Appendix 2 - Objective 2

Determination of the nature and behavior of coalbed methane product upon exposure to atmospheric conditions, upon surface discharge, and upon discharge and mixing with non-receiving water resources

Power Point Presentation - File title: Drake MSU Seminar.

Title: Coalbed Methane Product Water (Soda with a Twist)

Author: Ronald Drake, Drake Engineering, Helena, MT (subcontractor)

Content: a 16-frame power point presentation detailing the chemical equilibrium reactions dictating the behavior of bicarbonate-carbonate within coalbed methane product water of the Powder River Basin when exposed to atmospheric conditions. Rapid increases in coalbed methane product water sodicity, SAR, and pH at wellhead discharge point.

Ron Drake
Drake Engineering Incorporated
Helena, MT

Coal Bed Methane Product Water (Soda With a Twist)

The Twist Is Transition

- ✓ From wellhead to landscape CBM product water is always changing
- ✓ You can't interpret a CBM water analysis unless you know the water's history
- ✓ The aquifer is a closed system with a high partial pressure of carbon dioxide
- ✓ The landscape is an open system with low but variable partial pressure of carbon dioxide

Instability Breeds Uncertainty

- ✓ Bicarbonate rules! CBM product water is unstable
- ✓ Chemical changes begin when the water is pumped from the coal seam
- ✓ Primary chemical reactions are fast
  - Spontaneous pH and EC decrease
  - Spontaneous SAR increase
- ✓ Approach to ultimate equilibrium chemistry is controlled by liquid/gas mass transfer

Chemistry Fundamentals Work

- ✓ Carbonate chemistry of Ca and Mg determines changes in SAR and EC

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

- ✓ pH and alkalinity depend on partial pressure of carbon dioxide

Carbonate Chemistry

$$CaCO_3(s) + H^+ \Leftrightarrow Ca^{2+} + HCO_3^- \qquad K = 10^{1.99}$$

$$H_2CO_3^*(aq) \Leftrightarrow HCO_3^- + H^+ \qquad K = 10^{-6.38}$$

$$H_2O + CO_2(g) \Leftrightarrow H_2CO_3^* \qquad K = 10^{-1.41}$$

$$CaCO_3(s) + CO_2(g) + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^-$$

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

$$* \; H_2O + CO_2(g) \Rightarrow H_2O + CO_2(aq) \Rightarrow H_2CO_3$$

Other Useful Stuff

$$aA + bB \Leftrightarrow cC + dD$$

$$K_e = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$[solid] = [H_2O] = 1$$

