh #8 coal from the Penn State Coal Sample Bank are published, [Wang, et al. (2000)] and a detailed chemical analysis of the Argonne Premium Coal Sample series was performed by the U.S. Geological Survey [Palmer (1997)].

Synthetic coalbed methane produced water (SPW) was prepared from reagent grade salts to replicate the major and minor element composition for coalbed methane produced water reported by Davidson and coworkers (1995). A field sample of coalbed methane produced water (CBMW) was collected from the separator vessel at Consol Energy's carbon sequestration field test site in Marshall County, WV. This water was produced from a depth of 436 m (1430 ft.). The depth interval for CO₂-ECBM is expected to be the same as that for CBM production, i.e., 1000 to 5000 ft (305 to 1524 m).[White, et al. (2005)] Regression analysis of existing gas well data yields a temperature range of 23° to 45°C and a hydrostatic pressure range of 32 to 160 bar at these depths. Reactor conditions for this study were selected within this range.

The first series of experiments were carried out in a ½ -liter autoclave (Hastelloy C-276) manufactured by Progressive Equipment Corp. In a typical experiment, the reactor was charged with 70 grams of the nominally 1/2" (12.5 mm) size Pittsburgh seam coal sample and 150 mL of synthetic produced water in a total available reactor volume of 320 mL. The reactor was then purged/evacuated with nitrogen three times to remove any residual oxygen. Finally, a predetermined amount of CO₂ or N₂ was charged into the reactor to achieve the desired testing pressure ($P_{\text{Total}} \sim 50$ bar). The coal-water-gas mixture was heated to 40°C and maintained for seven days. Upon completion of each experiment, the reactor was cooled to room temperature, the remaining gas was vented, and the slurry removed. A digital pH meter (Sentron-1001 pH) was used to determine the pH of the produced water before and after reaction. A portion of the supernatant liquid was reserved for analysis, and then the liquid and solids were separated using a 0.45 micron membrane filter (Millipore - type HA). Filtration was aided by reduced pressure provided by a water aspirator. The collected coal pieces were rinsed with a small amount of deionized water, and then dried in a nitrogen-purged oven at 110°C. A small quantity of fine material remained on the membrane filter, but was not recovered. Portions of the filtered solutions were acidified (pH < 2.0) by adding trace metal grade nitric acid.

The second series of experiments were carried out in a set three identical 1.3-liter autoclaves (17/4PH-1150 stainless steel) manufactured by Thar Technologies, Inc. Two of these reactors were charged with 100 grams of the nominally 1/2" (12.5 mm) size Upper Freeport Argonne Premium Coal sample and 500 mL of the CONSOL produced water which had been deoxygenated under N₂ at slightly reduced pressure. The third reactor was loaded with only the 500 mL of deoxygenated CONSOL produced water. Each of the reactors was then purged/evacuated with nitrogen three times to remove any residual oxygen. Finally, a predetermined amount of CO₂ or N₂ was charged into each reactor to achieve the desired testing pressure ($P_{\text{Total}} = 53.4$ bar). The coal-water-gas mixtures were heated to 30°C and maintained for seven days. These Thar autoclaves are fitted with a sampling port which allowed removal of a portion (c. 100 mL) of the produced water for analysis after 24 hours reaction time (test pressure was reestablished by the addition of further CO₂ or N₂

after sampling). Upon completion of each experiment, the remaining gas was vented, and the slurry removed. The liquid and solids were separated, a portion of each supernatant liquid was reserved for anion analysis, and then the remainder acidified for metals analysis. The collected coal pieces were rinsed with a small amount of deionized water, and then dried in a nitrogen-purged oven at 40°C.

Metal concentrations were determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Perkin Elmer Optima 3000 ICP spectrometer. A low-flow gem cone nebulizer was employed so that solids loading could be accommodated, and a glass cyclonic spray chamber was employed to minimize contamination between analyses. The determinations were performed using an online internal standard to correct for variations during sample introduction. The reproducibility of the analytical results for metal cations by ICP is approximately 3 %; however, for samples containing suspended solids or colloids considerable additional uncertainty is introduced as the subsample is removed for digestion and dilution. Due to the high concentrations of alkali and alkaline earth metals in these solutions significant dilution was required; these dilutions were prepared using trace metal grade nitric acid in distilled, deionized water. The analysis of the CONSOL field sample of produced water reported below represents the average of twelve replicate determinations. The Series 1 solutions were analyzed only singly except for the synthetic produced water which was analyzed in triplicate, but four replicate determinations were analyzed for the Series 2 test solutions. Mercury was determined by cold-vapor atomic absorption (CVAA) from digested samples diluted 10-fold in 10% nitric acid. Reproducibility of mercury determination by CVAA at the sub-ppb level is *c.* 10 % in the absence of chemical species that interfere with tin chloride reduction of the Hg in solution.

Anion analysis was performed using a Dionex DX-600 ion chromatograph equipped with an electrochemical detector. The analytical column was a Dionex 4 mm IonPac AS11-HC with an IonPac AG11-HC guard column. A self-regenerating ASRS-Ultra suppressor was used. The eluent was 1 mM to 60 mM potassium hydroxide generated as needed using an EG-40 generator. Both linear (30 mM KOH) and multi-step gradient analyses were performed at 30 °C using an eluent flow rate of 1.5 mL/min. For Series 1, sample dilution necessary to determine chloride was 1/500; samples were analyzed at 1/50 and 10/25 dilutions to determine the fluoride, bromide, nitrate, and sulfate. Carbonate ion was resolved from the other analytes, but was not quantifiable because of CO₂ loss during sample filtration. For Series 2, sample dilution necessary to determine chloride was 1/2000; samples were analyzed at 1/20 and 10/25 dilutions to determine the fluoride, bromide, nitrate, sulfate, phosphate, thiosulfate, chromate, and iodide. One further dilution was also required for the samples reacted with coal to quantify higher concentrations of sulfate. Quantization limits, calculated at a 95% confidence interval (determined by weighted linear least-squares regression analysis of the individual anion calibration curves), ranged from 0.07 ppm to 0.3 ppm in an undiluted sample, and were raised according to the dilution necessary as noted with the results.

