

COALBED METHANE NATURAL GAS (CBNG) PRODUCED WATER: OUTFALLS AND DISPOSAL PONDS¹

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Abstract. Coalbed methane (CBNG) extraction is facilitated by pumping water from the aquifer. The majority of CBNG produced water is discharged into disposal ponds. The objective of this study was to examine the geochemistry of CBNG produced water in the Powder River Basin, Wyoming. Water samples from outfalls and corresponding disposal ponds in Cheyenne River (CHR), Belle Fourche River (BFR), Little Powder River (LPR), Powder River (PR), and Tongue River (TR) within the Powder River Basin (PRB) were collected over a period of three years. CBNG produced samples were monitored pH, electrical conductivity (EC), major elements [e.g., calcium (Ca), magnesium (Mg), sodium (Na), alkalinity], trace elements [e.g., iron (Fe), aluminum (Al), barium (Ba), arsenic (As), selenium (Se)]. From Na, Ca, and Mg measurements, sodium adsorption ratios (SAR) were calculated. Results suggest that Na, alkalinity, and pH all tend to increase, possibly due to environmental factors such as evaporation, while Ca decreased from outfalls to corresponding disposal ponds due to calcite precipitation. Trace elements concentrations in both outfalls and disposal ponds were below the discharge limit, however an increasing trend was observed in disposal ponds. Overall, these results are useful to develop management approaches for CBNG produced water and reclamation of disposal ponds.

Additional Key Words: Energy Demand, Clean Energy, Coalbed Methane, Produced Water, Reclamation of CBNG Disposal Ponds

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Introduction

Several western states within the US are extracting methane (natural gas) from coalbed deposits to supplement the nation's growing energy demands. Methane is formed deep in confined coalbed aquifers through biogeophysical processes and remains trapped by water pressure. Extraction of the methane requires pumping of water from the aquifer (produced water). It is estimated that a single CBNG well in the Powder River Basin may produce from 8 to 80 L of product water per minute, but this amount varies with aquifer that is being pumped and the density of the wells. At present, more than 20,000 wells are under production in the PRB and this number is expected to increase to at least 30,000 (RIENR, 2005). According to DeBruin et al., (2000), approximately 2 trillion L of product water will eventually be produced from CBNG extraction in Wyoming. Commonly 2 to 10 CBNG extraction wells are placed together in a manifold system discharging to a single point and releasing into constructed unlined holding ponds. These holding ponds are constructed with initial well pumping. The Wyoming DEQ considers this water as surface water of the state with Class 4C designation.

CBNG produced water can have high concentrations of soluble salts (McBeth et al., 2003a, 2003b; USDI-BLM, 2003; Rice et al., 2000) and could affect surrounding soils, vegetation, wildlife, and livestock. Beneficial uses proposed for CBNG produced water includes: irrigation, aquaculture, livestock and wildlife watering, and human drinking water (USDI-BLM, 2003). However, any potential beneficial use of produced water depends on the water quality. Few studies examined the quality of CBNG produced water and associated discharge ponds in the Powder River Basin (McBeth et al., 2003a, 2003b; Rice et al., 2000). For example, McBeth et al., (2003a, 2003b) monitored water quality of CBNG produced water at discharge points and associated discharge ponds in the southern and eastern portions of the PRB for 2 years. McBeth et al., (2003a, 2003b) studies had few sample sites, located primarily in the eastern half of the PRB. In general, these studies reported that water quality parameters such as SAR, salt concentration, and pH increased in discharge ponds. Studies conducted by Rice et al. (2000) examined only the chemistry of CBNG discharge water at the wellhead and did not consider disposal pond chemistry. In above studies, the geochemical changes and fate of SAR, salts, trace elements as a function of time were not fully understood. In addition, the CBNG produced water in the disposal pond undergoes geochemical processes such as ion complexation, adsorption, and precipitation. These processes control the fate of trace elements in disposal ponds. The

objectives of this research were to: 1) examine the chemistry of outfalls and corresponding disposal pond water and 2) determine potential beneficial uses for CBNG produced water in the Powder River Basin, Wyoming.