$$[gas] = p_{gas} = atmosphere$$

$$p_{CO_2} = 3.55 \times 10^{-4}\ atm$$

$$pH = -\log[H^+]$$

Determine Calcium Conc. From Calcite

$$CaCO_3(s) + CO_2(g) + H_2O \Leftrightarrow Ca^{2+} + 2HCO_3^-$$

yields

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

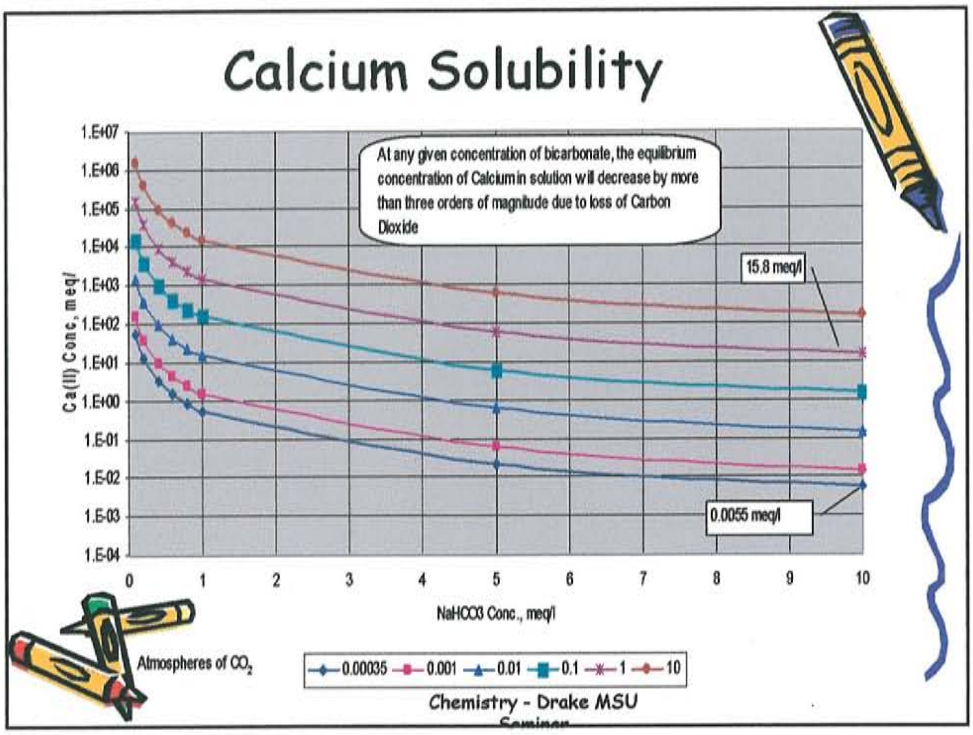
or

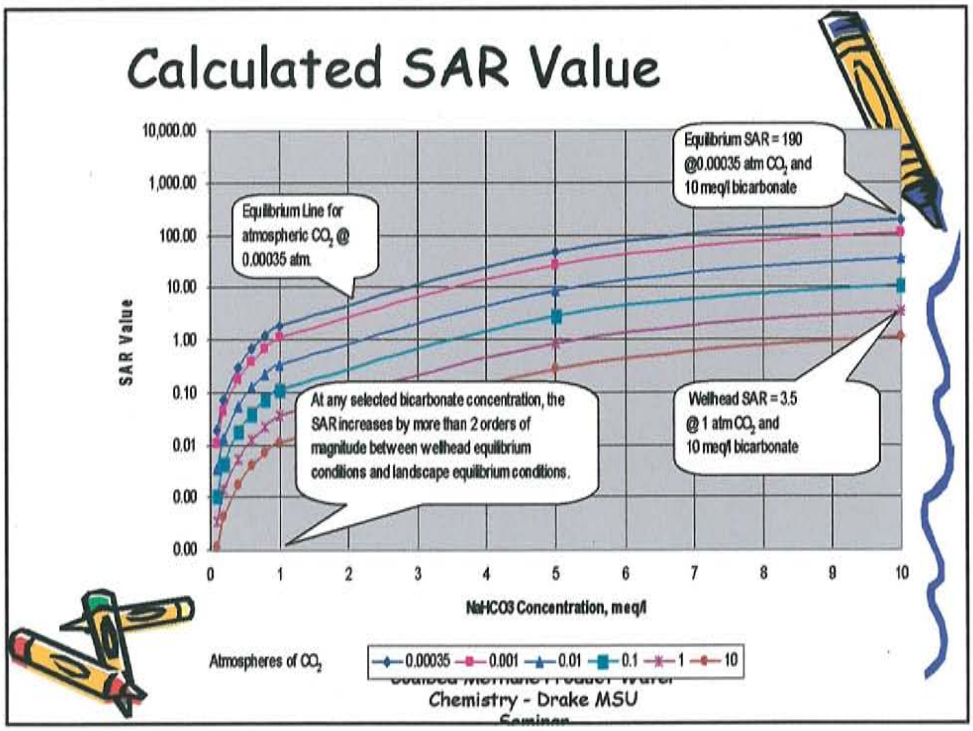
$$[Ca^{2+}] = \frac{10^{-5.80} \times [CO_2(g)]}{[HCO_3^-]^2}$$

Carbon dioxide partial pressure and bicarbonate concentration control calcium solubility in CBM water.

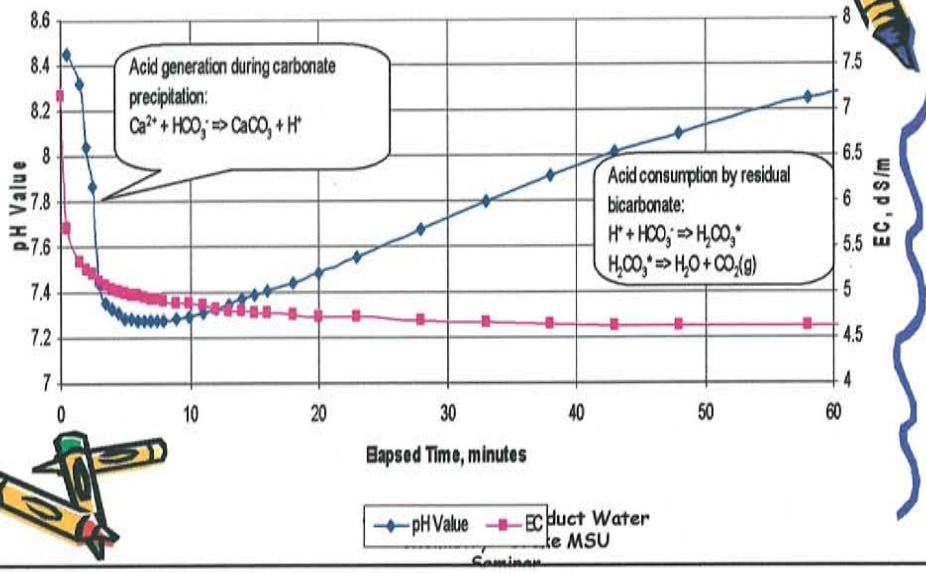
Remember SAR Definition

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


Calcium Solubility
At any given concentration of bicarbonate, the equilibrium concentration of Calcium in solution will decrease by more than three orders of magnitude due to loss of Carbon Dioxide
15.8 meq/l
0.0055 meq/l
Ca(II) Conc., meq/l
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
0 1 2 3 4 5 6 7 8 9 10
NaHCO3 Conc., meq/l
Atmospheres of CO_2
0.00035 0.001 0.01 0.1 1 10
Chemistry - Drake MSU


Calculated SAR Value
Equilibrium SAR = 190 @0.00035 atm CO_2 and 10 meq/l bicarbonate
Equilibrium Line for atmospheric CO_2 @ 0.00035 atm.
At any selected bicarbonate concentration, the SAR increases by more than 2 orders of magnitude between wellhead equilibrium conditions and landscape equilibrium conditions.
Wellhead SAR = 3.5 @ 1 atm CO_2 and 10 meq/l bicarbonate
SAR Value
10,000.00
1,000.00
100.00
10.00
1.00
0.10
0.01
0.00
0.00
0 1 2 3 4 5 6 7 8 9 10
NaHCO3 Concentration, meq/l
Atmospheres of CO_2
0.00035 0.001 0.01 0.1 1 10
Chemistry - Drake MSU

Mass Transfer of CO_2 Is Rate Limiting Step



SAR Reduction Requires

- ✓ Reduction of Na Concentration
  - Chemical Processing Equipment
  - Generation of Na Concentrate
- ✓ Increase of Ca and Mg Conc.
- ✓ Must Eliminate Bicarbonate Ion
  - Direct Acidification
  - Chemical Addition

Bicarbonate Elimination

Direct Acidification

$$HCO_3^- + H^+ \Rightarrow H_2CO_3^* \Rightarrow H_2O + CO_2(g)$$

$$CaCO_3(s) + H^+ \Rightarrow Ca^{2+} + HCO_3^-$$

Chemical Addition

$$CaSO_4 \bullet 2H_2O \Rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$

$$Ca^{2+} + HCO_3^- \Rightarrow CaCO_3(s) + H^+$$

Wrap-up

- ✓ Bicarbonate increases SAR by suppressing Ca and Mg solubility
- ✓ Ca and Mg carbonate precipitation is fast and generates hydronium ions
- ✓ Hydronium ions convert bicarbonate to carbonic acid
- ✓ Carbonic acid decomposition rate is limited by mass transfer of CO_2

Summary Rules of Thumb

- ✓Water with bicarbonate as the predominant anion will exhibit high SAR when equilibrated with the atmosphere
- ✓Water containing bicarbonate will rarely exhibit Ca and Mg above 1 meq/l
- ✓Therefore, SAR (quick-and-dirty) in bicarbonate water can be approximated by the Na concentration in meq/l

Ain't Chemistry Fun??!!

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Excel File - File title: CBM Product Water Chemistry - Part 1

Title: Chemistry transformations of sodium bicarbonate-rich coalbed methane product water over time when exposed to evapoconcentration - open impoundment/stream channel simulation.

Author: Holly Sessoms, Montana State University

Content: 3-graph Excel presentation, illustrating changes in three water compositions, coalbed methane product water salinity (EC - electrical conductance), sodicity (SAR), and acidity (pH) over a 202-hour mixing/atmospheric exposure time subject to surface evaporation.

