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Evaluation of Formation Water Chemistry: Bakken Shale.

Geoffrey Thyne and Patrick Brady

Abstract

Determination of in situ formation water chemistry is an essential component of reservoir management. This paper details the use of thermodynamic computer models to calculate reservoir pH and restore produced water analyses for prediction of scale formation. Bakken produced water samples were restored to formation conditions and calculations of scale formation performed. In situ pH is controlled by feldspar-clay equilibria. Calcite scale is readily formed due to changes in pH during pressure drop from in situ to surface conditions. The formation of anhydrite scale, which has been observed, is not predicted from the model. Formation of anhydrite and/or halite may be related to the localized conditions of increased salinity as water is partitioned into the gas phase during production.

Introduction

Accurate formation water chemistry is essential for the design of drilling and completion fluids, ensuring fluid compatibility, avoiding corrosion damage, souring, fines mobilization, clay swelling and scale precipitation, as well as design of surface fluid handling facilities (Abdou et al, 2011, Bader, 2007, Baraka-Lokmane and Sorbie, 2010, El-Said et al. 2009, Holubnyak et al. 2011, Kan et al. 2014, Kodel et al. 2010, Mosghadasi et al. 2004, Shosh and Li, 2013). In particular, the precipitation of calcium carbonate and sulfates, barium sulfate and iron scales in wellbores and surface facilities are an on-going problem for most fields (Mahmoud, 2014, Zahedzadeh et al. 2014). There are software packages available to calculate potential scaling (Haghtalab et al. 2014, Fu et al. 2013), but good predictions require accurate formation water chemistry (Zhang et al. 2010). And the water chemistry measured at the wellhead often differs that of the formation because of reactions that occur in transit. A thermodynamic approach must be applied to calculate the in situ water chemistry by accounting for the changes in pressure and temperature and their effect on chemical equilibria as production fluids rise in a borehole (Ahmadi et al. 2015). This paper presents an evaluation of Bakken reservoir fluids focusing on restoration of in situ conditions, especially pH (Kan et al. 2013), and evaluation of formation water chemistry scaling potential. The thermodynamic modeling used is a first step in evaluation restricted to static mode and does not explicitly account for flow (Fu et al. 2014).

The Bakken Shale is a prolific hydrocarbon producer in the Williston Basin. The Bakken is an intracratonic basin with a relatively simple structure that encompasses portions of South Dakota, North Dakota, Montana, Saskatchewan and Manitoba. The basin formation water is typically very saline due to dissolution of salts including anhydrite and halite (Bachu and Hitchon, 1996, Iampen and Rostron, 2000). The Bakken Formation ranges from 0 to 140 feet, thickening toward basin center (Tran et al. 2011). The productive middle member of the Bakken Formation is composed of silt-sized clay, carbonate and silicate minerals together with 5-10% organic matter. The Bakken Formation is considered to be an aquitard (Hitchon, 1996) and so is hydrologically isolated from the general west to east topographically-driven basinal flow in the aquifer units (Bachu and Hitchon, 1996). The low permeability of the shale has trapped generated oil within the shale further reducing permeability to water flow. No Bakken oil has escaped to the overlying Madison group (Ramakrishna et al. 2010).

Petrographic studies have shown the middle Bakken member is composed of slit-sized dolomite and mono-crystalline quartz with minor amounts of potassium feldspar, plagioclase, volcanic rock fragments, muscovite, calcareous grains and skeletal fragments. The authigenic phases are mostly carbonate cements, dolomite and calcite. Dolomite grains may have ferroan rims. Other authigenic features include quartz and K-feldspar overgrowths, and anhydrite and pyrite. Clays are predominantly illite (<5% expandable) and minor chlorite and kaolinite (Ashu, 2014, Kurtoglu et al. 2014, Pitman et al. 2001, Ramakrishna et al. 2010). There are no reports of halite in the middle Bakken, however, the underlying salt beds in the Middle Devonian Prairie Evaporite Formation do contain halite (Iampen and Rostron, 2000).