Materials and Methods

Study Area Description

Most CBNG development in Wyoming occurs in the eastern portion of the PRB. This basin is part of the Great Plains Missouri Plateau. The PRB is semiarid with average annual precipitation ranging from 30-60 cm and bounded by the Black Hills on the east, the Hartville Uplift to the south, the Big Horn Mountains on the west, and the Yellowstone River to the north (USDI-BLM, 2003). The PRB generally consists of high plains with elevations from 1,640-1,800m above sea level with rolling hills capped with clinker, a reddish brick created from surface coal combustion (USDI-BLM, 2003).

Major coal formations in the PRB include the Tertiary White River Formation and the Tertiary Tongue River Member of the Fort Union Formation (USDI-BLM, 2003). Soils in the PRB are dominated by Ustic Haplargids (clay loam), Ustic Calcicargids (fine loamy), and Ustic Torriorthents (loamy) (USDI-GS, 1986). The major river systems include the Cheyenne River (CHR), Belle Fourche River (BFR), Little Powder River (LPR), Powder River (PR) and Tongue River (TR). The Cheyenne River drains the southeast portion of the PRB while the Belle Fourche River drains the eastern portion of the basin. The Little Powder River drains the northern portion of the basin while the Powder River drains the northwestern portion of the basin. The Tongue River flows north from Wyoming into the Yellowstone River. These are perennial rivers and tributaries of the Missouri River.

The surface streams that contribute to CHR, BFR, LPR, PR, and TR have intermittent or ephemeral flows regulated by snowmelt or storm events. Major land uses in the PRB include ranching, livestock production, coal and uranium extraction, and methane extraction (USDI-BLM, 2003). Discharge of CBNG produced water increases overall flow of receiving tributaries, which drain through local soils and plant communities. Subsequently, these processes influence the quality of the receiving water.

Site Selection

Site selection and sample collection was coordinated after consulting with: WYDEQ, Wyoming Water Development Commission (WY-WDC), Coalbed Methane Industry, Wyoming

Landowners and Citizens, U.S. Geological Survey (USGS), Wyoming State Geological Survey (WYSGS), U.S. Environmental Protection Agency (USEPA), Colorado, and Montana to avoid duplication of efforts. Site selection was based on geographic location, focusing on CBNG development in Tongue, Powder River, and Little Powder River watersheds due to their poor product water quality. Access to sites was based on landowner involvement. Twenty-six sites were selected within 5 Wyoming watersheds (Fig. 1) to obtain CBNG produced water disposal point and associated disposal pond samples. Specific data collection included 7 sites from each of the Little Powder River and Powder River watersheds, 3 sites from Cheyenne River watershed, 4 sites from Belle Fourche River watershed, and 5 sites from Tongue River watershed.

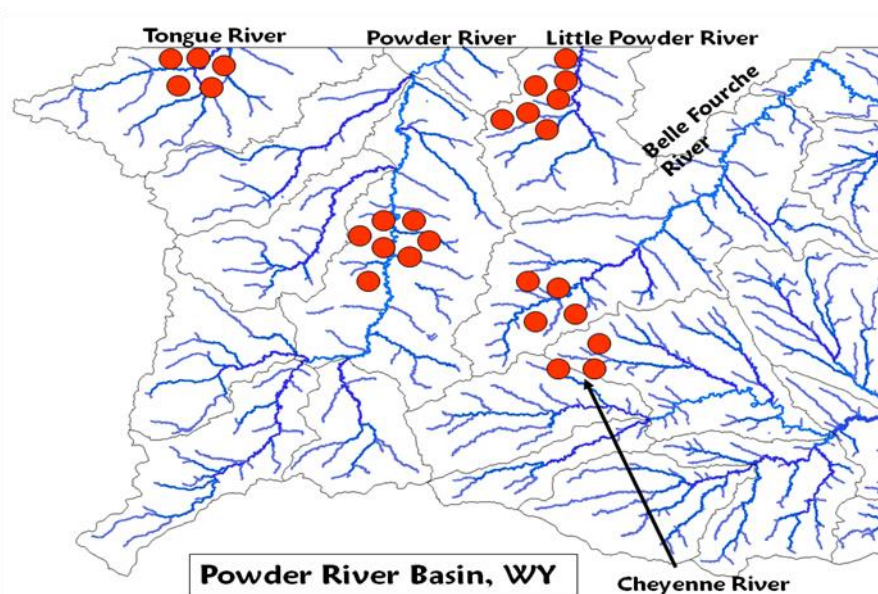


Figure 1. CBNG outfalls and disposal sampling sites in the Powder River Basin, WY (not to scale).

