

Chemical Changes in Coal Bed Methane Product Water Over Time

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It is widely known that coal bed methane (CBM) development in the Powder River Basin of Wyoming and Montana produces considerable amounts of discharge water. The majority of this product water is discharged into surface channels and evaporation reservoirs. The chemical properties of CBM product water at or near the point of discharge are rigorously monitored and generally well known. However, as product water



mixes with surface water and achieves equilibrium with the atmosphere, product water chemistry changes. Principle chemical properties of interest that potentially experience change are electrical conductivity (EC), pH, and sodium adsorption ratio (SAR). Changes in water chemistry are of concern for many downstream water users, namely those considering the suitability of product water or blended water for irrigation purposes.

Hypothesis

When sodium bicarbonate-rich CBM product water is discharged into surface water or applied to the, soluble sodium bicarbonate in the water will initiate precipitation of calcium carbonate, causing SAR values to increase. Correspondingly, EC values will decrease slightly or remain relatively stable due to small amounts of ion (Ca^{+2}) precipitation. The dissolution of sodium bicarbonate will also cause pH to increase.

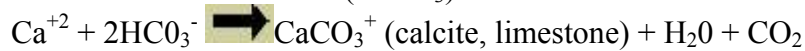
Chemistry

Coal bed methane product water chemistry is highly variable throughout the Powder River Basin. However, generalizations about product water can be made. For instance, product water at the point of outfall and discharge most often has a pH of 7.0 to 7.5 and is considered fairly neutral. Product water is also known to be sodium bicarbonate

(NaHCO₃) rich and surface water and soils of the region are known to be calcium (Ca²⁺) rich (Rice et al., 2000). When product water is exposed to the atmosphere, discharged into surface water or applied to soil, sodium bicarbonate undergoes the following reaction:



Free carbonate (CO₃⁻²) in the solution is now available to bind with calcium in the surface water or soil to form calcium carbonate (CaCO₃).



Calcium carbonate (limestone) is relatively insoluble and precipitates out of solution. The loss of Ca²⁺ in solution causes an increase in the ratio of sodium to calcium + magnesium, and SAR increases (Rhodes et al., 1973).

$$\text{SAR} = \text{Na}^+ / \sqrt{[(\text{Ca}^{+2} + \text{Mg}^{+2})/2]}$$

This increase in SAR can be predicted and is expressed as the adjusted SAR when these values are reported in meq/L. An adjusted SAR, when considering CBM product water, is probably more representative of irrigation water quality and suitability than an unadjusted SAR. The dissolution of NaHCO₃ also causes pH to increase with the formation of sodium hydroxide (NaOH):



Experiment 1: Experimental Design and Results

To better understand chemical changes of CBM product water, two short-term experiments were conducted on waters of varying chemistry simulating possible CBM product water and surface water. The first experiment involved assessment of the changes in each of five synthesized water qualities upon exposure to the atmosphere (Table 1). Water qualities 1 and 2 (WQ1, WQ2) were intended to mimic Powder River water qualities. Water qualities 3 and 4 (WQ3, WQ4) were designed to mimic a saline product water, and water quality 5 (WQ5) was designed to mimic a saline-sodic water quality. The five water qualities were mixed based on product water recipes determined from successive runs of MINTEQA2 simulation model. Three replications of each water quality were allowed to sit for 12 days while being slowly circulated to simulate continuous mixing. Each container containing a replication of a respective water quality had a lid placed on top of the container throughout the entire experiment to minimize evapoconcentration. Samples from each product water were collected from each container approximately two times per day over a 12-day period and analyzed for EC, pH, and SAR. The average resulting chemistry for four water qualities at the end of 12 days, excluding water quality 1, reflected a 51% increase in SAR and a 4% decrease in EC (Table 1). Changes in EC, SAR, and pH values for all water qualities are presented in Table 1 and Figures 1 through 3.



Table 1. Initial, final, and percent change in water chemistry for five water qualities over a 12 day time period with minimal evapoconcentration.