In petroleum reservoirs, water-rock reaction rates are anticipated to quickly reach chemical equilibrium with silicate and carbonate minerals within weeks to months after introduction of non-equilibrium fluids (Houston et al. 2007). Standard geochemical modeling codes can restore parameters such as calcium, alkalinity and pH to reservoir values by assuming equilibrium with formation minerals before production (Miller et al. 1976, Fu et al. 2013, Haghtalab et al. 2014, Holubnyak et al. 2011). In the Bakken, production of oil is preceded by formation of fracture networks to facilitate flow. The hydraulic fracturing process forces large volumes of fluid into the formation (LaFollette et al. 2012). This fluid is mostly low salinity water together with proppants and chemicals that is forced into the low permeability rock under pressure. Pressure is then released and hydrocarbons flow to the well. The return of injected fluids is termed flowback. During flowback the chemistry of the produced water gradually changes from pure fracturing and completion fluids to mixtures with formation water. In the Bakken, between 15 to 40% of the injected fluid does not return to the surface but instead remains in the formation (Boschee, 2014). The fluid entrained in the formation continues to mix and react with formation water, reservoir minerals and organic matter. Most wells deplete rapidly and reach stable low rates within a year. The life span of Bakken wells is three to four years.

Data

Chemical analyses of Bakken Formation water were compiled from the USGS Produced Waters database and several literature sources (Griffin et al. 2014, Gupta et al. 2012, Kurtoglu et al, 2014, Zhou et al. 2014a, Zhou et al. 2014b). The samples were from depths of 10,000 to 12,000 feet. The initial dataset had 423 samples from the USGS database and 12 samples from the other literature sources. Samples with missing data for the major solutes were discarded with the exception of five samples lacking alkalinity. An average value was substituted in those cases assuming carbonate equilibrium. Next, the charge balance was calculated and samples with charge imbalance greater than ±10% were removed from further evaluation. In a few cases careful examination of the analyses showed obvious errors in data entry that could be corrected to restore charge balance. Total dissolved solids (TDS) were measured on less than 10% of the samples so the TDS was calculated as the sum of the major solutes. Solutes are dominantly sodium and chloride with some potassium, calcium and magnesium, bicarbonate and sulfate with minor amounts of iron, barium, boron, and strontium. The final dataset had 369 samples with calculated TDS ranging from 963 mg/l to 343,833 mg/l. The higher salinity data is consistent with reported water chemistry in Williston basin formation waters (Iampen and Rostron, 2000).

The productive interval of the middle Bakken has a narrow range of depths. Reported sample depths ranged from 9,834 to 11,134 feet, averaging 10,227 feet. In situ temperature was calculated for samples that reported depth using the geothermal gradient and reported depth. The average temperature was 123°C with temperatures ranging from 106 to 133°C. For simplicity we use 120°C during calculations for samples that did not report depth or temperature.

Formation water samples from the Bakken are generally very saline with total dissolved solids as high as 350,000 mg/l. Figure 1 shows a Piper plot for the Bakken formation water analyses. The plot shows the solutes are mainly Na and Cl with minor amounts of Ca in some lower TDS samples. Figure 2 shows the TDS versus chloride content for the water samples together with an imbedded figure showing the distribution of values. The histogram shows that most samples have higher TDS, but there are samples with low TDS that form a distinct population. The linear regression line for the data has an r^2 of 0.99 and a y-intercept of 2,570 ppm TDS. The injected water in the Bakken has total salinity of approximately 5,000 ppm (Kurtoglu, 2014). Samples with low TDS probably represent early flowback in which the majority of the water is composed of hydraulic fracturing fluid rather than formation brine. Water from adjacent formations may be derived from hydraulic fractures that reach out of the relatively thin Bakken formation. Evaluation of 544 samples from the overlying Madison and Mission Creek and underlying Winnipegosis Formations using the same methodology were made. Samples used were from the same area as the Bakken samples, and sometimes the same field. The evaluation shows similar water compositions as the Bakken, so the lower salinity samples are not a result of contributions from the adjacent formations.

Petrographic examination of the Bakken shows the presence of quartz and K-spar including late stage overgrowths, dolomite and calcite, pyrite and occasional anhydrite, but no halite. In addition, the clay minerals illite, kaolinite, and chlorite were reported. We anticipate that the formation water should be in equilibrium with quartz, carbonate minerals and anhydrite given the rate of rock-water reactions at high temperature (106-133ºC).