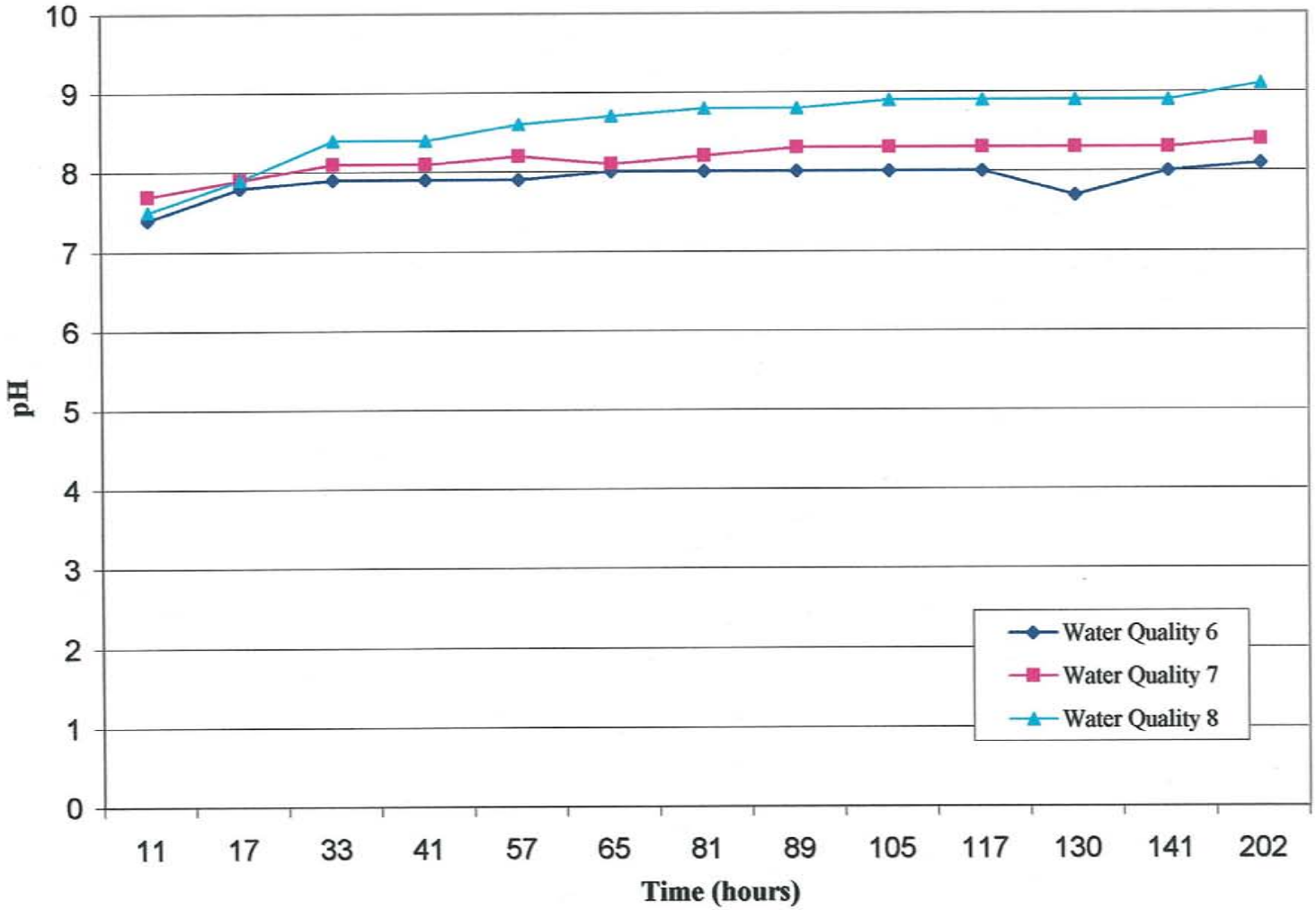


Figure 4. pH of three simulated CBM product waters of varying quality over a 9 day period of agitation in an open container at atmospheric pressure, i.e., in the presence of evapoconcentration.