	Initial pH	Final pH	Initial EC	Final EC	Initial SAR	Final SAR	% Change EC	% Change SAR
WQ1	7.77	8.5	1.67	1.38	3.1	6.51	-17.37	110.00
WQ2	7.58	8.09	3.21	3	2.19	3.25	-6.54	48.40
WQ3	7.94	8.64	3.02	2.92	9.49	14.67	-3.31	54.58
WQ4	7.53	8.3	3.8	3.62	8.69	13.51	-4.74	55.47
WQ5	7.39	8.87	6.87	6.73	16.98	24.98	-2.04	47.11
Average % Change (excluding WQ1)							-4.16	51.39

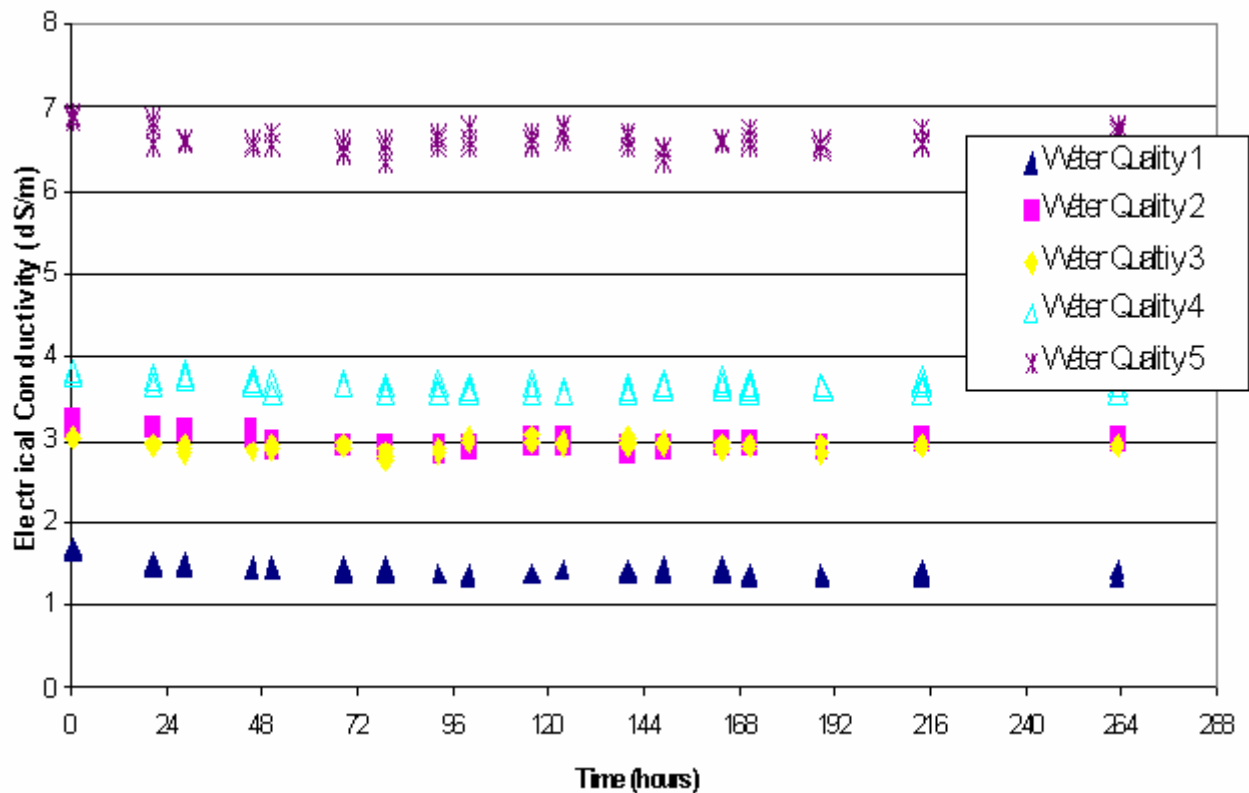


Figure 1. Electrical Conductivity (EC, dS/m) of five simulated CBM product waters of varying quality over a 12 day period of agitation without evapoconcentration (closed container at atmospheric pressure).