The assumption of equilibrium with quartz at 120ºC can be tested. Figure 3 shows quartz saturation indices plotted against total dissolved solids for Bakken samples with dissolved silica analyses. The data show that the produced water samples are at, or near, equilibrium with respect to quartz; given the uncertainties in temperature and the possible effects of scale formation during rise to the surface, it is likely that formation waters are in equilibrium with quartz. This calculation is in agreement with the observations of late-stage quartz overgrowths (Pitman et al. 2001).

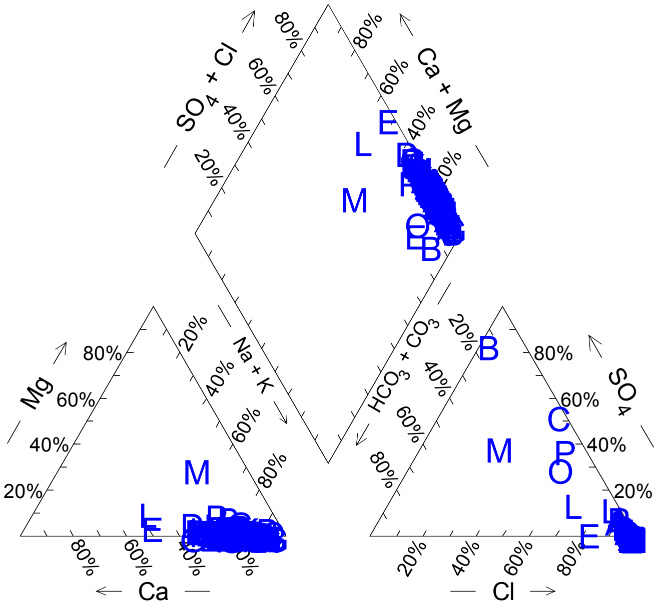

Figure 1. Piper plot of all Bakken samples.

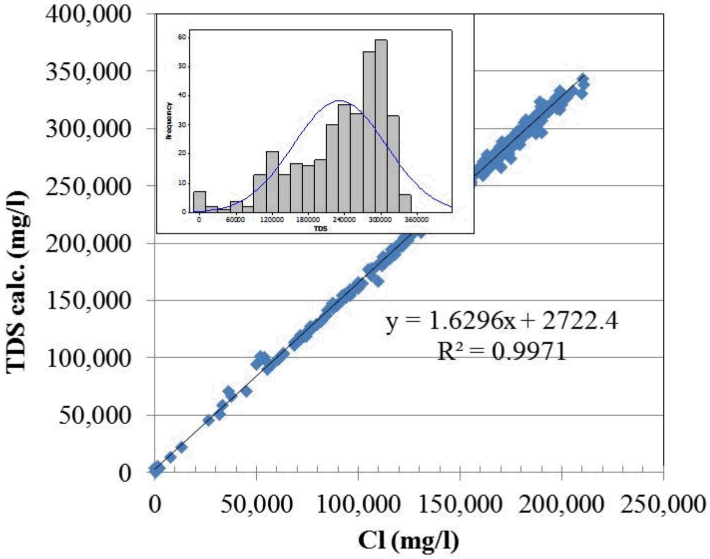

Figure 2. Total dissolved solids (calculated) versus chloride. Inset histogram shows the distribution of TDS in the Bakken produced water database.