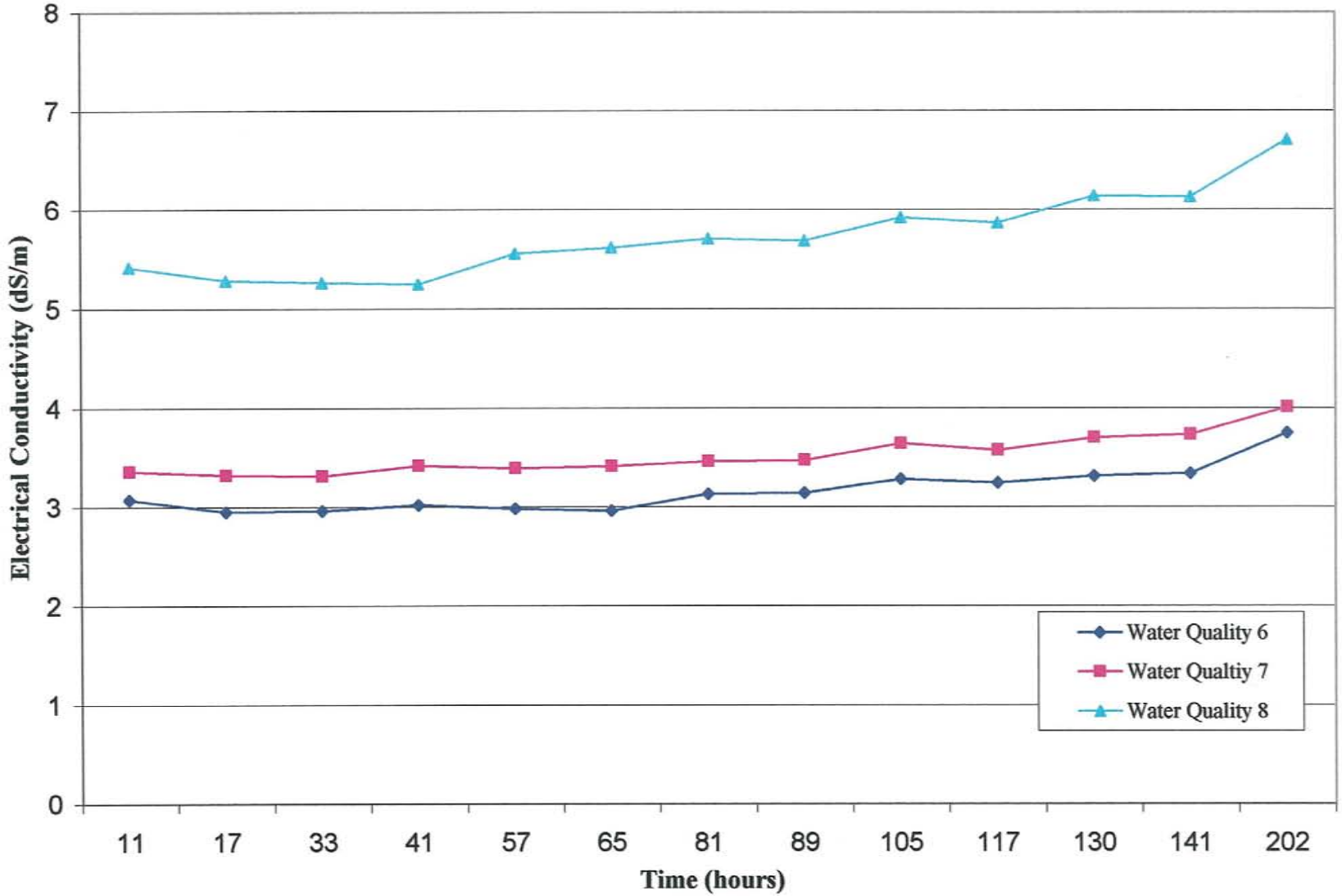


Figure 5. Electrical conductivity (EC, dS/m) of three simulated CBM product waters of differing quality over a 9 day period of agitation in an open container at atmospheric pressure, i.e., in the presence of evapoconcentration.

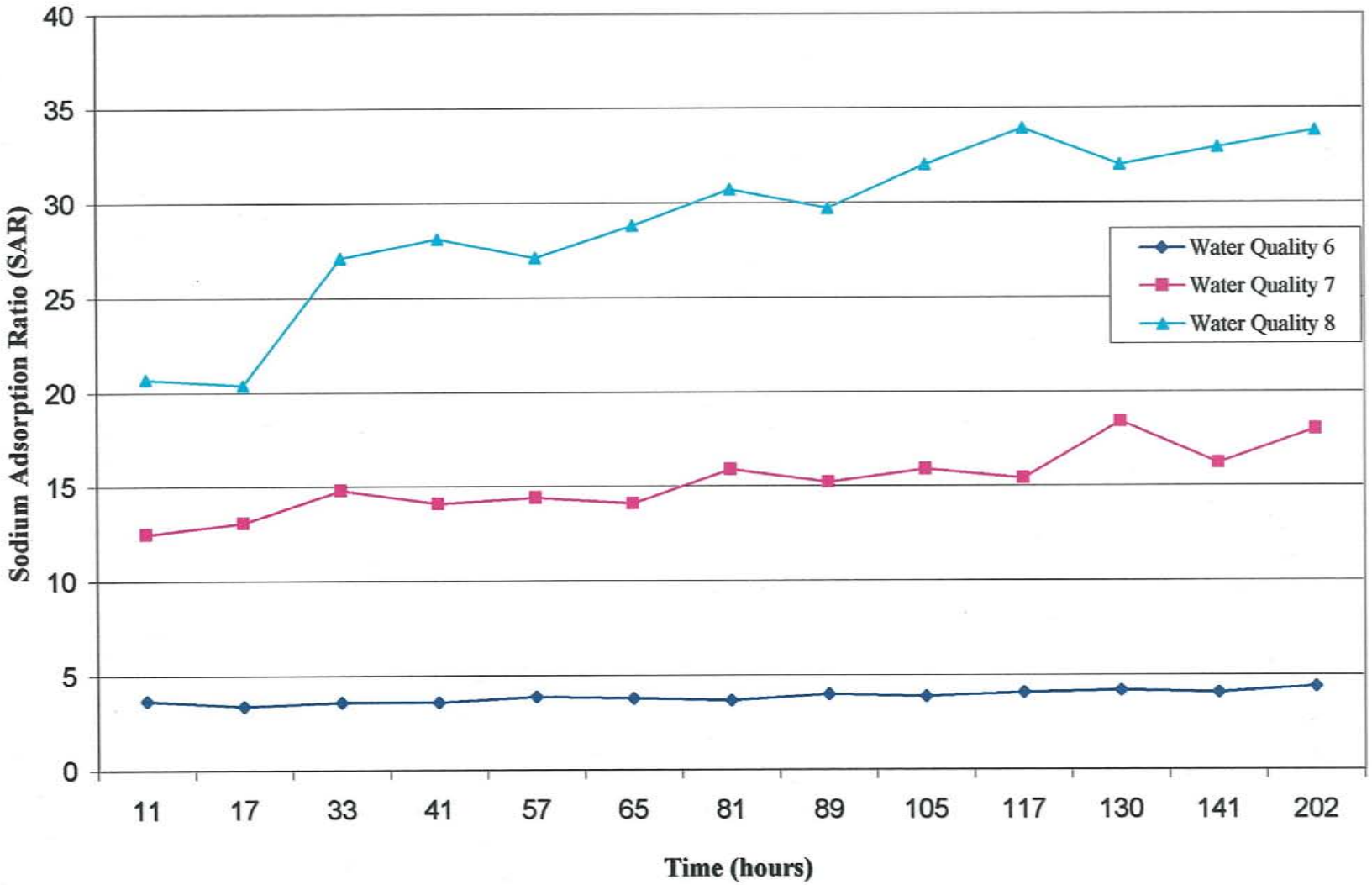


Figure 6. Sodium Adsorption Ratio of three simulated CBM product waters of differing quality over a 9 day period of agitation in an open container at atmospheric pressure, i.e., in the presence of evapoconcentration.

Excel File - File title: CBM Product Water Chemistry - Part 2

Title: Chemistry transformations of sodium bicarbonate-rich coalbed methane product water over time in the absence of evapoconcentration - closed system, no evaporation permitted.

Author: Holly Sessoms, Montana State University

Content: 3-graph Excel presentation, illustrating changes in three water compositions, coalbed methane product water salinity (EC - electrical conductance), sodicity (SAR), and acidity (pH) over a 270-hour mixing time in the absence of evaporation.