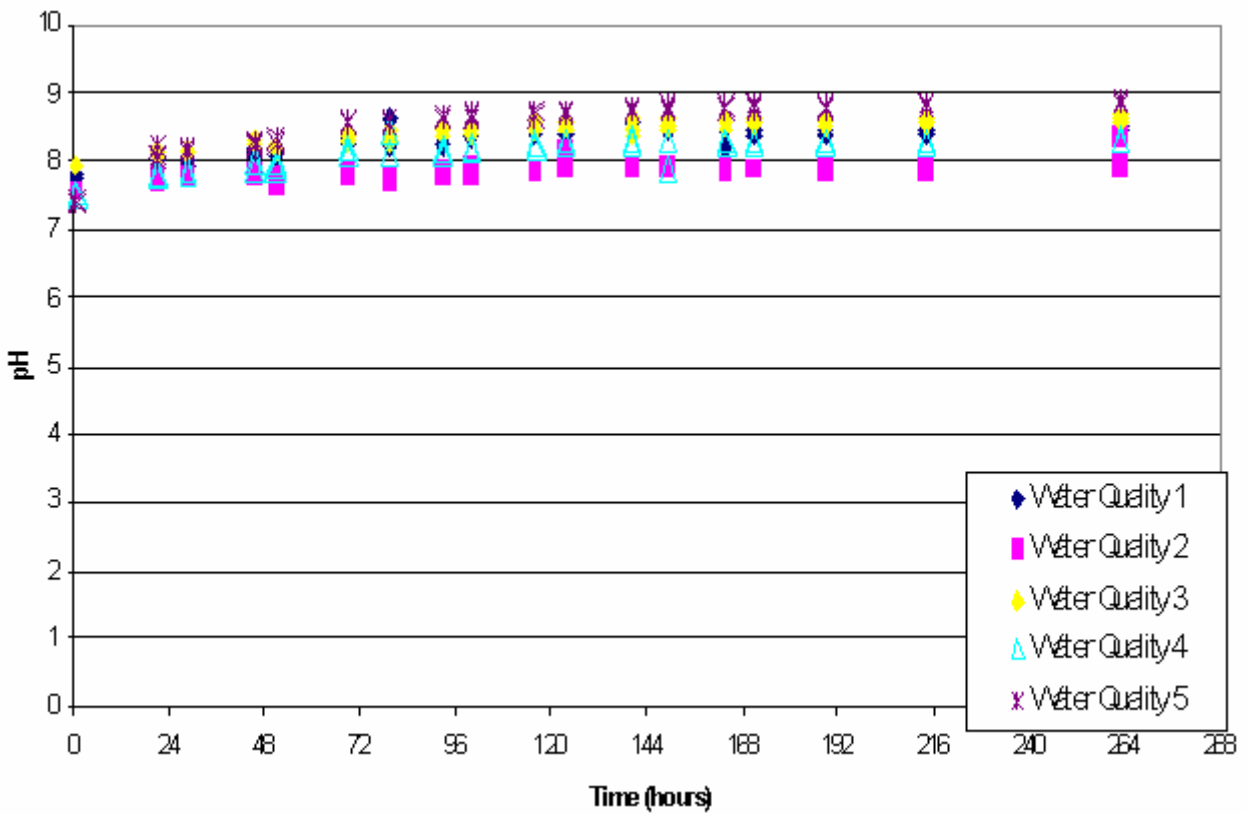


Figure 2. pH of five simulated CBM product waters of varying quality over a 12 day period of agitation without evapoconcentration (closed container at atmospheric pressure).