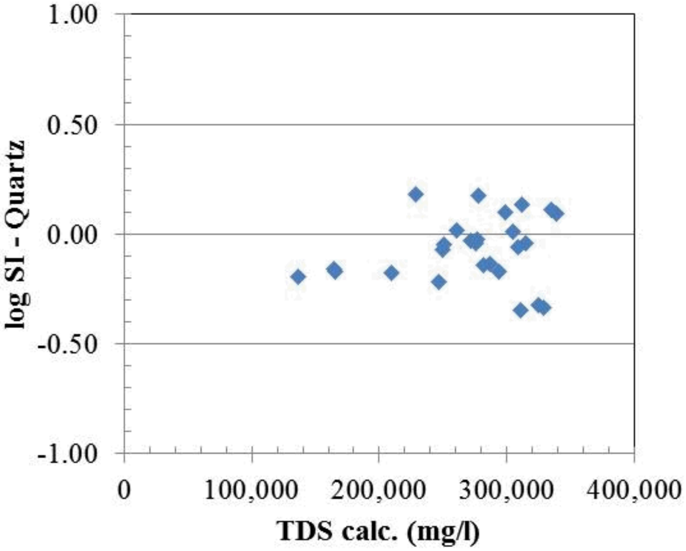

Figure 3. Calculated log SI (saturation index) for quartz at 100ºC versus total dissolved solids (calculated). Saturation with respect to quartz is equal to 0 in units of log SI. Calculated using GWB (b-dot) and llnl database.

The highly saline formation water in the Bakken means the ionic strength of the solution is greater than 4. In default mode PHREEQC (Parkhurst and Appelo, 1999) uses the Davies activity model while GWB uses the B-dot formulation (Bethke, 1996), but both modeling tools also include their own versions of a Pitzer database. In high ionic strength solutions, the use of traditional activity coefficient models such as the Davies equation or the extended Deybe-Huckel (B-dot) is not always correct. Instead, the Pitzer activity coefficient model is often used given its widespread adoption for multicomponent electrolytes and extensive parameterization in salt systems (Bethke, 1996).

To evaluate which activity model is the most effective for the Bakken we used PHREEQC to calculate the saturation for the mineral anhydrite with the PHREEQC, llnl and Pitzer databases. The PHREEQC and llnl databases use the default activity model, while the Pitzer database uses the ion-pair activity formulation. The calculated saturation for quartz and anhydrite should be relatively insensitive to pH, allowing the calculations to be made with field pH values. During production some calcite is precipitated and the temperature is lowered. Both of these processes should cause under-saturation of the produced water with respect to anhydrite since calcium is removed from solution and anhydrite solubility is retrograde, that is increases as temperature is lowered.

Figure 4 shows the results of the saturation index (SI) versus TDS for anhydrite. The Pitzer activity formulation produces saturation indices for anhydrite that are unlikely – persistent over-saturation – given that, if saturated, anhydrite should precipitate rapidly. The PHREEQC database gives more plausible results, but still shows many samples that are over-saturated. The llnl database produces the results most consistent with the observed mineralogy, and will be used for the rest of the calculations.

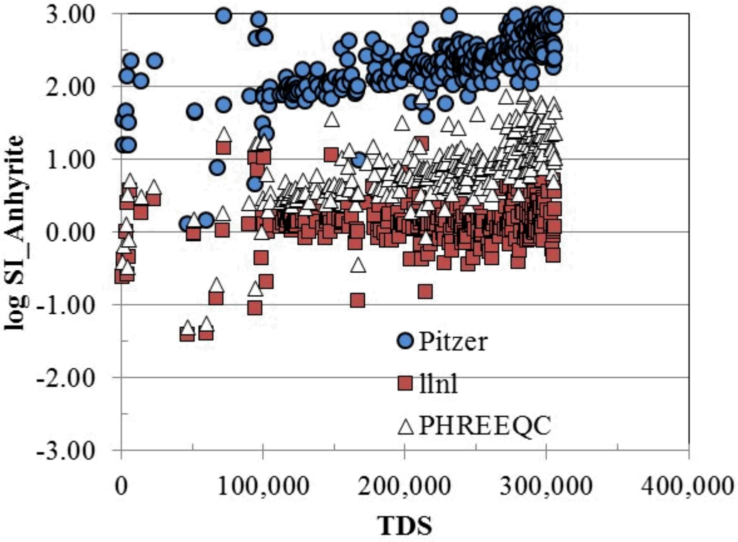

Figure 4. Calculated calcite saturation indices for anhydrite versus TDS for Bakken samples. Calculation were made using three different databases.

Restoration of in situ Formation Water Chemistry

We restore in situ formation water chemistry by first considering pH as carbonate mineral solubility depends strongly on pH. Carbonate scales typically form in response to an increase in pH that usually accompanies CO_2 degassing during production of fluids. We assume that the formation water is in equilibrium with the reservoir minerals, specifically carbonate minerals.