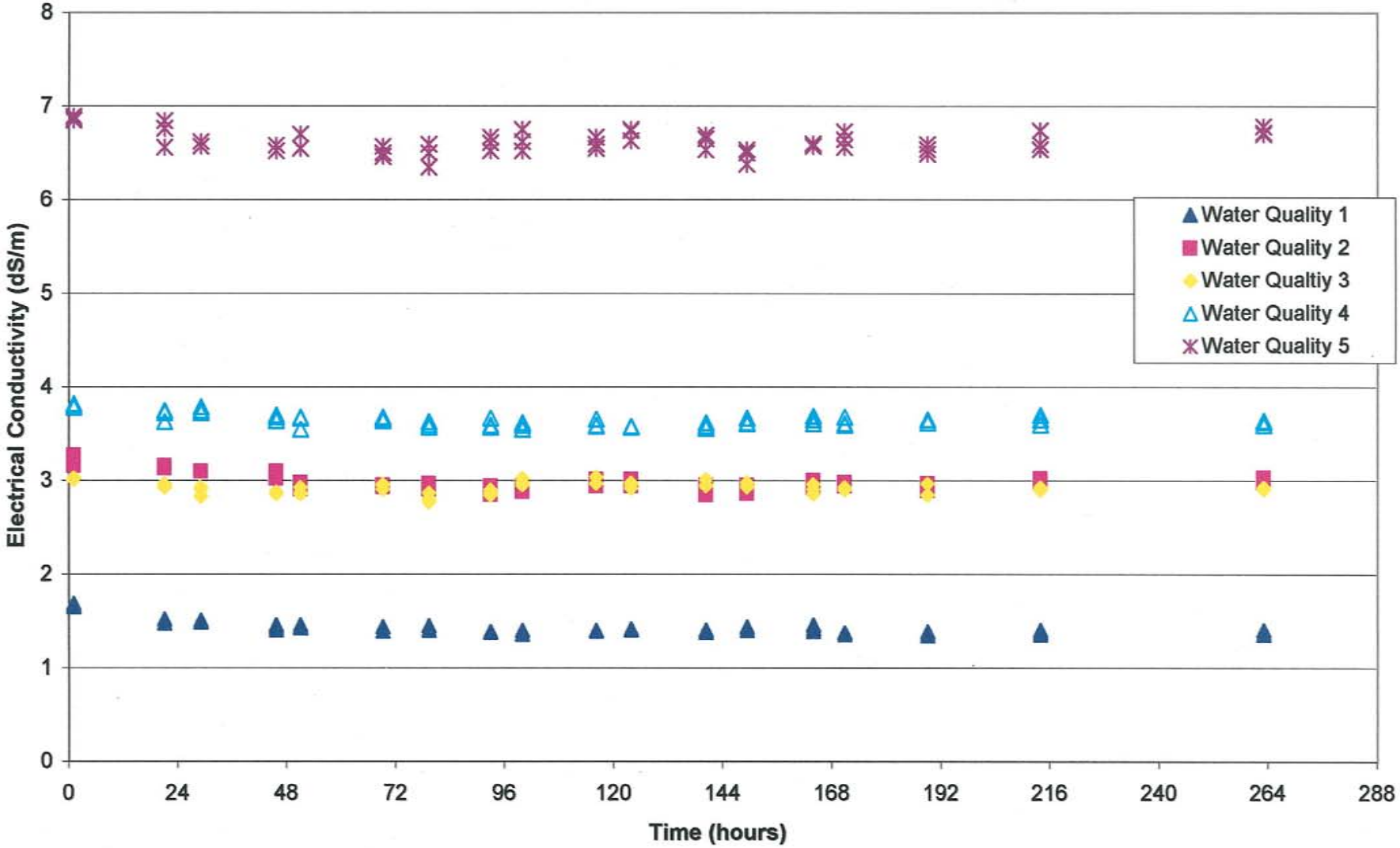


Figure 1. Electrical Conductivity (EC, dS/m) of five simulated CBM product waters of varying quality over a 12 day period of agitation without evapoconcentration, i.e., closed container at atmospheric pressure.