Sample Collection and Analysis

CBNG water samples from each outfall and corresponding discharge pond were collected once during the summers of 2003, 2004, and 2005. Before sample collection, field measurements including pH, conductivity, temperature, ORP (oxidation and reduction potential), and dissolved oxygen were taken from each CBNG outfall and associated pond with an Orion Model 1230 Multi-Probe. Exact locations for pond measurements were taken directly away from

outfall, and were chosen upon pH stabilization at different distances from discharge point. Sample locations were identified using GPS markers.

Chemical Analysis

Duplicate water samples of outfalls and discharge ponds were taken from each site. Samples were transported in ice coolers (2° C) to the University of Wyoming Water Quality Laboratory. Each sample was filtered through 0.45µm filter and subdivided: half were acidified to pH of 2.0 with concentrated nitric acid (HNO₃), and half were left unacidified. Acidified samples were analyzed for Ca, Na, Mg, K, Fe, Al, Cr, Mn, Pb, Cu, Zn, As, Se, Mo, Cd, Ba and B by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), and un-acidified samples were analyzed for SO₄²⁻, Cl⁻, F⁻, NO₃³⁻ and PO₄³⁻ using Ion Chromatography (IC). Total alkalinity on unacidified samples was determined by acid titration method.

Quality Control

The quality control/quality assurances protocols such as duplicate sampling and analysis, trip blanks, and known concentrations of reference standards were included. Standard laboratory procedures were used for all analytical analyses and pH, EC, and alkalinity measurements (APHA, 1992). All analyses were performed following CFR 40, Part 1, Chapter 36 procedures.

Geochemical Modeling & SAR Calculations

The geochemical model MINTEQA2 was used to verify analytical data accuracy with calculated charge balances and to calculate ion activities (Brown and Allison, 1992). This model uses chemical data, pH, alkalinity, and redox couples to calculate ion activities, ion complexes, and saturation indices. The SAR values were calculated from Ca, Na and Mg concentrations (Hanson et al., 1993). Typically SAR is used to predict sodicity hazards, particularly with irrigation waters (Hanson et al., 1993). Irrigation with high SAR waters on clayey soils could lead to low water infiltration, high run off, and increased soil erosion (Hanson et al., 1993; McBeth et al., 2003a).

Results and Discussion

The pH in outfalls ranged between 6.9 and 7.9 and was stable between years, while discharge pond pH ranged between 7.6 and 9.6 and varied between years. Results suggest that outfall water pH is stable and controlled by the geologic formation and the concentration of dissolved CO₂ confined in the aquifer (Patz et al., 2004). Pond water pH is much more varied, most likely

due to the degassing of CO₂ from the produced water and its interaction with local soils (McBeth et al., 2003a). Discharge pond water pH is primarily controlled by the ambient concentration of atmospheric CO₂ and calcite precipitation, wetland plants, and evaporation (McBeth et al., 2003a). Like pH, EC and Na were elevated in the discharge ponds. Increased EC from outfalls to discharge ponds can be attributed to the overall increase in Na and HCO₃⁻ from outfalls (Rice et al., 2000). The increase in discharge pond Na is likely due to the discharge of Na rich water from CBNG outfalls, and subsequent evaporation. Continual evaporation concentrates Na in the ponds. Unlike pH, EC, and Na, Ca decreased from outfalls to discharge ponds.