Calculation of pH

As produced fluids are brought to the surface, degassing and shifts in temperature result in disequilibrium (Ahmadi et al. 2015). In the Bakken produced water samples, the measured pH values range between 5.6 and 8.2, but those measurements were made at the surface at lower temperatures (4-35ºC) and pressures (1 bar) than prevail in the formation. To assess the degree of dis-equilibrium we have initially calculated the saturation index for calcite using the reported pH and dissolved calcium and alkalinity (see figure 3).

In order to calculate in situ pH, we assume that in situ pH is controlled by silicate mineral buffering (feldspar and clay) at reservoir conditions (Baccar and Fritz, 1993, Helgeson et al. 1993, Hutcheon et al., 1993, Smith and Ehrenberg, 1989). The pH set by the silicate buffer controls the pCO_2 and carbonate alkalinity through carbonate equilibrium rather than having the pH controlled by carbonate buffering of CO_2 produced by organic maturation (Lundegard and Land, 1989).

The *in situ* pH is estimated by assuming K-feldspar/Kaolinite equilibrium at reservoir temperatures, using log K ≈-3.8 (Smith and Ehrenberg, 1989) and the dissolved potassium values for each water sample (Equation 1).

$$H^+ + KAlSi_3O_8 + 1/2H_2O \leftrightarrow 1/2Al_2Si_2O_5(OH)_4 + K^+ + 2SiO_{2,qtz}$$

$$a_{K+}/10^{3.8} = a_{H+} \qquad (1)$$

First, we calculate the a_{K+} using the reported pH and potassium value for each analysis with the PHREEQC-llnl database. This database is common to both computer codes and contains the carbonate, chloride and sulfate minerals of interest. This calculated a_{K+} value is then used to calculate the in situ pH value using Equation 1. The procedure is then iterated to converge on a final value. There was no change in calculated pH after the second iteration.

We evaluate the calculated pH values by plotting the adjusted data on the mineral stability diagram for this system (Güler and Thyne, 2004). Figure 5 shows the mineral stability diagram for the K-spar-illite system with the produced water analyses after the in situ pH is calculated using GWB. All the data is clustered near the phase boundaries for kaolinite-K-feldspar, illite-K-feldspar or the K-feldspar-illite-kaolinite.

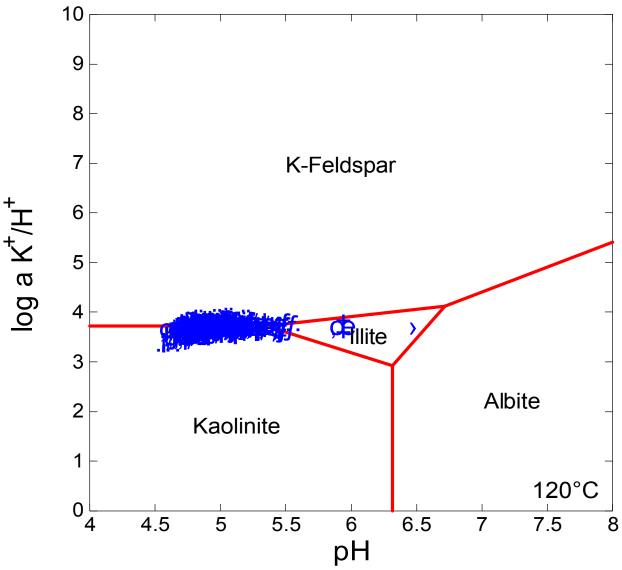

Figure 5. Phase diagram for K_2O-NaO-SiO_2-MgO-Al_2O_3-H_2O system at 120°C with the 368 Bakken water samples plotted (symbols). Diagram made using GWB ACT2 module (Bethke, 1996).

Figure 6 shows the calculated in situ pH values for all the samples with mean values of 5.08 using the GWB and 5.1 using the PHREEQC. The difference in calculated pH for each model is a result of slightly different calculated values of a_{K+}. The field pH values are shifted an average of 1 pH unit lower.

