

# Geochemical Constraints on Selection of CBM Product Water Management Strategies

Presented by Ron Drake, Drake Engineering Incorporated, Helena, MT, with funding support from LRES Department, Montana State University

## ABSTRACT

CBM product water from Montana and Wyoming plays is chemically unstable and may exhibit profound changes in composition after withdrawal from the aquifer. Spontaneous changes in CBM product water composition are likely to impair its suitability for beneficial use on the landscape. Understanding the fundamental chemical behavior of CBM product water is key to designing and implementing successful water management strategies at any desired scale.

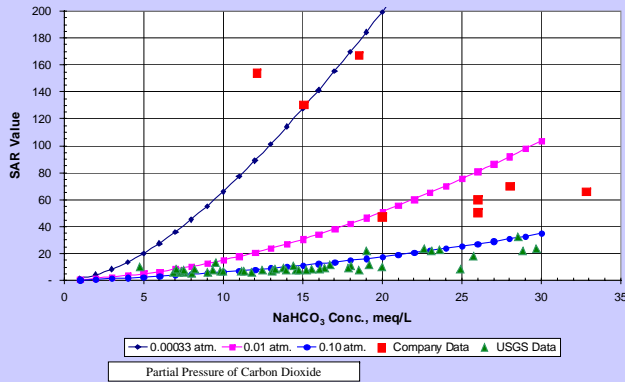
Laboratory investigations confirm results of geochemical modeling that show equilibrium sodium adsorption ratio (SAR) is controlled by concentration of bicarbonate that suppresses solubility of Ca and Mg. Liquid/gas mass transfer of carbon dioxide controls rate of approach to chemical equilibrium.

## GEOCHEMICAL MODELING OF OBSERVED PHENOMENAE

MINTQA2 geochemical modeling software was used to calculate equilibrium compositions of sodium bicarbonate solutions over calcite and dolomite at various partial pressures of carbon dioxide. Modeled equilibrium concentrations of soluble Na, Ca, and Mg were used to calculate SAR values as a function of initial concentration of sodium bicarbonate and equilibrium partial pressure of carbon dioxide. Model results show that relatively low (0.10 atmospheres) partial pressures of carbon dioxide over sodium bicarbonate solutions in contact with calcite and dolomite will generate solutions exhibiting the characteristic chemical signature of CBM water produced from Powder River Basin (PRB) coal aquifers.

$$SAR = \frac{[Na^+]}{\sqrt{\frac{[Ca^{2+}] + [Mg^{2+}]}{2}}} \quad [C] = meq/l$$

## Calculated Equilibrium SAR Values of NaHCO<sub>3</sub> Solutions Over Calcite and Dolomite at Selected Partial Pressures of CO<sub>2</sub>

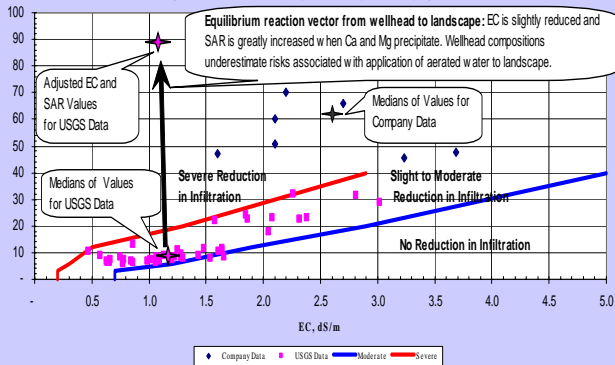


Geochemical modeling using MINTQA2 software shows that samples of CBM product water, obtained by the USGS, exhibit compositions that would be expected of water in equilibrium with calcite and dolomite under a partial pressure of about 0.10 atmospheres of carbon dioxide. Limited sample data provided by several developers in the Powder River Basin indicate waters in transition from aquifer and approaching landscape equilibrium conditions.

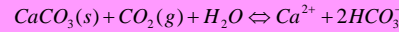
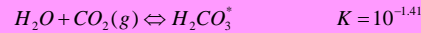
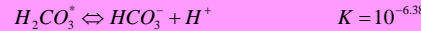
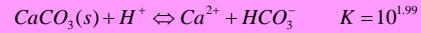
Geochemical modeling of the equilibrium reaction vector produced by aeration of CBM product water shows that composition data taken from wellhead samples seriously underestimate the risks associated with applying water to the landscape. EC is slightly reduced and SAR is greatly increased as Ca and Mg are precipitated from solution.

## Effect of CBM Water Quality on Infiltration

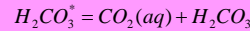
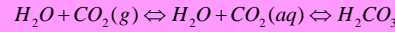
Guidelines per Ayers and Weston, "Water Quality for Agriculture", FAO Irrigation and Drainage Paper 29, (Rev. 0, 1985)