X-ray diffraction (XRD) characterization of the solid reaction products was conducted using a PANalytical X'pert Pro powder diffractometer with a Cu X-ray source at 45 kV and 40 mA. The coal samples were crushed and mounted as powders on glass sample holders for analysis. The XRD patterns were typically recorded over a 2 θ range of 8° to 70°. Phase identification was verified by comparison to the ICDD inorganic compound powder diffraction database.

Pieces of the coal samples were also selected for optical microscopic examination. The selected pieces were placed in one inch diameter plastic sample cups and surrounded by epoxy. The epoxy

was allowed to harden overnight and the samples were ground and polished following standard coal petrographic preparation procedures to produce a surface for optical microscopic examination. The samples were ground on 240, 400, and 600 grit silicon carbide papers, and then polished with 0.5 micron and 0.05 micron alumina suspension. The samples were observed using a Leitz Orthoplan research microscope with reflected light and a 20x oil immersion objective. Total observed magnification was 200x. Photomicrographs of selected areas were taken with a Canon PowerShot G5 digital camera.

RESULTS:

Conditions for the individual experiments and the measured pH values are given in Table 1. As can be seen from the table, the pressure of CO₂ decreased during the first series of experiments due to solubility in the SPW and reaction with the solution and coal. In the second series of experiments, the pressure was maintained at constant pressure by addition of further CO₂. The synthetic produced water was initially prepared using sodium carbonate to supply all of the dissolved bicarbonate/carbonate: this resulted in a solution with higher pH than is typical of produced water. The synthetic produced water was tested both as prepared, and after a suitable pH adjustment with hydrochloric acid. The pH tabulated for the field sample of coalbed methane produced water is for the stored, deoxygenated sample used for these test; the pH value at the time of collection in the field was 5.405 at 22°C.

Table 1.

	Reactants	Initial pH	Supernate pH	Filtrate pH	P _T Initial (bar)	P _T Final (bar)
Series 1						
1	CO ₂ + SPW	10.73	6.08	6.06	50.9	46.3
2	N ₂ + SPW + coal	10.73	6.30	6.75	52.9	52.7
3	CO ₂ + SPW + coal	10.73	6.07	6.50	48.6	43.7
4	CO ₂ + SPW + coal	7.74	5.72	6.24	49.1	43.5
5	N ₂ + SPW + coal	7.56	6.25	7.20	54.0	53.2
Series 2						
1	CBMW + N ₂	6.48	6.68		53.4	53.4
2	CBMW + N ₂ + coal	6.48	6.02		53.4	53.4
3	CBMW + CO ₂ + coal	6.48	4.91		53.4	53.4

Series 1: Synthetic Produced Water with Pittsburgh #8 As-Mined Coal

Microscopic examination of the post-reaction samples clearly indicated that there were physical changes on the coal surface. The coal samples reacted with CO₂ and synthetic produced water showed a multi-colored stain along the cleats and fractures (see Figure 1). These stains could be followed along the length of the fractures, and indicate sites where there were chemical reactions between coal minerals and the mixture of synthetic produced water and CO₂. Some of the stains appeared to be more intense (not shown) along boundaries of larger fractures. However, after the seven day reaction period, there were still locations in the samples where it appeared that no reaction had taken place. These areas were usually located in a matrix of vitrinite.

X-ray diffraction (XRD) characterization of the Pittsburgh seam coal indicates that the mineral matter is approximately 75-80% amorphous. The crystalline minerals present, identified in Figure

2, are low symmetry quartz and kaolinite with small amounts of illite and marcasite. Figure 3 shows a comparison of the coal samples before and after reaction, illustrating the effect of exposure to CO₂-saturated produced water at two initial pH values. Partial loss of crystalline phases (quartz, kaolinite, and illite) is observed for Run 3, which was conducted with high initial pH. Essentially all of the crystalline minerals (illite, kaolinite, quartz, and marcasite) were removed in the sample from Run 4, which was conducted with an initial pH more typical of coalbed methane produced water. These experimental results with respect to clay minerals confirm the results predicted by simulation: White and coworkers (2005) predicted that illite and kaolinite would be dissolved from coal by formation water acidified by high pressure CO₂.

Table 2 compares the composition of the synthetic produced water before and after reaction with CO₂ and Pittsburgh seam coal. Also included for comparison are the National Drinking Water Standard limits and the recommended/average values for the Pittsburgh #8 Argonne Premium Coal. Table 3 compares the composition of the synthetic produced water before and after reaction with N₂ and Pittsburgh seam coal. Comparison of the analytical results obtained for the as-prepared synthetic produced water and the two pH-adjusted SPW samples (Runs 4 & 5) shows reasonable reproducibility except for somewhat high uncertainties in the determination of aluminum, silicon, and barium. This is consistent with well-known difficulties in the accurate determination of trace levels of aluminum and silicon, and reflects the fact that the as-prepared SPW was faintly turbid due to slight supersaturation with respect to barium sulfate. The trace elements silver, arsenic, molybdenum, lead, antimony, selenium, titanium, thallium, vanadium, and iodine remained below our quantization limits in all samples and have therefore been omitted from Tables 2 & 3. Also not shown are concentration results for chromium and nickel, two major components of Hastalloy C-276, which showed large increases in the SPW + CO₂ run without coal present and may have been elevated by corrosion damage to the reaction vessel. (Only the bottom portion of the reactor is teflon lined, the cap is not coated.)