The geochemical model MINTEQA2 predicted that most discharge ponds are oversaturated with respect to calcite. When Ca concentration is oversaturated with respect to calcite, Ca can precipitate as calcite (Drever, 1997). For example, outfall Ca concentrations decreased from 17.0 mg/L to 13.2 mg/L in the discharge ponds. When calcite precipitates it also buffers the water pH to around 8.3, similar to observed CBNG discharge pond pH. There were no differences between outfall and discharge pond Mg and alkalinity. Magnesium was varied, but did not indicate any trend between outfalls and discharge ponds. Alkalinity was higher in discharge ponds (772.5 mg/L) than outfalls (458.5 mg/L). Alkalinity increased in discharge ponds due to the increased pond pH. A possible explanation why alkalinity was not different between outfalls and discharge ponds is because of large variation in alkalinity within outfalls. In outfalls, alkalinity varied between 315.0 and 2425.4 mg/L, while discharge pond alkalinity varied between 645.3 and 2609.6 mg/L.

The CBNG outfalls and corresponding discharge ponds in the CHR and BFR were stable from 2003 through 2005. The mean SAR values for both outfalls and discharge ponds were similar (Fig. 2). The acceptable SAR range is 8-10, however depends on soil and plant factors. The CBNG discharge waters from CHR were slightly more reactive than BFR. The CHR discharge pond SAR increased from 5.3 to 6.8 from 2003 to 2005. The LPR produced waters were moderately reactive due to changes in Ca and Na concentrations in disposal ponds. The overall SAR increased from 10 to 15 in disposal ponds. This increase in SAR in pond water was probably due to a combination factors including evaporation, increase in outfalls Na and decrease in Ca in pond water. Outfalls and discharge ponds in TR had the most chemical changes between years than the previous CBNG water samples. The TR had highest SAR in

outfalls or disposal ponds when compared with any other watersheds in the PRB. The outfalls SAR was 40 and decreased to 34 in disposal ponds.

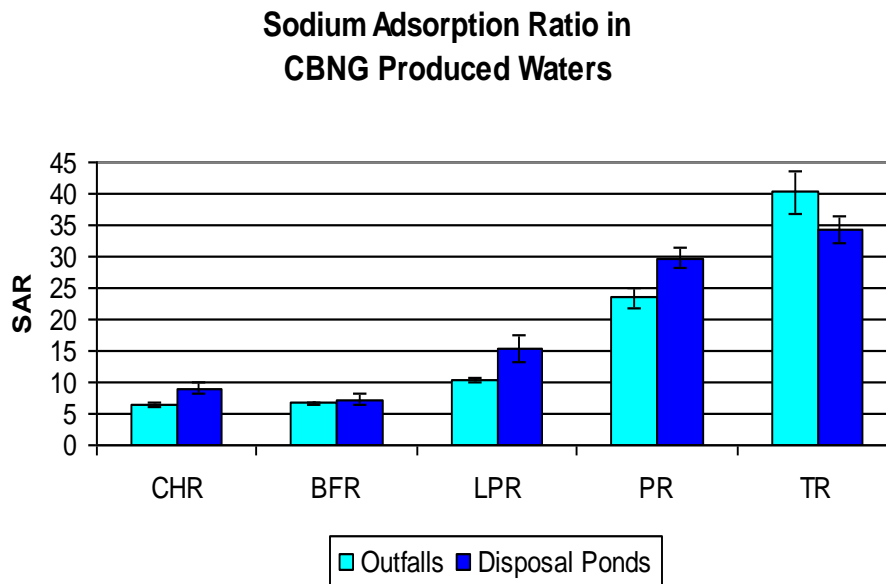


Figure 2. Sodium adsorption ratio of CBNG outfalls and corresponding disposal ponds in the PRB.