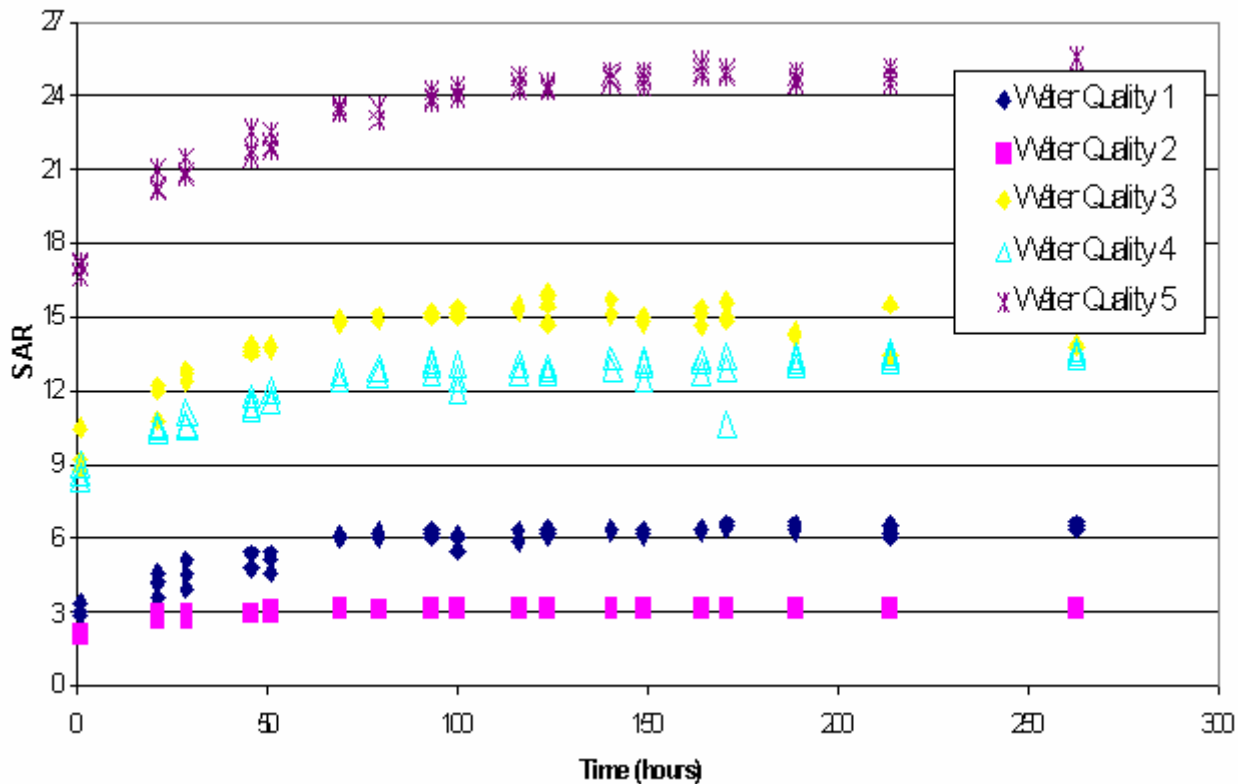


Figure 3. Sodium Adsorption Ratio (SAR) of five simulated CBM product waters of varying quality over a 12 day period of agitation without evapoconcentration (closed container at atmospheric pressure).

Experiment 2: Experimental Design and Results

The second experiment was intended to evaluate the effect of exposure of CBM product water to the atmosphere and evapoconcentration on resulting water chemistry. Three waters of varying chemistry were subjected to the same analysis as in the first experiment, but in containers without lids, for a nine-day period. Water quality 6 (WQ6) was designed to resemble Powder River water. Water quality 7 (WQ7) was designed to resemble saline product water and had an initial EC of 3.36 dS/m, an initial pH of 7.7, and an SAR of 12.5. Water quality 8 (WQ8) was designed to resemble a saline-sodic CBM product water with an initial EC of 5.42 dS/m, initial pH of 7.5, and initial SAR of 20.7. The ending water chemistry reflected an average increase in SAR of 42% and a 22% increase in EC values (Table 2). Changes in EC, SAR, and pH values for all water qualities are demonstrated in Table 2 and Figures 4 through 6.

Table 2. Initial, final, and % change in water chemistry for three water qualities over a 9 day time period: subject to evapoconcentration.

	Initial pH	Final pH	Initial EC	Final EC	Initial SAR	Final SAR	% Change EC	% Change SAR
WQ6	7.4	8.1	3.07	3.75	3.7	4.4	22.15	18.92
WQ7	7.7	8.4	3.36	4.01	12.5	18	19.35	44.00
WQ8	7.5	9.1	6.42	6.71	20.7	33.8	23.80	63.29
Average % Change							21.77	42.07