In Run 1, the as-prepared synthetic produced water was allowed to react with CO₂ at 40 °C and 50 bar. The supernatant liquid (see Table 2) recovered from this run contained appreciably less calcium, barium, and copper than was present in the starting produced water suggesting possible segregation of precipitated calcite from the slurry during sampling. The liquid filtrate (see Table 2) contained substantially decreased amounts of calcium, iron, barium, and boron compared to the as-prepared SPW. Also significantly decreased were the trace elements: cobalt, copper, and manganese. This is consistent with calcite and hydrous iron hydroxide precipitation and partial loss of trace elements due to coprecipitation/occlusion. Unfortunately, significant concentration *increases* were also observed for strontium, aluminum, fluoride, bromide, and sulfate, and for the trace elements zinc, and phosphorus in both the supernate and filtrate samples. These observed increases in certain elements may have been introduced from some contamination of the sample by carryover from a previous, unrelated experiment known to contain substantial amounts of these elements.

For the nitrogen-SPW-coal runs (Table 3), the supernatant liquid contains substantially increased amounts of iron, sulfur/sulfate, and aluminum. The increased amounts of iron and sulfur/sulfate are consistent with the pyrite/marcasite oxidation in humid air [Jerz and Rimstidt (2004)] as the coal was being prepared, or in acidic solution [Descostes, et al. (2004)] during testing due to incomplete exclusion of dissolved oxygen from the synthetic produced water. The increased aluminum reflects the fact that our synthetic produced water was only an approximation of the natural fluid, and not in

equilibrium with the mineral phases of the coal. Also significantly increased are cobalt, manganese, and zinc. The observed concentration increase of these transition metals may have been due to impurities from the dissolved pyrite/marcasite; however, contamination of the sample by corrosion damage to the reactor cannot be ruled out since cobalt and manganese are minor components of Hastalloy C-276. The liquid filtrate, however, shows substantially *decreased* amounts of aluminum, boron, barium, calcium (Run 2), iron, and silicon (Run 2) compared to the as-prepared SPW. In the pH adjusted SPW (Run 5), the calcium and silicon concentrations remain unchanged by sample filtration. Only sulfur/sulfate, bromide, and phosphorus are increased in comparison to the as-prepared SPW. This is consistent with precipitation of hydrous iron hydroxides, barium sulfate and possibly calcium sulfate (Run 2), and partial loss of minor and trace elements due to coprecipitation/occlusion.

For Run 3, reaction of CO₂ and coal in the as-prepared SPW, the supernatant liquid contains substantially increased amounts of iron, sulfur/sulfate, aluminum, potassium, strontium, and bromide. Also significantly increased are the trace elements: cobalt, manganese, and zinc. Comparison of the supernatant liquid from Run 3 to that from the run without coal shows increased calcium, iron, potassium, bromide, and sulfur/sulfate. The trace elements cobalt and manganese are also increased relative to the run without coal. The concentration of barium, silicon, and fluoride, and of the trace elements copper, phosphorus, and zinc are significantly lowered in the supernatant liquid from Run 3 when compared to the run without coal. Once again, the observed compositional changes in the SPW are consistent with pyrite oxidation, partial dissolution of other coal minerals, and possible leaching of calcium from the coal matrix. The composition of the liquid filtrate from Run 3 is quite similar to that of the supernate except for aluminum, iron, cobalt, and copper. This is consistent with precipitation of hydrous iron hydroxides, and partial loss of these trace elements due to coprecipitation/occlusion. Comparison of the filtrate from Run 3 to the run without coal shows substantially higher concentrations of calcium, iron, potassium, and sulfur/sulfate. The trace elements cobalt and manganese are also increased in the filtrate relative to the concentration observed without coal present. Concentrations of aluminum, silicon, and barium were significantly decreased in the filtrate from Run 3 compared to the filtrate from the run without coal present.

For Run 4, reaction of CO₂ and coal in the pH-adjusted SPW, the supernatant liquid contains substantially increased amounts of iron, sulfur/sulfate, calcium, aluminum, silicon, strontium, and bromide compared to the as-prepared, pH-adjusted SPW. Also significantly increased are the trace elements: beryllium, cadmium, cobalt, mercury, manganese, and zinc. Supernate concentrations of barium and boron are decreased compared to the starting SPW. The composition of the liquid filtrate from Run 4 is quite similar to that of the supernate. Comparing the supernatant liquid from Run 3 to that from Run 4 shows that adjusting the pH downward to a value more characteristic of the pH of typical CBM produced waters significantly increased aluminum, iron, and the trace metal manganese, but decreased sulfur/sulfate and bromide. Comparing the filtrates from these two runs shows that adjusting the pH downward significantly increased the aluminum, iron, and barium, and the trace metals cobalt, and manganese remaining in solution, but decreased sulfur/sulfate and bromide.