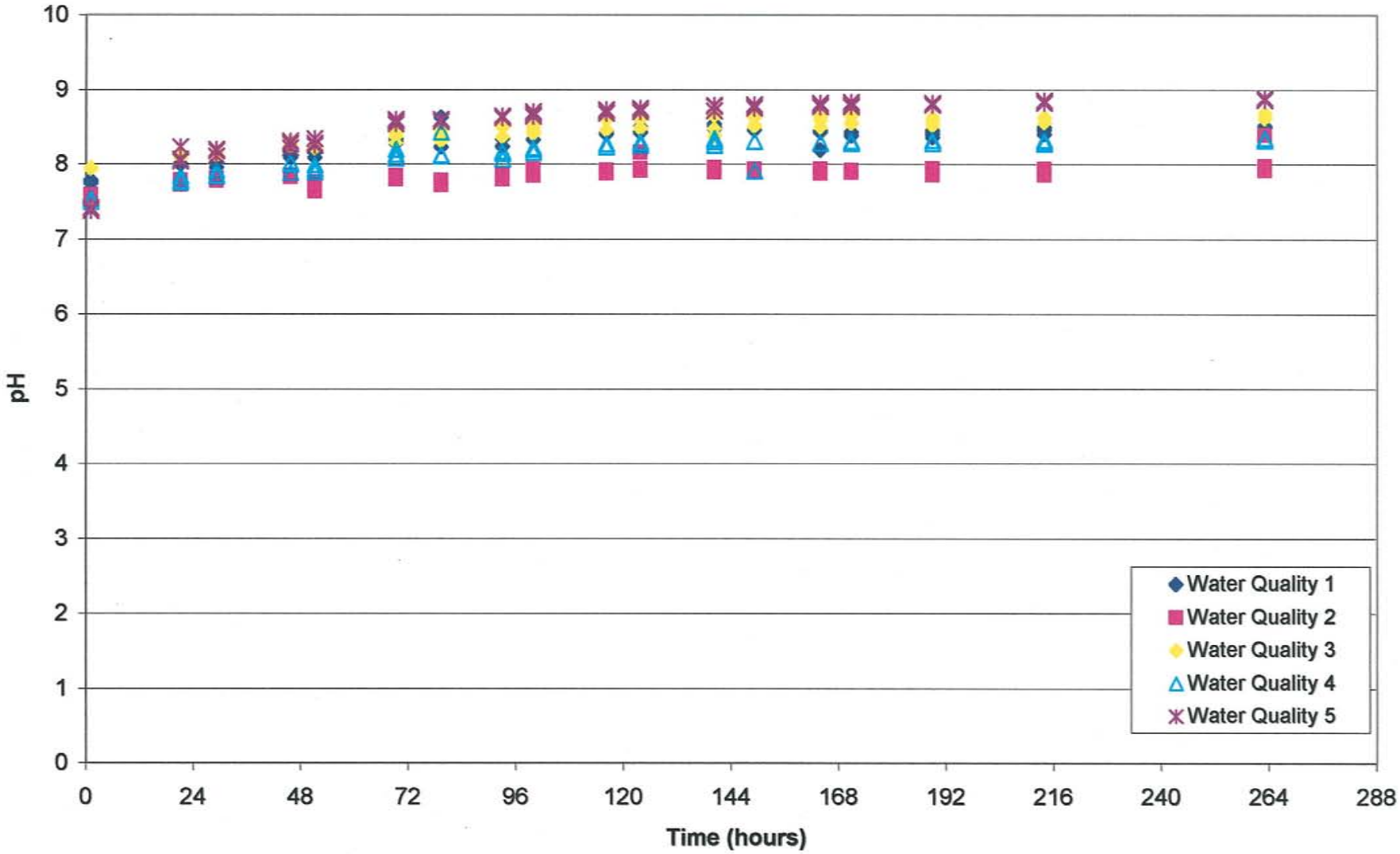


Figure 2. pH of five simulated CBM product waters of varying quality over a 12 day period of agitation without evapoconcentration, i.e., closed container at atmospheric pressure.