The TR produced waters are unique compared to other CBNG produced waters in that they undergo a remediation technique that acidifies the water with sulfuric acid. Commonly referred to as Sulfur Burners, the machines convert sulfur pellets into sulfuric acid and mix with outfall water (pH ~ <4.0) before entering the discharge pond. The “acidification” lowers discharge pond pH and alkalinity, causing many of the carbonates to dissolve, artificially increasing Ca and Mg. Since SAR is a ratio between Na/Ca and Mg, this process lowers SAR. Though SAR is considered high, landowners are using it for irrigation. Continued irrigation of this high SAR water can eventually cause sodic soil conditions (Hanson et al., 1993) and lead to severe degradation of once fertile soils

The dissolved trace elemental concentrations which showed most changes between outfalls versus corresponding disposal ponds are shown in Figures 3-6. Aluminum concentrations were very low (<500 µg/L) in outfalls or disposal ponds in all watersheds, except for outfalls for TR (Fig. 3). In this watershed the Al in outfalls was as high as 2000 µg/L. These high Al concentrations are due to the acidification process of outfall water. However, Al concentrations decreased to <500 µg/L in disposal ponds. We expected these results because of high pH of

disposal ponds, which precipitate Al as $\text{Al}(\text{OH})_3$. Similarly, outfalls Ba concentrations tend to decrease by 50-60% (data not shown) when they reach corresponding disposal ponds.

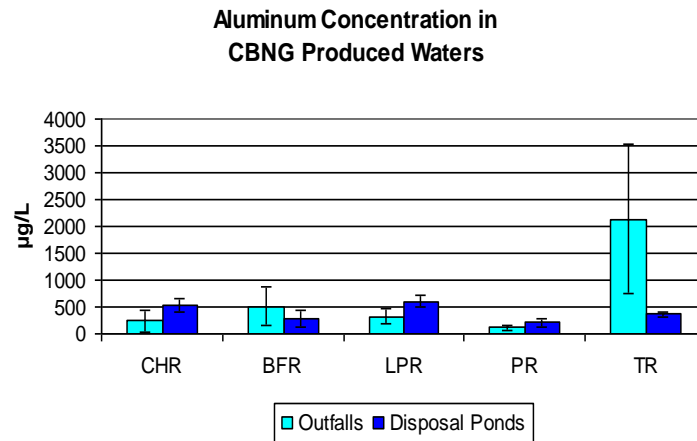


Figure 3. Aluminum concentrations in CBNG outfalls and corresponding disposal ponds in the PRB.

Iron concentrations in general were lower in outfalls ($<100 \mu\text{g/L}$). However, Fe concentrations increased significantly in disposal ponds (Fig. 4). For example, Fe concentrations as high as $450 \mu\text{g/L}$ were recorded in the disposal ponds of BFR. High Fe concentrations observed in the disposal ponds are attributed to the high pH and increased solubility of Fe anionic solution species. Previous studies on CBNG disposal ponds also reported similar results (McBeth et al., 2003b).

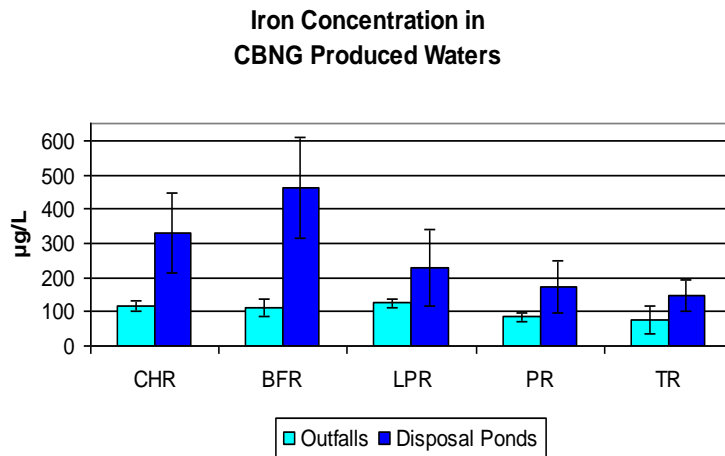


Figure 4. Iron concentrations in CBNG outfalls and corresponding disposal ponds in the PRB.

Mean Se and As concentrations in water samples from outfalls and from disposal ponds across all watersheds in the PRB are shown in Fig. 5 and 6. These results suggest that Se concentration increases from the outfalls to the disposal ponds (Fig. 5). However, the Se concentrations whether in outfalls or in disposal ponds are very low (<2.5 µg/L).