Comparison of the supernatant liquid compositions from runs with CO₂ to those with N₂ shows that carbon dioxide addition significantly increased the dissolution of aluminum (initial pH = 7.6), calcium, potassium, strontium, bromide, and possibly zinc, but may have decreased copper dissolution. Comparing the filtrates from these runs shows that CO₂ addition significantly increased the aluminum, barium, calcium, iron, potassium, strontium, and bromide and the trace metals

copper, manganese, and zinc remaining in solution, but may have decreased sulfur/sulfate.

Series 2: Field-Collected Coalbed Methane Produced Water with Upper Freeport Argonne Premium Coal Sample

X-ray diffraction (XRD) characterization and microscopic examination of the post-reaction samples of the Upper Freeport premium coal indicates were similar to those described above; the mineral matter is primarily amorphous with some crystalline low symmetry quartz, kaolinite, and small amounts of illite and pyrite. Comparison of these coal samples before and after reaction also showed partial loss to near complete removal of crystalline phases during reaction. The “stained” reaction front along the cleats and fractures was less pronounced, however.

Table 4 compares the composition of the CONSOL coalbed methane produced water before and after reaction with Upper Freeport coal with and without CO₂ present. Vessel 1 results constitute a reactor blank with only produced water and nitrogen charged to the autoclave. Also included for comparison are the National Drinking Water Standard limits (values shown in parenthesis are National Secondary Drinking Water Regulation guidelines), and the recommended/average values for the Upper Freeport Argonne Premium Coal. As was pointed out above, the analytical results obtained for the coalbed methane produced water are the average of twelve replicate determinations and show reasonable reproducibility except for high uncertainties in the determination of aluminum, silicon, boron, copper, and zinc. This is consistent with well-known difficulties in the accurate determination of trace levels of aluminum, silicon, and boron. These results also indicate a possible interference in our procedures which preclude accurately determination of trace copper or zinc. The trace elements silver, cadmium, molybdenum, titanium, vanadium, and fluoride remained below our quantization limits in all samples and have therefore been omitted from Table 4. Also not shown are concentration results for phosphate ion which remained below our quantization limit of 0.4 mg/L in all anion samples.

Comparing the water composition for the reactor blank experiment (Vessel 1) to the as-received produced water shows an increase in concentration for each of the constituents of the 17/4PH-1150 stainless steel except phosphorus which decreased. Lead and iodide ion were also increased in the blank. For the nitrogen+CBMW+coal test (Vessel 2), the post-reaction solution contains substantially increased amounts of calcium, sulfur/sulfate, cobalt, chromium, iron, manganese, and nickel (with the components of the stainless steel being substantially higher than for the reactor blank). The increased amounts of iron and sulfur/sulfate are consistent with the pyrite oxidation as discussed above, despite precautions to improve exclusion of dissolved oxygen from the produced water and to avoid exposing the Argonne premium coal sample to room air prior to charging it to the vessels. The increased calcium concentration (and possibly the trace metals) reflects the fact that our produced water was not in equilibrium with the mineral phases of this coal sample, even though both were from the Freeport seam. The reaction liquid shows substantially decreased amounts of barium and phosphorous compared to the as-received CBMW. It is also interesting to note that for several of the minor and trace metals and for sulfur/sulfate the concentration after 24 hours reaction time is substantially higher than for seven days, suggesting initial dissolution from the coal followed by reprecipitation into other phases.

For the reaction of CO₂ and Upper Freeport coal in the CBMW, the solution contains substantially increased (relative to the N₂ only tests, both the produced water only *and* the CBMW + coal tests) amounts of calcium, magnesium, iron, sulfur/sulfate, and aluminum. Also significantly increased

are the trace elements: arsenic, beryllium, chromium, mercury, and thallium. Comparison of the analyses after one day and one week shows increased cobalt, manganese, and nickel remained in the solution phase after one week when bicarbonate was present. Once again several of the minor and trace metals and for sulfur/sulfate concentrations after seven days are substantially lower than for initially measured for 24 hours reaction, suggesting initial dissolution from the coal followed by reprecipitation into other phases. As was observed for the first series of tests, these compositional changes in the CBMW are consistent with pyrite oxidation, partial dissolution of other coal minerals, and possible leaching of calcium from the coal matrix, followed by precipitation of hydrous iron hydroxides and metal sulfates with partial loss of some trace elements due to coprecipitation/occlusion.

CONCLUSIONS:

Petrographic analysis of the post-reaction coal samples clearly showed tracks of mobility along the face and butt cleats of Pittsburgh seam coal reacted with CO₂ gas and synthetic coalbed methane produced water. Partial to near complete loss of crystalline mineral phases in the post reaction coal samples were observed by XRD analysis for both Pittsburgh seam coal and the Upper Freeport Argonne premium coal. Mineral dissolution was due, at least in part, to the fact that neither the "average" produced water simulated nor field-collected coalbed methane produced water from another depth/location is necessarily in equilibrium with the minerals present in the coal sampled. For example, this is especially true for the aluminosilicate minerals since in the case of synthetic produced since aluminum and silicon were not specifically added, and the equilibrium concentration of these elements in groundwater is known to be quite sensitive to temperature and pressure. Changes in the composition of the synthetic and field-collected produced waters provide evidence of numerous chemical reactions, including pyrite oxidation and dissolution, and calcium extraction. Also, the addition of CO₂ to the system contributed to further lowering of the pH, in addition to the pH decrease resulting from oxidation/dissolution of pyrite and precipitation of hydrous iron hydroxides, which contributes to enhanced dissolution of the mineral phases identified. Comparison of synthetic produced water compositions for SPW + Pittsburgh #8 coal runs with and without CO₂ addition shows obvious enhancement in the dissolution of several major and minor elements from the coal matrix, including aluminum, barium, calcium, iron, potassium, strontium, and bromide. Comparison of field-collected coalbed methane produced water compositions for CBMW + Upper Freeport premium coal tests with and without CO₂ addition shows similar obvious enhancement in the dissolution of several major and minor elements from the coal matrix, including aluminum, calcium, magnesium, iron, and sulfur/sulfate.