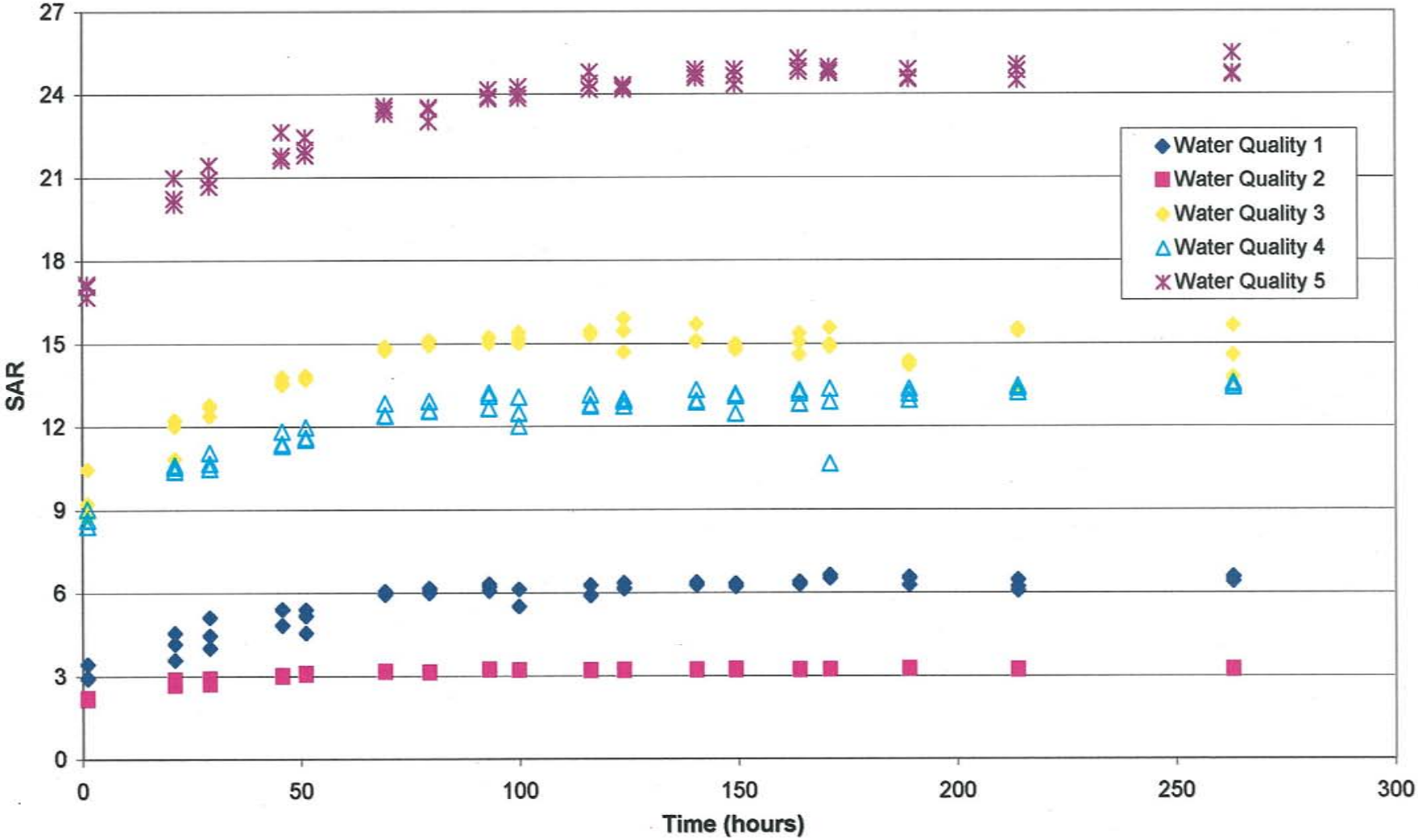


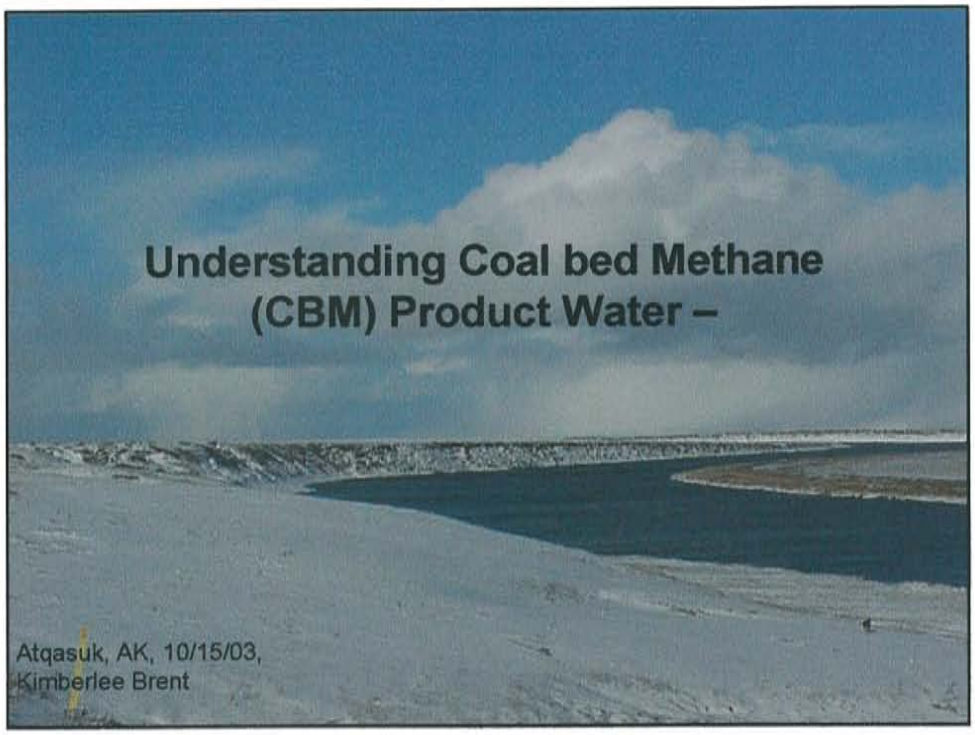
Figure 3. Sodium Adsorption Ratio (SAR) of five simulated CBM product waters of varying quality over a 12 day period of agitation without evapoconcentration, i.e., closed container at atmospheric pressure.

Power Point Presentation - File title: Bauder_CBM Water

Title: Understanding Coal bed Methane (CBM) Product Water –

Author: James W. Bauder, Montana State University

Content: 14-frame power point presentation explaining the process of biogenic methane production, water chemistry transformations during methane genesis, the evolution of coalbed methane product water including the dissolution of sodium bicarbonate and subsequent precipitation of calcium carbonate, results of benchtop and field monitoring studies documenting changes in chemistry of coalbed methane product water upon exposure to atmospheric conditions, with resultant elevation in sodicity (SAR), salinity (EC) due to evapoconcentration, and pH.



Coal bed methane (CH_4) product water

CBM, coal formations, H_2O

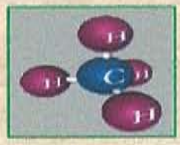
Jim Bauder
Water Quality Specialist
Montana State University

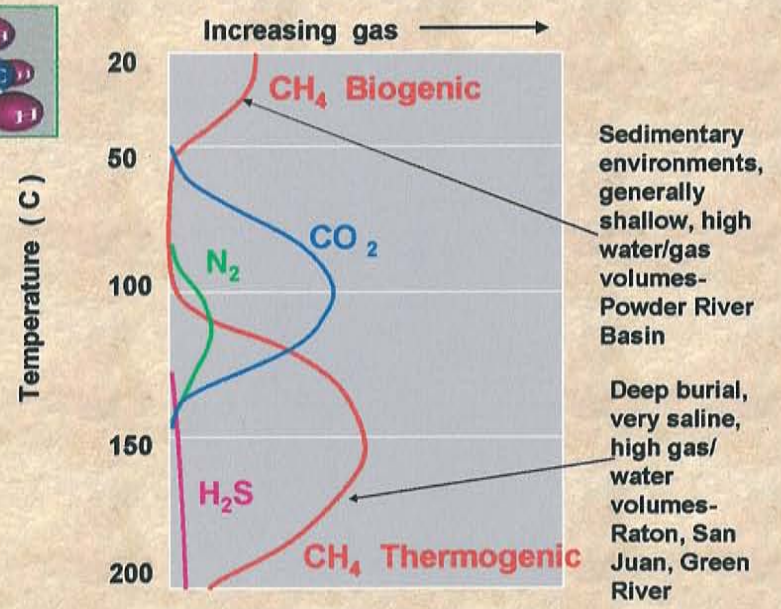
About Methane

- Geologic events– ***thermogenic***
  - Thermal decomposition of organic matter under high heat and pressure - catagenesis
- Biological events "bugs" – ***biogenic***
- Marsh gas – CH_4 - Natural gas -
  - methanogenesis
  - Fermentation and dissociation of acetate
    - CH_3--|--CO_2^- + H → CH_4 + CO_2
  - Reduction of CO_2 formed during respiration
    - CO_2 + 8H → CH_4 + $2H_2O$

3

Relative Generation of Gas during Coalification





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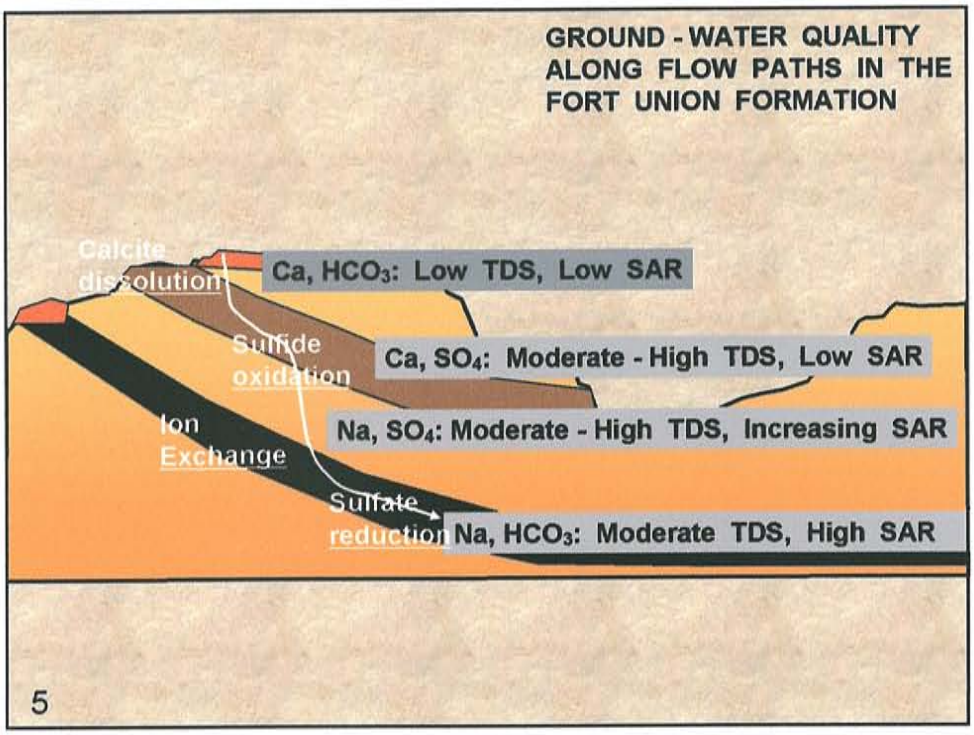