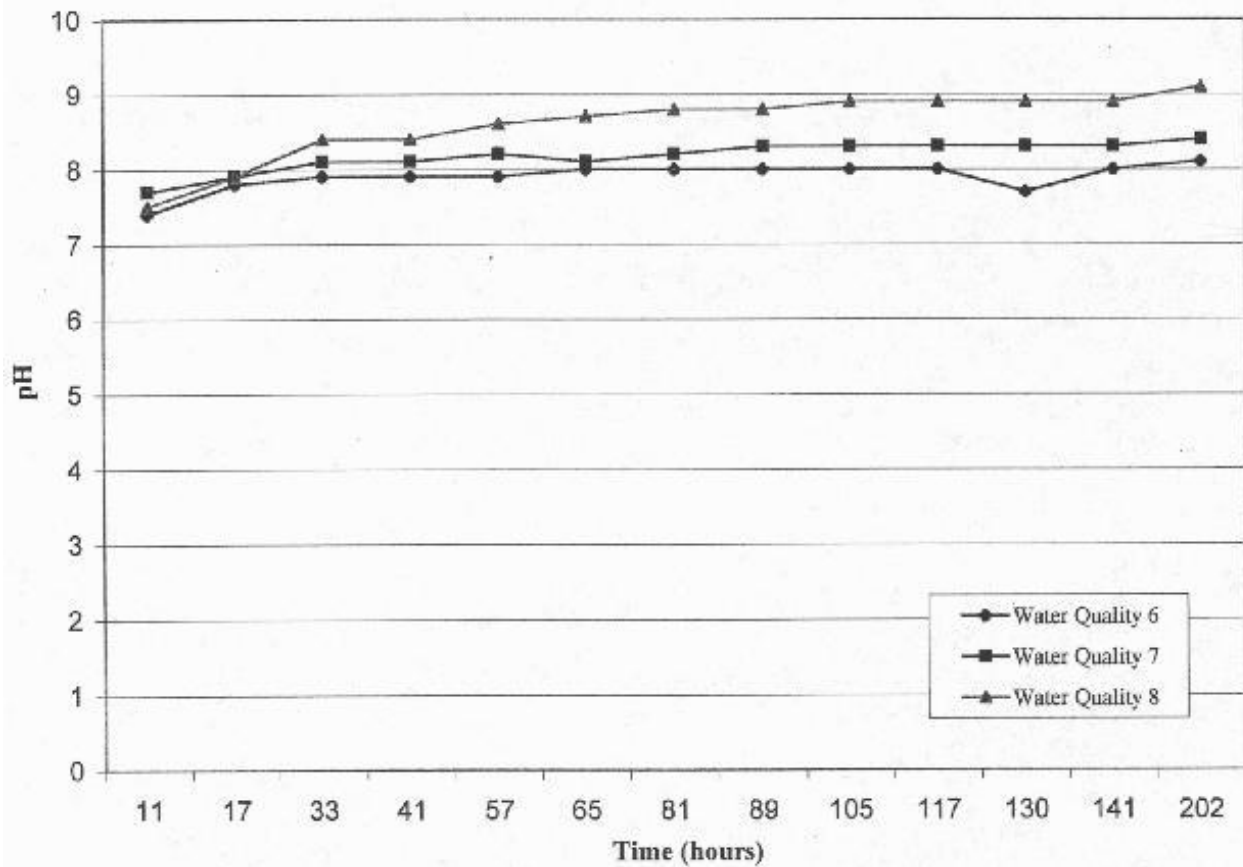


Figure 4. pH of three simulated CBM product waters of varying quality over a 9 day period of agitation in an open container at atmospheric pressure (in the presence of evapoconcentration).