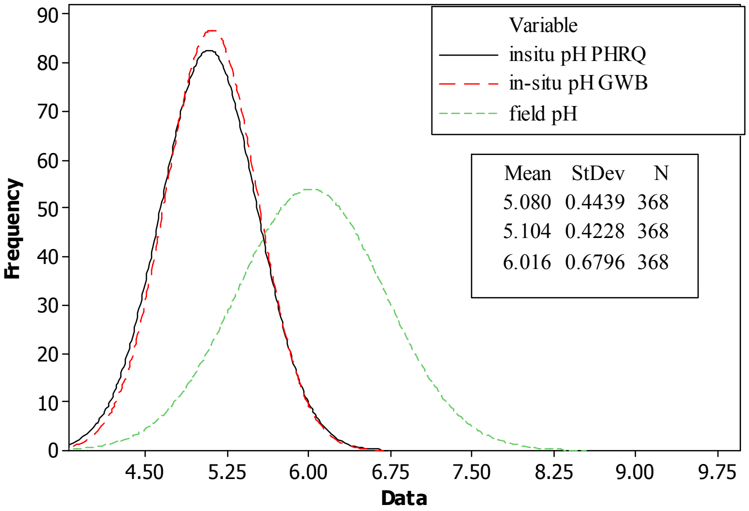

Figure 6. Reported and in situ pH values (calculated for Kspar-Illite equilibrium and potassium activities derived with GWB and PHREEQC using the Pitzer activity model) of water analyses at 120ºC.

The calcite saturation indices calculated with the restored (in situ) pH values are shown in Figure 7. The saturation indices for the restored pH values plot at or slightly under-saturated in comparison with saturation indices calculated using reported pH. The samples are slightly under-saturated, to saturated at reservoir conditions. The near-saturation with respect to calcite calculated when using reservoir pH values and reported chemical values is reasonable because of the presence of calcite in the formation and its relatively high reactivity. Produced fluids precipitate calcite scale during production in Bakken wells (Cenergy et al. 2011, Wylde et al. 2012).

Figure 8 shows calculated pCO_2 versus TDS for field and restored values. As an independent metric we calculated the pCO_2 value of about 1.5 bar (log pCO_2 of 0.1), based on CO_2 gas analysis of 0.57 mole% (Wocken et al. 2013) and an average depth of 10,227. The calculated values show good agreement with the measured CO_2 content of produced gas further supporting the restored pH values. The values for pCO_2 of the produced water samples center around1 bar at reservoir pH. Most of the reported analyses do not have pCO_2 values near atmospheric (log $pCO_2 = -3.5$) indicating that the samples had not fully equilibrated with surface conditions. Therefore, Bakken produced water can precipitate more calcite if given sufficient time to reach equilibrium. This process will occur in the separators and surface installations.

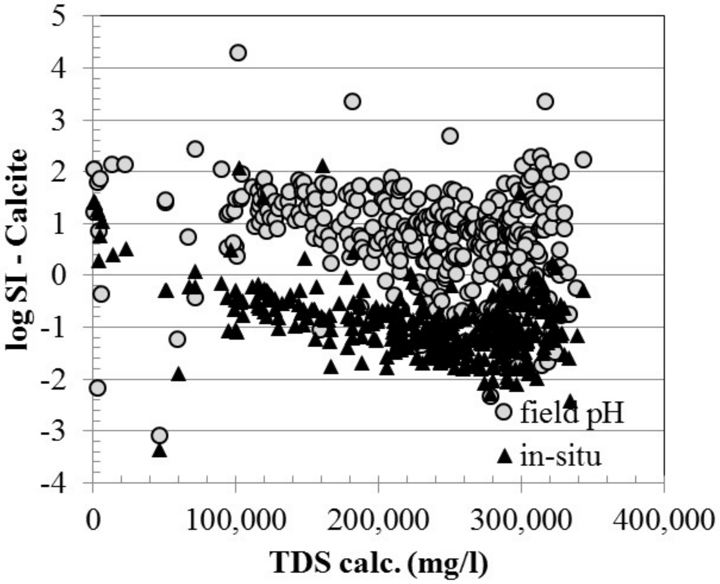

Figure 7. Calculated calcite saturation index for field and in situ pH (PHREEQC with llnl database.