Evaluation of mobilization of trace elements from these experiments is complicated by the oxidation of pyrite/marcasite and by the quenching to room temperature & pressure and further loss of CO₂ during the filtration that was necessary for analysis. For example, the run with only synthetic produced water and CO₂ showed significantly decreased amounts of calcium, iron, barium, and boron and the trace elements cobalt, copper, and manganese in the post-reaction solution, indicating hydrous iron hydroxide and perhaps calcite precipitation and partial loss of trace elements due to coprecipitation/occlusion. In the second series of tests with improved oxygen exclusion, trace element mobilization was examined by comparing N₂-only tests, both the produced water only *and* the CBMW + coal tests, to the reaction of CO₂ and Upper Freeport coal in the CBMW. In this series, substantially increased concentrations of the trace elements arsenic, beryllium, chromium, mercury, and thallium were observed, but once again results suggest initial dissolution of some mineral phases from the coal followed by reprecipitation of minor and trace

elements into other phases. In actual CO₂-ECBM operations, iron sulfide oxidation may be avoided if the CO₂ to be sequestered does not contain dissolved oxygen. Significant concentration increases were observed for the trace elements arsenic(UF), beryllium, cadmium(PITT), chromium(UF), mercury, thallium(UF), and zinc(PITT), and probably also for cobalt, manganese and nickel. Observed increases in aluminum, iron, arsenic, cadmium, and chromium are potentially of concern, but beryllium and mercury remained below drinking water standards.

DISCLAIMER

Reference in this paper to any specific commercial product, process, or service is to facilitate understanding and does not imply endorsement by the United States Department of Energy.

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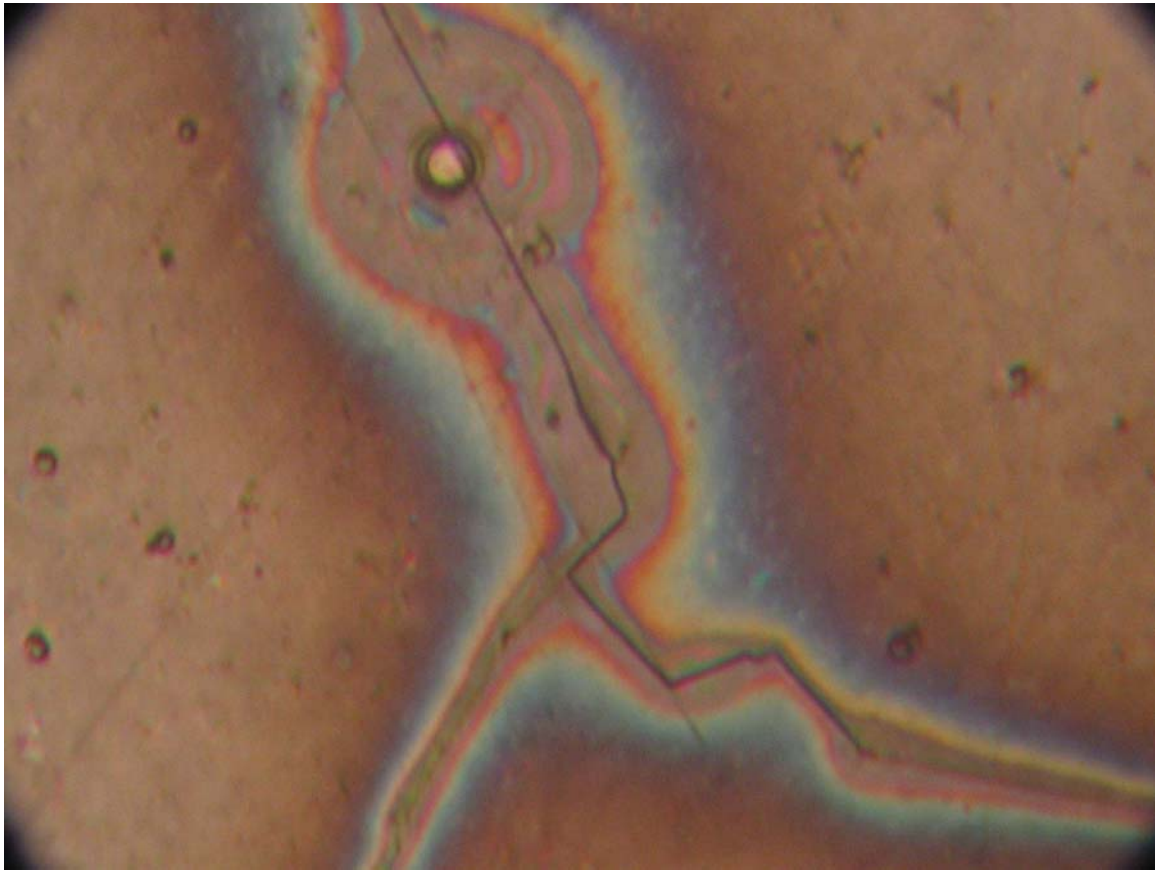