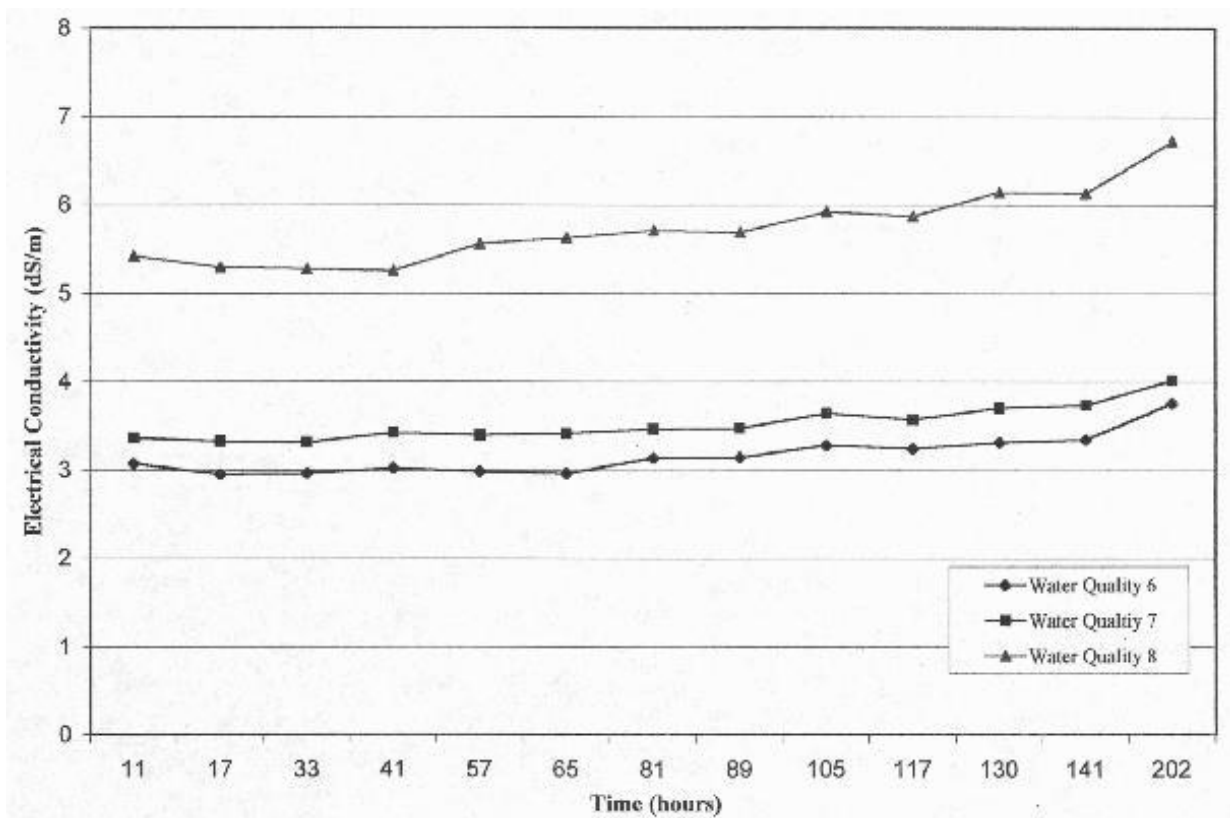


Figure 5. Electrical conductivity (EC, dS/m) of three simulated CBM product waters of differing quality over a 9 day period of agitation in an open container at atmospheric pressure (in the presence of evapoconcentration).