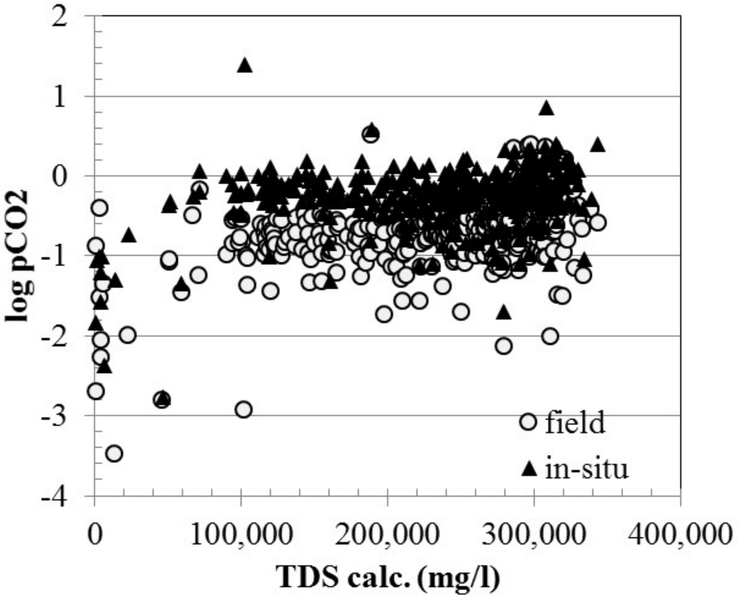

Figure 8. Plot of calculated pCO_2 versus TDS for Bakken water samples assuming equilibrium with calcite and in situ pH (PHREEQC with llnl database).

Figure 9 shows the calculated saturation indices for halite and anhydrite. The calculated values are reasonable since while there is no halite in the Bakken, the Williston basin brines are known to be derived from halite dissolution. The high degree of under-saturation for halite in the lower TDS samples is consistent with dilution of normal brines by drilling and completion fluids. The presence of anhydrite in the formation is consistent with the calculated saturation or near saturation for the produced water samples.

The general approach of correcting pH values to in situ conditions and restoring water analyses for changes during production produces reasonable results. Some of the simplifications such as using an average temperature for samples lacking data introduce uncertainty, but the overall trends are consistent with the expected results. The approach is effective for carbonate scale prediction. Analysis of the scale shows it is about 90% calcite with 10% composed of anhydrite and halite and small amounts of iron minerals.

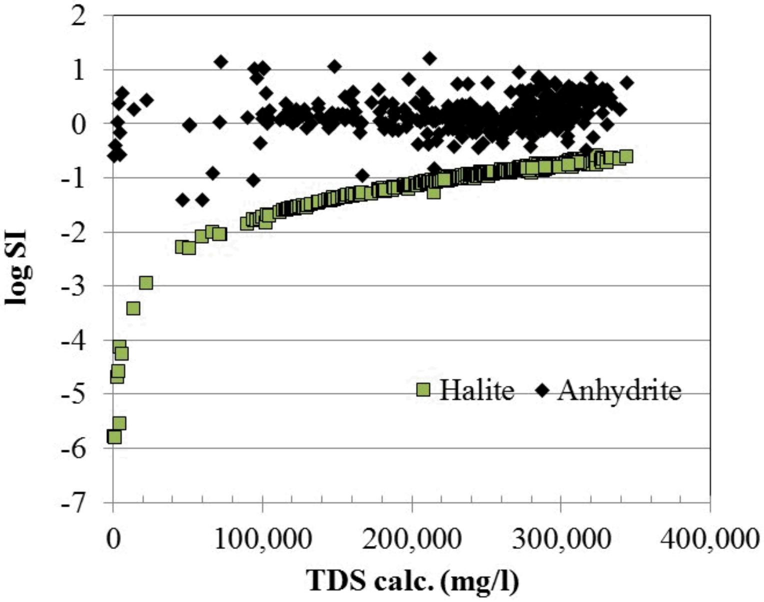

Figure 9. Saturation indices for Anhydrite and Halite versus TDS for Bakken produced water samples. Saturation is equal to zero for log SI.