## CARBONATE CHEMISTRY EXPLAINS CBM WATER INSTABILITY



$$K_{sum} = 10^{-5.80}$$



Rearranging and Solving for concentration of Ca in solution yields:

$$K = 10^{-5.80} = \frac{[Ca^{2+}][HCO_3^-]^2}{[CO_2(g)]}$$

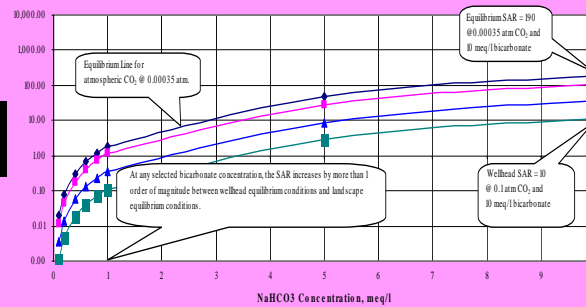
or

$$[Ca^{2+}] = \frac{10^{-5.80} \times [CO_2(g)]}{[HCO_3^-]^2}$$

## Bicarbonate Suppresses Ca and Mg Solubility

Similar relationships can be derived for magnesite and dolomite. In all cases the concentration of Ca and Mg in solution varies directly with the partial pressure of carbon dioxide and inversely with the square of the concentration of bicarbonate ion. The partial pressure of carbon dioxide in the atmosphere is about 0.00033 atmospheres, or considerably less than the estimated equilibrium partial pressure (~0.10 atm.) in the aquifer. As CBM product water loses dissolved carbon dioxide and approaches equilibrium with the atmosphere, Ca and Mg precipitate to form carbonate minerals. Sodium remains in solution. At bicarbonate concentrations above 5 meq/L, equilibrium concentrations of soluble Ca and Mg drop below about 0.1 meq/L. As a result, SAR values increase rapidly with increasing bicarbonate in solution.

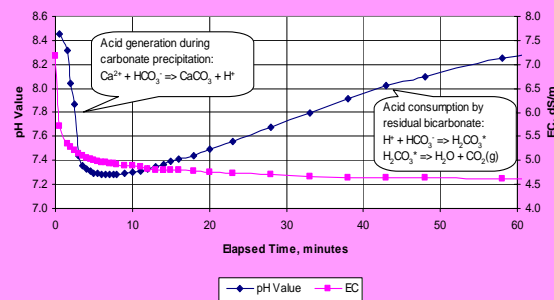
## Calculated SAR Value Based on Calcite Solubility



Atmospheres of CO<sub>2</sub>

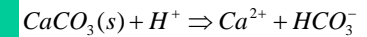
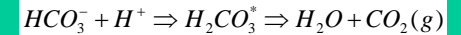
- 0.00033 (blue diamonds)
- 0.001 (magenta squares)
- 0.01 (green triangles)
- 0.1 (red squares)

## CO<sub>2</sub> Mass Transfer Controls Rate of Approach to Equilibrium

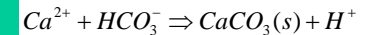
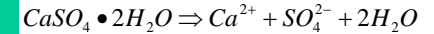


## SAR Reduction Without Sodium Removal

### Direct Acidification



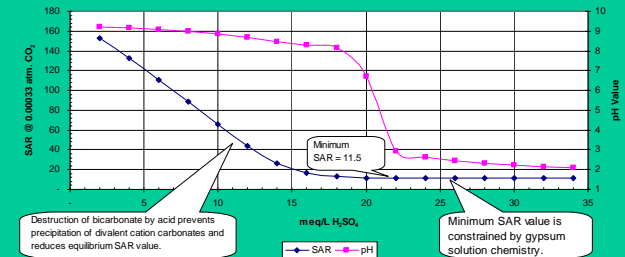
### Gypsum Addition



Direct acidification and treatment with gypsum both act to substitute sulfate for bicarbonate anions and thus retard precipitation of divalent cation carbonates. CBM product water measured at the wellhead contains significant dissolved Ca and Mg. Direct acidification at the wellhead accompanied by aeration to promote degassing can minimize increases in SAR due to precipitation of divalent cation carbonates. SAR reductions accompanying CBM water treatment with sulfuric acid are constrained by rapid reduction in water pH at the titration endpoint. If sulfuric acid acidification is performed over calcite, the pH remains slightly above neutral and the minimum SAR is governed by gypsum solubility. Gypsum solubility limits successful treatment to CBM product waters exhibiting sodium concentrations below about 15 meq/L. Sodium removal will likely be required for adequate SAR management of CBM product waters that have undergone evaporative concentration or otherwise exhibit Na concentrations above about 15 meq/L.

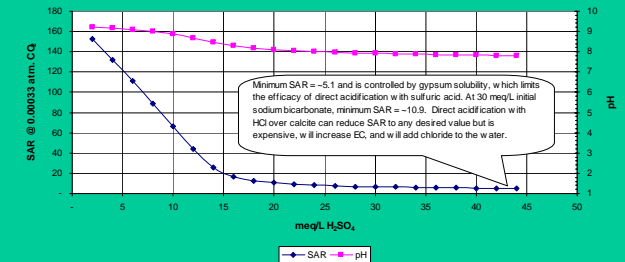
## Direct Acidification of CBM Product Water

15 meq/L NaHCO<sub>3</sub>, 5 meq/L Ca(HCO<sub>3</sub>)<sub>2</sub>, Titrated With H<sub>2</sub>SO<sub>4</sub>



## Direct Acidification of CBM Water Over Calcite

15 meq/L NaHCO<sub>3</sub>, 5 meq/L Ca(HCO<sub>3</sub>)<sub>2</sub>, Titrated With H<sub>2</sub>SO<sub>4</sub>



## Equilibrium SAR of NaHCO<sub>3</sub> Solutions Over Gypsum @ 0.00033 atm. CO<sub>2</sub>