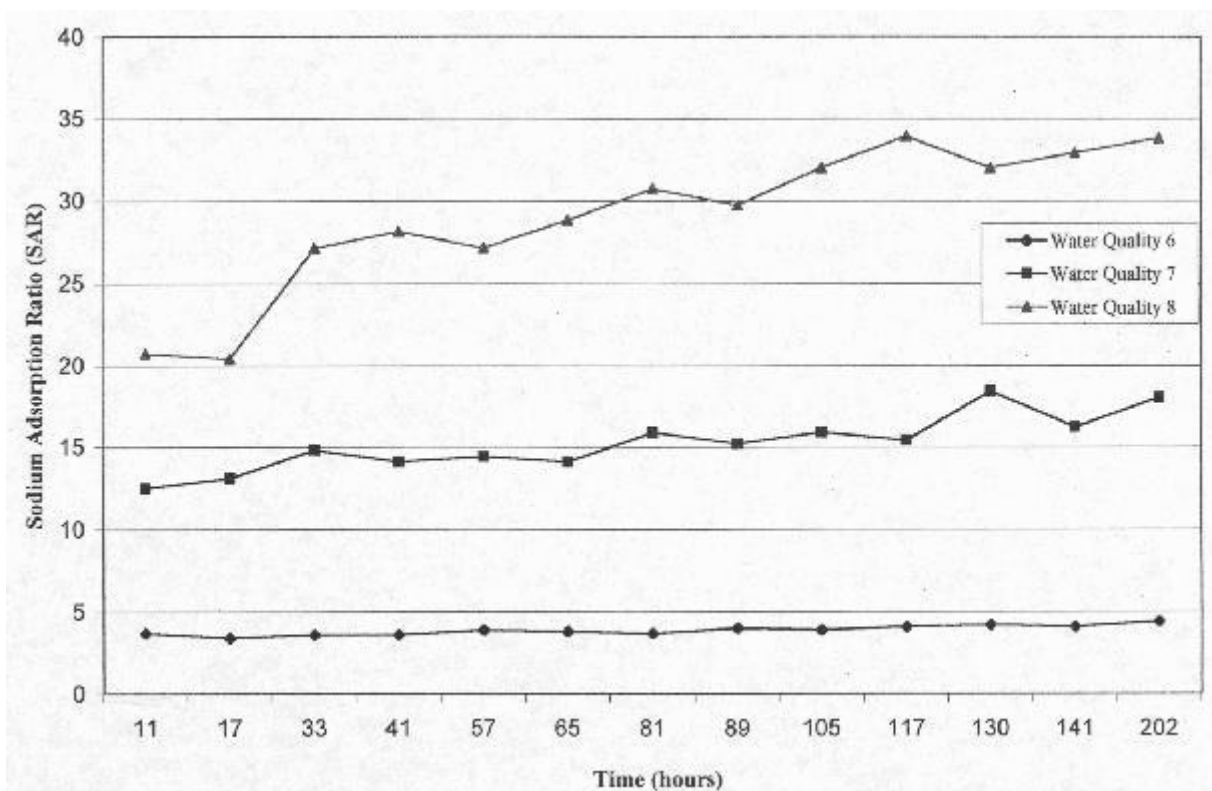


Figure 6. Sodium Adsorption Ratio of three simulated CBM product waters of differing quality over a 9 day period of agitation in an open container at atmospheric pressure (in the presence of evapoconcentration).

Discussion

An issue of concern for CBM producers and irrigators in the Powder River Basin is sodium adsorption ratio (SAR). As previously explained, SAR expresses the ratio of sodium to calcium and magnesium in water or soil solution. A high SAR indicates a high exchangeable sodium percentage. Without adequate amounts of calcium and magnesium in solution to counteract its effects, sodium will bind onto clay particles and cause the soil to disperse. Dispersed clay particles will move into pores previously available for air and water infiltration. High SAR's will induce poor permeability in the soil, create seals or crusts at the soil surface, and increase runoff and erosion. Dispersive tendencies of irrigation water vary between soil types, with montmorillonitic clays being the most easily dispersed (Miller and Gardiner, 1997). In general, soils with higher clay content disperse more easily than coarser soils. Notably, montmorillonitic clays are common in southeast Montana and northeast Wyoming.

Generally, the SAR of CBM product water at a discharge point or that of surface water at the point of measurement reflects one set of equilibrium conditions which might be somewhat different than the conditions experienced at the soil surface, down gradient in channel, or in the soil solution. Where adjusted SAR becomes important is in dealing

with ground water (and CBM product water at the point of discharge to the surface) and soil water (soil solution). The actual calcium concentration of the resultant soil water may be lower than the calcium concentration of irrigation water, i.e., calcium concentration may decrease within the impoundment, channel, or soil environment due to calcite precipitation. This reduction in calcium concentration subsequently affects the resultant SAR, as shown here.

The lower "equilibrium" calcium concentration in the stream channel, at the point of water contact with the stream channel, or within soil water (less than the equilibrium concentration of calcium in the surface irrigation water) occurs because the calcium level is controlled by the dissolution or precipitation of calcium carbonate (CaCO₃).

Increases in SAR and pH in stream channels below CBM outfalls have been documented by other research. DeJoia observed a consistent increase in pH and SAR and a decrease in EC from the outfall of the CBM well to the nozzle of a pivot irrigation system. Table 3 illustrates the changes observed.

Source	pH	SAR	EC (Uhmhos/cm)
Outfall	7.5	20-26	3,800-4,200
Pump	8.2	27-30	2,600
Nozzle	8.7	32	2,900

Patz looked at the change in CBM water chemistry from the CBM discharge point down gradient over uplands and within Burger Draw and Sue Draw, Wyoming - two ephemeral stream channels. She observed an increase in pH and SAR and a decrease in EC and calcium (due to precipitation on calcium carbonate). After residence time in an impoundment, the pH and SAR increased and EC and calcium decreased downstream from the impoundment. Table 4 illustrates the changes observed (Patz, 2000).