Discussion

The calcite saturation index calculated using measured pH values produce a degree of super-saturation that is not realistic. The in situ pH correction assumes the pH is determined by silicate mineral buffering and produces in situ pH values that average 1 standard pH unit lower than field measurements. The calculated pCO_2 values using the thermodynamic model pH values agree closely with the actual gas analysis offering an independent approach to validate the methodology.

Water analyses impacted by scale formation will have calcium and bicarbonate analytical values lower than reservoir values. We can restore the water analyses to in situ values by adding calcite to the reported solutions to reach equilibrium with calcite and anhydrite at reservoir pH (Hitchon, 1996). Using this approach we restore several water analyses and then simulate production changes. A model for Bakken brine (SN 17150000) assumed equilibrium with calcite and anhydrite as the starting condition. Scale precipitation is simulated by using the restored chemistry as the starting point and then lowering temperature to 25°C and CO_2 fugacity to atmospheric.

The calculations show that calcite scale could be as much as 0.045 grams per liter, while the precipitation of halite and anhydrite is not likely except for the most saline samples. This means early flowback will produce little or no halite or anhydrite, but later produced water may generate these other scales as TDS approaches formation water levels, consistent with observations (Wylde et al. 2012).

The Bakken wells produce significant amounts of scale, mostly calcite with minor anhydrite and halite (Cenergy et al. 2011, Wylde et al. 2012). The severity of scaling is related to time of production with relatively early (Cenergy et al. 2011) and later periods (Wylde et al. 2012) being the most difficult. The average water volume used in the Bakken is about 900,000 gallons/well (LaFollette et al. 2012). For a Bakken well that produces water at about 1500 barrels/month for 48 months (about 3M gallons of fluid), this equates to approximately 2 million gallons of formation water during well life assuming complete recovery of fracking fluid.

Using this assumption that represent maximum value as fluid production generally declines during well life. Table 1 shows an example of calculated scale volume. In the model the calcite scale forms early in the production process consistent with the observations of scale in production tubing and surface equipment (Cenergy et al, 2011). It may occur in the fractures and near well-bore area depending on the amount of pressure reduction. This analysis does not consider some additional sources of scaling. First, the local cooling and pressure drops that can occur in fractures or near perforations as gas flashes from oil. This process will produce calcite scale by lowering pressure and shifting pH. The pressure drop can also produce a separate gas phase that will cause water to partition into the gas out of the aqueous phase increasing the salinity locally. Under those conditions the salinity may increase enough to precipitate anhydrite and halite from the saline produced water.

Table 1. Amount of calculated scale for Bakken produced water sample.

		Scale			
PW (lbs/mo)	PW (bbls/mo)	calcite	4 years	cm^3/month	in^3/month
		(kg/month)	(kg)		
3,507	10	0.07	3	26	2
17,535	50	0.36	17	132	8
87,675	250	1.79	86	659	40
175,350	500	3.57	171	1,318	80
263,025	750	5.36	257	1,977	121
350,700	1000	7.14	343	2,636	161
438,375	1250	8.93	429	3,295	201
526,050	1500	10.72	514	3,954	241
613,725	1750	12.50	600	4,613	282
701,400	2000	14.29	686	5,272	322

1500 bbls/month of bakken brine for 48 months is 3.03 million gallons of water, scaling potenital is based on sample SN 17150000

Conclusions

A thermodynamic approach to restoring formation water was performed for pH by assuming that in situ pH and portions of the water chemistry is controlled by mineral equilibrium. The technique produces realistic results for the Bakken formation. Most produced water has not reached equilibrium with surface conditions as indicated by elevated pCO_2 values calculated from the reported analyses.

The results show that calcite scale formation is highly dependent on pressure reduction rather than temperature changes and will be produced in the both production tubing and surface facilities. Calcite scale potential appears to be less in the lower TDS flowback and is greater in higher TDS brine later in well life.

Anhydrite and halite scale is possible, but probably only when produced water salinity increases, such as during water partitioning into the gas phase raising salinity locally. Thus, anhydrite and halite scale formation is not predicted for most produced water samples. Only the very saline water is produced after flowback later in the well history is likely to be able to form these scales.

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