Figure 1. Reaction Stain following fracture (cleat) in Run 3 Sample — = 20 microns

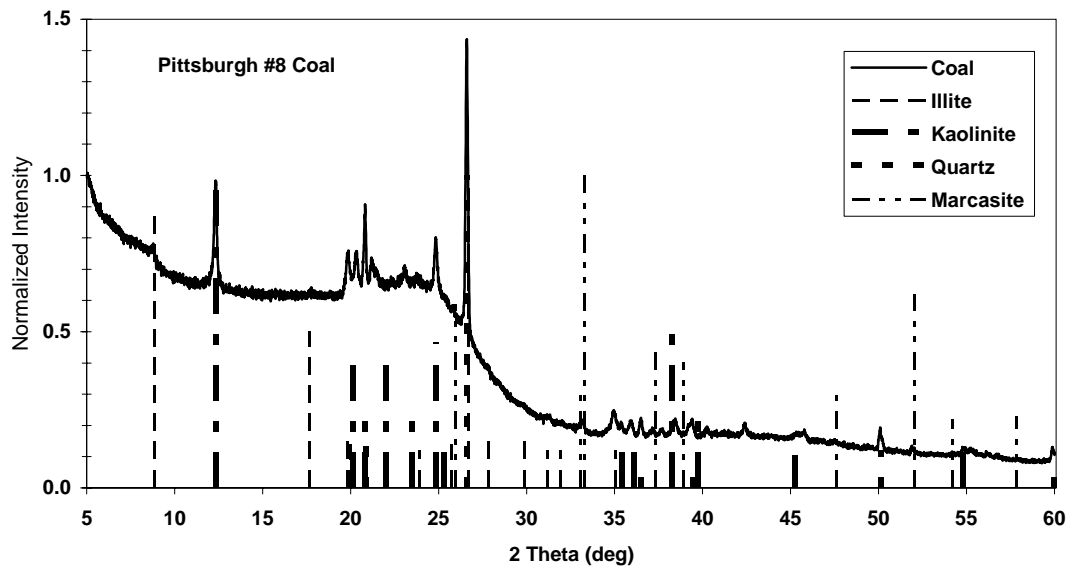


Figure 2. XRD of Pittsburgh seam coal with mineral phases identified.

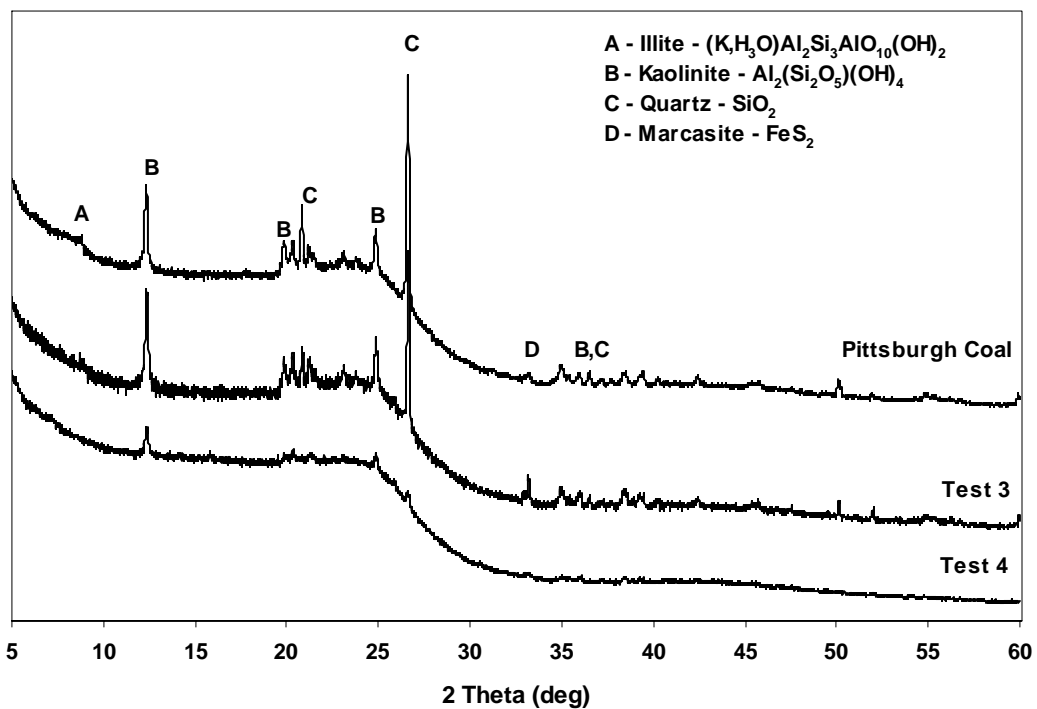


Figure 3. Comparison of the as-received coal and reacted coal from Runs 3 and 4.