CBM Product Water Chemistry

- CBM product water is bicarbonate rich and 'confined' (under pressure) in coal seams.
- When product water is exposed to the atmosphere, discharged into surface water or applied to soil, sodium bicarbonate undergoes the following reaction:

$$NaHCO_3 \Rightarrow H^+ + CO_3^{-2} + Na^+$$

(See poster by R. Drake, 2003; also Van Voast, 2003)

CBM Product Water Chemistry

- Free carbonate (CO_3^{-2}) in solution is now available to bind with calcium in the surface water or soil to form calcium carbonate, i.e., limestone or calcite.

$$Ca^{+2} + 2HCO_3^- \rightarrow CaCO_3^- + H_20 + CO_2$$

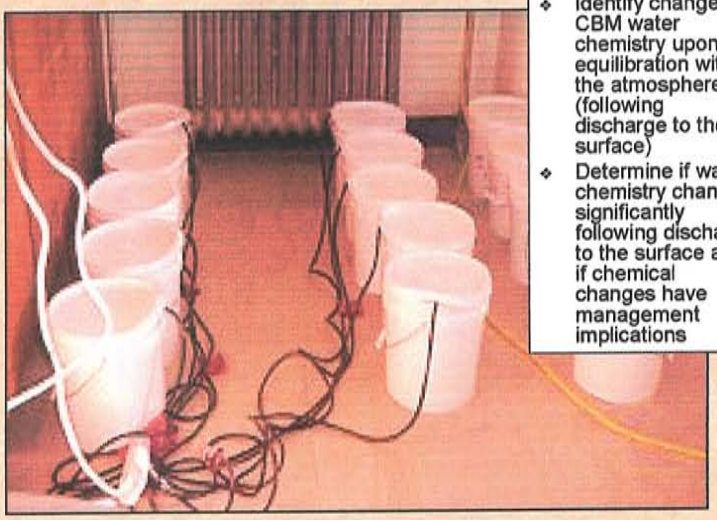
CBM Product Water Chemistry

- The dissolution of sodium bicarbonate ($NaHCO_3^{-)}$ also causes pH to increase

$$Na^+ + H^+ CO_3 \Rightarrow CO_2 + Na^+ + OH^-$$

Chemical changes to CBM product water upon discharge to the surface

Holly Sessoms, M.S.



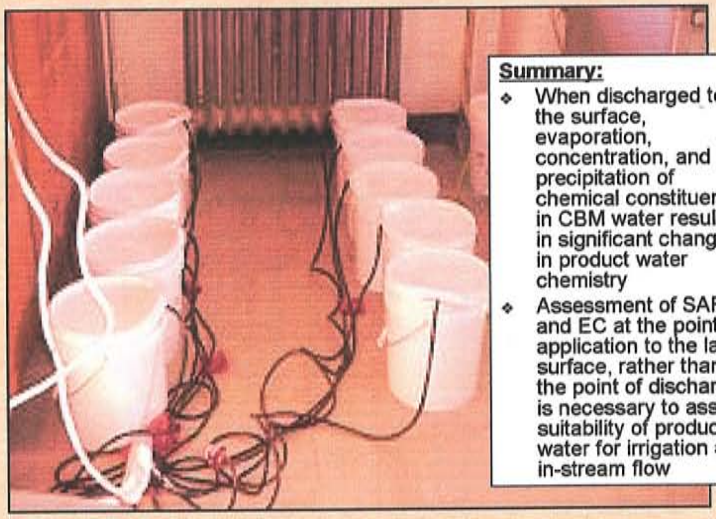
Objectives:

- Identify changes to CBM water chemistry upon equilibration with the atmosphere (following discharge to the surface)
- Determine if water chemistry changes significantly following discharge to the surface and if chemical changes have management implications

9

Chemical changes to CBM product water upon discharge to the surface

Holly Sessoms, M.S.



Summary:

- When discharged to the surface, evaporation, concentration, and precipitation of chemical constituents in CBM water results in significant changes in product water chemistry
- Assessment of SAR and EC at the point of application to the land surface, rather than at the point of discharge, is necessary to assess suitability of product water for irrigation and in-stream flow

10

Change in water chemistry for three water qualities over a 9 day time period (subject to evapoconcentration).

	Initial vs. Final pH	Initial vs. Final EC (dS/m)	Initial vs. Final SAR	% Change EC	% Change SAR	% Change pH
Powder River	**7.4 / 8.1**	**3.07 / 3.75**	**3.7 / 4.4**	22.15	18.92	9.5
CBM	**7.7 / 8.4**	**3.36 / 4.01**	**12.5 / 18.0**	19.35	44.00	9.1
Saline-sodic CBM	**7.5 / 9.1**	**5.42 / 6.71**	**20.7 / 33.8**	23.80	63.29	21.3
			Average % Change:	**21.77**	**42.07**	**13.3**

11

Changes in product water chemistry - from discharge to downstream location:

	Mean values			
	pH --	**EC dS/m**	**SAR practical**	**SAR true**
Sue Draw DC 1	**7.13**	**4.30**	**24.76**	**33.5**
Site 3	**8.54**	**4.20**	**29.74**	**44.1**
Site 4 (below res.)	**9.15**	**4.27**	**32.46**	**53.4**
% Change: (discharge to Site 4)	**28.3% increase**	**<1% decrease**	**31.1% increase**	**59.4% increase**

Source: Patz, Marji J. Coalbed Methane Product Water Chemistry on Burger Draw, Wyoming, M.S., Department of Renewable Resources. University of Wyoming. May, 2002.

12

Change from outfall to irrigation

- Aaron DeJoia
  - Cascade Earth Sciences
  - Kingsbury site, WY, 2002

Source	pH	SAR	EC mmhos/cm
Outfall	7.5	20-26	3.8-4.2
Pump	8.2	27-30	2.6
Irrigation Nozzle	8.7	32	2.9

13

CBM Product Water Chemistry

- In summary, sodium bicarbonate-rich CBM product water can initiate the precipitation of calcium carbonate causing:
  - SAR increase
  - EC decrease slightly
  - pH increase