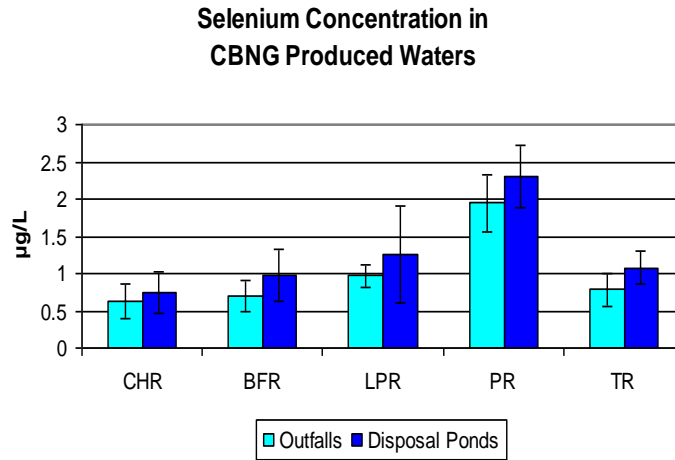


Figure 5. Selenium concentrations in CBNG outfalls and corresponding disposal ponds in the PRB.

Arsenic concentrations also very low in outfalls across all the watersheds (<1 µg/L), however, increased significantly in all disposal ponds (Fig. 6). For example, in LPR watershed As concentrations were 10 µg/L in disposal ponds.

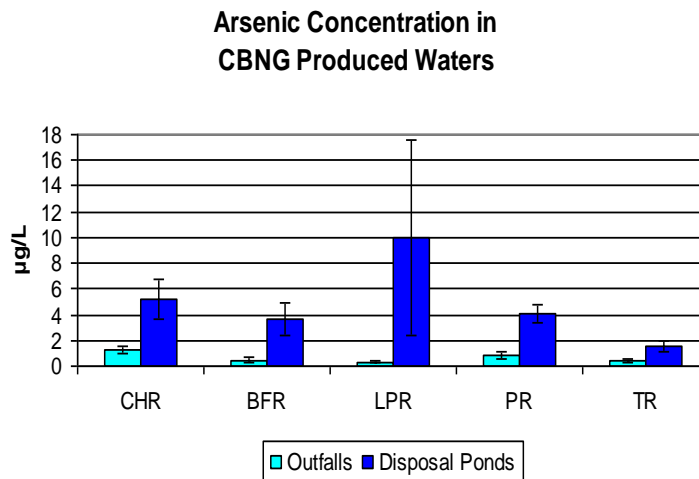


Figure 6. Arsenic concentrations in CBNG outfalls and corresponding disposal ponds in the PRB.

Arsenic in general has been identified as a major contaminant of groundwater resources and a public health concern (Bunnell, 2007). Further investigation of As concentrations in water samples from disposal ponds revealed an incremental increase from year to year across all watersheds. Many studies have identified that As solubility is directly related to adsorption and desorption processes of metal oxides and hydroxides (Stumm and Morgan, 1996). In semi-arid alkaline environments, mineral oxides and hydroxides tend to have a negative surface charge. In nature, As is an anion, thus it is expected to be soluble and mobile in these watersheds and increase in concentration over time in disposal ponds.

Conclusions

The pH and salt concentration of CBNG produced water increases moving from CHR to TR basin. Moving from north and west toward deeper coal seams within the PRB produces saline, alkaline and high SAR water. Overall results of this study suggest that CBNG produced outfall water dominated by Na^+ and HCO_3^- and higher dissolved CO_2 , which buffers the pH of outfall water between 7 and 8. When CBNG outfall water is discharged into a disposal pond, CO_2 degases from the disposal ponds and pH increases to 8-9. Under high pH environments, solubility and availability of trace elements (e.g., arsenic, selenium,) increases in CBNG disposal ponds. The high pH environment in disposal pond also enhances the precipitation of CaCO_3 . Subsequently, precipitation of CaCO_3 increases the SAR of disposal pond water. Increased SAR in some disposal ponds acts as sediment sealing and prevents downward movement of trace elements.

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