Table 3.		Calculated Composition	As Prepared Produced H ₂ O pH = 10.73	Run 2 Supernate pH = 6.3	Run 2 Filtrate pH = 6.75	Run 5 pH Adjusted H ₂ O pH = 7.56	Run 5 Supernate pH = 6.25	Run 5 Filtrate pH = 7.2
major & minor elements								
Al	mg/L		0.84	1.61	0.44	0.60	2.30	0.72
B	mg/L		1.86	817	668			
Ba	mg/L	3.514	3.77	959	277	2.21	0.890	0.276
Ca	mg/L	89.12	91.0	78.5	27.3	52.1	104	105
Fe	mg/L	10.70	15.4	22.3	8.35	7.05	32.4	4.24
K	mg/L	9.645	11.0	10.2	10.0	9.19	11.5	11.4
Mg	mg/L	29.99	28.9	32.8	31.9	28.2	35.0	35.5
Na	mg/L	1910	2170	2230	2120	1940	2020	2020
S	mg/L	4.470	8.77	79.5	75.6	4.61	119	120
Si	mg/L		5.67	3.11	2.75	0.399	2.30	2.23
Sr	mg/L	3.788	3.35	4.51	2.83			
trace elements								
Be	μg/L		< 3	< 3	< 3			
Cd	μg/L		< 15	< 15	< 15			
Co	μg/L		39.3	82.2	< 30			
Cu	μg/L		251	155	119			
Mn	μg/L		71.5	370	59.8	34.0	613	571
P	μg/L		304	434	431	<150	268	<150
Zn	μg/L		180	737	163	2.6	4.78	4.49
anions								
F	mg/L	3.221	1.63	1.37	2.0			
Cl	mg/L	2499	2515	2698	2665			
Br	mg/L		0.44	0.59	0.80			
NO₃⁻	mg/L	5.362	6.10	6.32	6.97			
HCO₃⁻	mg/L	597.7						
SO₄⁼	mg/L	13.39	15.7	221	218			
PO₄⁻³	mg/L		<0.35	<0.35	<0.35			

Table 3. Comparison of the composition of synthetic coalbed methane produced water before and after reaction with Pittsburgh seam coal under 53 bar N₂ pressure.

Table 2		Calculated Composition	As Prepared Produced H ₂ O pH = 10.73	Run 1 Supernate pH = 6.08	Run 1 Filtrate pH = 6.06	Run 3 Supernate pH = 6.07	Run 3 Filtrate pH = 6.5	Run 4 pH Adjusted H ₂ O pH = 7.74	Run 4 Supernate pH = 5.72	Run 4 Filtrate pH = 6.24	EPA Drinking Water Standard	Pittsburgh # 8 Coal [13,18]		
major & minor elements														
Al	mg/L		0.84	1.60	1.48	1.83	0.75	0.44	4.77	3.30	(0.05)	9.9	mg/g	Al
B	mg/L		1.86	1.15	0.85	0.79	0.70	1.01	0.65	0.61		0.048	mg/g	B
Ba	mg/L	3.514	3.77	1.86	1.15	1.01	0.39	2.84	1.17	1.10	2	0.040	mg/g	Ba
Ca	mg/L	89.12	91.0	39.4	18.0	117	116	65.0	129	124		1.97	mg/g	Ca
Fe	mg/L	10.70	15.4	14.3	7.44	30.1	19.7	10.0	44.4	43.5		13.3	mg/g	Fe
K	mg/L	9.645	11.0	13.1	12.0	20.3	19.9	11.8	16.0	15.6	(0.3)	1.11	mg/g	K
Mg	mg/L	29.99	28.9	27.8	27.0	33.4	33.0	35.2	42.3	42.0		0.36	mg/g	Mg
Na	mg/L	1910	2170	2300	2190	2290	2220	2185	2340	2335		0.33	mg/g	Na
S	mg/L	4.470	8.77	10.5	13.3	93.3	91.5	5.43	51	51.4			mg/g	S
Si	mg/L		5.67	5.38	4.62	2.65	2.55	0.84	2.44	2.34		18.6	mg/g	Si
Sr	mg/L	3.788	3.35	9.65	8.07	9.15	8.95	2.68	6.92	6.79		0.064	mg/g	Sr
trace elements														
Be	μg/L		< 3	< 3	< 3	< 3	< 3	0.37	0.75	0.9	4	0.77	μg/g	Be
Cd	μg/L		< 15	< 15	< 15	< 15	< 15	3.0	5.8	6.4	5	0.08	μg/g	Cd
Co	μg/L		39.3	45.8	16.4	93.9	43.3	8.0	74.5	65.5		2.6	μg/g	Co
Cu	μg/L		251	141	141	81.8	188	131	105	109	1300	5.8	μg/g	Cu
Hg	μg/L							0.100	0.154	0.154	2	0.16	μg/g	Hg
Mn	μg/L		71.5	83.5	37.4	265	244	41.0	558	557	(50)	19	μg/g	Mn
P	μg/L		304	920	470	< 300	341	< 300	< 300	< 300		100	μg/g	P
Zn	μg/L		180	3970	2140	688	615	38.2	655	635	(5,000)	8.3	μg/g	Zn
Anions														
F	mg/L	3.221	1.63	2.34	2.98	1.17	1.69	1.38	1.39	1.35	4.0		mg/g	F
Cl	mg/L	2499	2515	2646	2643	2776	2755	2896	3018	3052	(250)	12.3	mg/g	Cl
Br	mg/L		0.44	0.89	1.19	1.22	1.33	0.37	0.68	0.66			mg/g	Br
NO₃⁻	mg/L	5.362	6.10	7.33	7.86	7.16	7.00	5.80	6.14	6.92	10		mg/g	NO₃⁻
HCO₃⁻	mg/L	597.7											mg/g	HCO₃⁻
SO₄⁼	mg/L	13.39	15.7	21.9	21.3	257	247	14.2	146	153	(250)	10.9	mg/g	S
PO₄³⁻	mg/L		<0.35	<0.35	<0.35	<0.35	<0.35	<0.35	<0.35	<0.35			mg/g	PO₄³⁻

Table 2. Comparison of the composition of synthetic coalbed methane produced water before and after reaction with CO₂ and Pittsburgh seam coal. The National Drinking Water Standard limits and the elemental analysis of Pittsburgh #8 coal are also included for comparison.