Source	pH	SAR	Ca	EC
CBM discharge 1	7.04	23.44	47.80	4.30
Burger Draw downstream from CBM 1	8.39	27.4	30.80	4.21
CBM discharge 2	7.13	24.76	51.55	4.30
Sue Draw downstream from CBM 2	8.54	32.46	28.66	4.24
Sue Draw downstream from impoundment	9.15	--	13.40	--

If precipitation occurs within the soil solution environment, the final calcium concentration in the soil solution may be less than that indicated by chemical analyses of irrigation or CBM product water. This, in turn, will increase the relative amount of exchangeable sodium, so that an adjustment must be made to the SAR to reflect the equilibrium calcium concentration. This adjustment depends in part on the concentrations of calcium and bicarbonate in the irrigation water and the salinity of the irrigation water. Typically, adjustment of the SAR value to account for calcium precipitation will result in an increase in the SAR of 10 to 25%. Patz (2002) reported in-stream increases in SAR of 9.5 - 31% in Burger Draw, Wyoming. Salinity increased approximately 10% down gradient in this same study.

Defining acceptable SAR values for irrigators is difficult because of varying soil types across the landscape, and also because of a well known relationship between SAR values and EC values. In general, ECs of high enough values are able to counteract the dispersive effects of high SAR. This is due to the fact that low-electrolyte water tends to flow into spaces, or pores, between clay particles more readily than high-electrolyte water (Hanson et al., 1999). The water carries with it fine clays that will settle into these pores and clog them, thus reducing permeability of the soil. Regardless of the SAR value of irrigation water, infiltration will increase with increases in salinity concentration (Hansen et al., 1999).

Conclusions

Research reported herein demonstrates the significance of assessment of SAR at the point of application to the land surface and not necessarily at the point of outfall or exposure of CBM product water to the atmosphere. Evaporation, concentration, and precipitation within the stream channel, impoundment, or soil may alter the soil solution chemistry significantly from the outfall water chemistry or the irrigation water chemistry.

The most significant issue to realize here is that any assessment of sodium hazard of irrigation water which is based on an unadjusted SAR value, particularly when HCO_3^- is present in abundance, as in the case of the Tongue River and Powder River, is at best representative of a "best case" scenario.

What is the significance of the changes in EC, pH, and SAR observed in these experiments? Typically, for reporting and permitting CBM product water discharges, water samples are collected for analyses at the point of outfall, i.e., the point of discharge to the atmosphere. The findings of the research reported herein illustrate the potential change that product water chemistry can undergo between the point of outfall (into a stream, channel, impoundment) and the point of dispersal to the land surface. Consequently, the need exists for adjusting the SAR of product water to account for calcite precipitation. Numeric standards should be defined for specific points of compliance or considerations for in-stream changes in pH, EC, and SAR need to be made

when defining numeric standards for water bodies. Point of compliance permitting is most likely more representative than outfall or impoundment compliance.

Lastly, pH should also be considered when evaluating the appropriateness of product water for irrigation purposes. Soil and water pH is commonly understood in terms of pH scale, with 7.0 being neutral, pH 4 strongly acidic, and pH 9 strongly alkaline. The pH of CBM product water is generally 7.0 to 7.5 upon discharge and increases thereafter as demonstrated in the sort term experiment. The major effect of high pH values is to lower the availability of plant nutrients such as phosphorous and plant micronutrients, specifically iron, zinc, copper, and manganese (Miller and Gardiner, 1997). A pH of 9 will reduce growth in most plants, and is fatal to some species.

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A significant amount of the material contained and extracted from the Western Fertilizer Handbook is also contained in Agricultural Salinity and Drainage. Other significant reference materials identified in this publication include Agricultural Salinity Assessment and Management, edited by K. K. Tanji and published by the American Society of Civil Engineers in 1990 and the United Nations Food and Agricultural Organization (FAO) publication, Irrigation and Drainage Paper 29, Water Quality for Agriculture, by R. S. Ayers and D. W. Westcot.

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