Table 4	CBMW	s.d.	Vessel 1				Vessel 2				Vessel 3				Drinking Water Standard	Upper Freeport [13]			
			Day 1	s.d.	Day 7	s.d.	Day 1	s.d.	Day 7	s.d.	Day 1	s.d.	Day 7	s.d.					
major & minor elements																			
Al	mg/L	1.69	1.25	0.42	0.27	0.34	0.08	12.1	0.2	1.04	0.03	32.1	0.3	11.6	0.1	(0.05)	15.8	mg/g	Al
Ba	mg/L	0.99	0.08	0.55	0.02	0.50	0.01	0.49	0.03	0.50	0.02	0.48	0.02	0.50	0.01	2	0.056	mg/g	Ba
Ca	mg/L	201	7	204	7	201	4	241	5	246	4	302	4	354	3		4.20	mg/g	Ca
Fe	mg/L	1.65	0.15	2.33	0.32	9.15	0.05	502	23	107.1	0.6	896	54	309	2	(0.3)	18.0	mg/g	Fe
K	mg/L	23300	531	22250	71			22250	354			22500	424				2.80	mg/g	K
Mg	mg/L	16.6	0.4	16.9	0.9	16.3	0.1	17.5	0.4	16.8	0.2	21.0	0.3	19.2	0.2		0.80	mg/g	Mg
Na	mg/L	870	68	762	11	776	7	771	16	787	6	787	19	797	5		0.33	mg/g	Na
S	mg/L	139	1	141	3	144	3	542	12	249	1	856	20	458	6			mg/g	S
Si	mg/L	4.3	1.3	7.2	0.3	14.9	0.7	7.6	0.6	14.3	0.5	6.8	0.6	14.2	0.5		26.3	mg/g	Si
Sr	mg/L	5.75	0.07	5.80	0.09	5.90	0.05	5.94	0.14	6.06	0.05	6.08	0.18	6.28	0.04		0.057	mg/g	Sr
trace elements																			
As	ug/L	<DL		12	15	<DL		21	37	25	7	95	48	123	8	10	16.7	ug/g	As
B	ug/L	65	90	97	28	142	15	85	9	121	9	97	12	148	10		38000	ug/g	B
Be	ug/L	<DL		0.79	1.01	0.40	0.32	0.52	0.12	<DL		3.61	0.80	2.03	0.32	4	1.5	ug/g	Be
Co	ug/L	<DL		<DL		<DL		273	8	49	4	212	5	107	5		5.2	ug/g	Co
Cr	ug/L	<DL		482	282	554	56	5098	1226	4317	150	8920	3047	4735	62	100	22.0	ug/g	Cr
Cu	ug/L	1060	1494	76	45	8	9	565	15	33	19	760	18	<DL		1300	18.9	ug/g	Cu
Hg	ug/L	0.0078	0.0022	0.0078	0.0019	0.0080	0.0009	n/d		0.0045	0.0011	n/d		0.022	0.009	2	0.39	ug/g	Hg
Mn	ug/L	488	39	1822	195	624	4	2580	65	1062	37	2965	112	2081	26	(50)	43	ug/g	Mn
Ni	ug/L	6	8	473	239	332	5	5245	136	1338	107	4763	220	2500	50		15	ug/g	Ni
P	ug/L	2877	305	1704	138	1518	95	556	197	656	74	770	141	707	54		70	ug/g	P
Pb	ug/L	<DL		673	1279	240	155	280	80	246	277	301	57	264	86	15	7.5	ug/g	Pb
Sb	ug/L	<DL		16	25	21	10	64	46	17	11	11	9	<DL		6	0.51	ug/g	Sb
Se	ug/L	<DL		12	4	<DL		43	38	44	34	<DL		54	14	50	1.9	ug/g	Se
Tl	ug/L	<DL		<DL		<DL		52	16	<DL		113	29	43	22		8.9	ug/g	Tl
Zn	ug/L	951	935	167	35	78	25	431	18	61	16	568	7	276	10	(5,000)	20.0	ug/g	Zn
anions																			
Cl	mg/L	23213	392	23315	52	23662	58	22945	15	23720	71	23439	43	23542	83	(250)		mg/L	Cl
Br	mg/L	15.7	0.2	15.7	0.6	16.0	0.9	16.2	1.1	16.5	1.1	17.2	1.9	16.4	1.1			mg/L	Br
SO ₄ ⁼	mg/L	127	19	97.8	0.6	120.8	1.3	3176	55	796	10	4500	55	2092	13	(250)		mg/L	SO ₄ ⁼
S ₂ O ₃ ⁼	mg/L	<QL		1.8	0.3	<QL		1.4	0.6	2.2	0.3	<QL		2.5	0.9			mg/L	S ₂ O ₃ ⁼
CrO ₄ ⁼	mg/L	<QL		1.7	0.4	<QL		<QL		1.6	0.4	<QL		0.7	0.5			mg/L	CrO ₄ ⁼
I	mg/L	<QL		10.2	0.7	12.8	0.5	13.7	1.7	13.3	0.2	<QL		16.2	0.5			mg/L	I

Table 4. Comparison of the composition of field-sampled coalbed methane produced water before and after reaction with N₂, CO₂, and Upper Freeport coal. The National Drinking Water Standard limits and the elemental analysis of this Argonne premium coal are also included for comparison.