IMPROVING CONNATE WATER SALINITY ANALYSIS ON PRESERVED CLAY RICH CORES

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ABSTRACT

Water saturation in exploration, appraisal and early development wells is usually computed from resistivity logs. The assumption that water properties in the aquifer are the same as those in the oil leg needs to be proved, not assumed. The use of core can be used to obtain more representative formation water resistivity values, which will improve water saturation calculations in hydrocarbon bearing zones.

Core cut from a hydrocarbon leg with OBM can provide an estimate of the formation water salinity by extracting salts (Dean Stark crush and leach) or by expelling formation brine by ultra centrifuging the samples. Correctly calculating formation brine salinity from Dean Stark crush and leach protocol requires corrections for additional anion and cation produced by mineral dissolution and mineral reactions. If clay is present, then clay bound water corrections maybe required. Ultra centrifuging core samples may only produce a few drops of brine, particularly if core is high on structure and water saturations are at or near irreducible saturations. These few drops are sufficient to obtain ambient conditions measurement of water resistivity, and complete chemical analyses if attention to sample handling and analysis protocol is strictly followed.

INTRODUCTION

Water saturation for the majority of exploration, appraisal and early development wells is computed from resistivity logs. It is common practice to assume water composition in a hydrocarbon leg is exactly the same as the underlying aquifer. This assumption is rarely challenged unless computed water saturations do not match other information, such as capillary pressure, Dean Stark water saturations or NMR. All resistivity based water saturation models require water resistivity in the hydrocarbon leg.

Formation water resistivity in hydrocarbon legs can be determined by extracting fluids or salts from core. Core based techniques have been around for many years [1, 2], but are not widely adopted. To determine formation water resistivity accurately in the reservoir, conventional core would best be cut using oil based muds (OBM), and core plugs cut and preserved correctly at the wellsite.

Results of the Dean Stark crush and leach and ultra centrifuging are presented in this paper and have been prequalified for used in clay rich reservoirs (about 25% total clay by XRD for this study.

EXPERIMENTAL PROTOCOLS AND RESULTS

Dean Stark Crush and Leach

When Dean Stark crush and leach technique is conducted correctly, it is a reliable method to determine salinity in a hydrocarbon bearing interval. This technique has a good chance of success when no water is introduced or removed from the core. If water is being added to the core from a second source (mud used to cut the core, or fluids used to cut the plug) then all introduced fluids need to have tracers added so that corrections can be made. C. Pan [3] has shown that Dean Stark crush and leach results for sandstones are reasonably good. Results on carbonate samples are less satisfactory due to the mineral dissolution during the extraction.

Chloride levels are not generally altered by mineral dissolution and this makes it an ideal species to determine salinity. The caveat with this technique is that it is limited to formation waters that are primarily chloride based and as such is not appropriate in every hydrocarbon province. Chloride levels will be elevated when solid salts (halite and sylvite) exist in the formation. When correctly conducted Dean Stark will remove all; free water, capillary bound water, and clay bound water. It is generally accepted that free water and capillary bound water have the same or very similar salinities, where as clay bound water is cation and anion free [4]. In this study, the effects of clay bound water (CBW) are accounted for to obtain more representative free water salinity. Clay bound water corrections were not discussed in Pan's paper [3].

The methodology used to test updated procedures is listed below:

Select five core plugs with permeability > 5md and significant clay bound water volume

1) Fully clean these samples, with a final step of flow through cleaning using methanol
2) Dry plugs in a vacuum oven and constant humidity oven, measure initial porosity, permeability and grain density
3) Pressure saturate plug with a known makeup brine, ensure rock / brine equilibration by flowing five pore volume of brine per day through each plug until plug resistivity remained constant for a minimum of 48 hours
4) De-saturate core plugs to irreducible water saturation using porous plate technique (air / water)
5) Perform the updated "Dean Stark crush and leach procedures" [5]
6) Analyze distilled water blank, standard stock solutions that cover the likely concentration range, and leached salt solution (leachate can be split between multiple chemical analysis labs for quality control
7) Correct salinity data using the updated dilution correction factor, and make clay bound water corrections based on the weight differences between vacuum and constant humidity drying at 60 °C and 55% % relative humidity (RH)
8) Compare fully corrected Dean Stark crush and leach data to initial makeup brine composition

In Table 1 are presented the Dean-Stark extraction water production for the five samples and the amount of clay bound water as determined by the weight difference between constant humidity and vacuum dried samples. In Table 2 are presented the chemical analysis of the leachates resulting from the extraction by adding about 1.55 grams of distilled water per gram of Dean-Stark extracted plug.

To convert the leachate concentrations in Table 2 back to the original undiluted brine requires three corrections, which are explained below and results provided in Table 3.

1. Determine the dilution factor which is the ratio of the weight of water added during extraction to the original weight of brine. However the original weight of brine is not known, only the original weight of water (Dean-Stark water production). The equation below calculates dilution factor:

   $$DF = Wt_{solvent}/(Conc_{salt}*(Wt_{solvent} - Wt_{H2O}) + Wt_{H2O}) \quad \text{(equ. 1)}$$

   DF = dilution factor
   Wt_{H2O} = weight of water extracted from Dean Stark (g)
   $Wt_{solvent}$ = weight of water used to dissolve all salt from the crushed sample (g)
   $Conc_{salt}$ = TDS (mg/kg) * 10^{-6} or TDS = 1.695* Cl conc. (mg/kg)
   Where all weights must be accurate to within ±0.01 g and:
2. However as is shown later (Table 3) the salinity (TDS) of back-calculated brine TDS is too high due to the addition of chemicals from the core which then affects the dilution factor. This problem is eliminated by calculating the TDS of the leachates from the chloride concentration with an assumed TDS/Cl ratio of 1.695.
3. The Dean-Stark water production in equ 1 is corrected for the clay bound water by subtracting the grain in weight from constant humidity drying from DS production.

The results in Table 3 show that reactive ions including; sulfate, bicarbonate, bromide, strontium and barium are elevated in the leached brine, compared with the makeup brine compositions. Elevated sulfate is usually due to pyrite oxidation in the plug, this is in line with the previously published results [3]. When pyrite oxidation occurs, one of the by-products is sulfur oxoacids (sulfate and thiosulfate). These sulfur oxoacids can then dissolve carbonate, if present, to form bicarbonate. Oxidation of just 1% of pyrite (1% by wt) will results in 6835 ppm sulfate in a 20% porosity rock with an Sw of 25%.

The appearance of other ions during the core leaching process is the result of mineral dissolution, or desorption. Some of ions were not present or at very different concentrations in the original synthetic brine (Table 3) and thus must be sourced from the rock itself. As such, these ions should not be used to determine the true total dissolved solids (TDS) concentration otherwise results will be too high. It is recommended to only use chlorine for calculation of true formation salinity and TDS, by using a constant TDS/Cl ratio of 1.695 when formation water salinity is unknown. This factor is based on the average of formation waters dominated by NaCl. In the study reported here, since the composition of the saturating brine is known we have used its TDS/Cl ratio of 1.663. It is also critical to use the correct concentration units, mg/l or mg/kg for the calculation, as density becomes an important term at high salinities.

All water samples were sent to an independent laboratory for analysis using IC/ICP (Ion Chromatograph for anion analysis and Inductively Couple Plasma for cation analysis). After clay bound water corrections are made the average error between analyzed chloride concentration and original makeup brine chloride concentration is 3%. Before clay bound water corrections the average error between analyzed chloride concentration and the original makeup brine chloride concentration is -7%. The agreement between milliequivalent sum of cations versus sum of anions was -1.0 ± 0.62%.

The volume of clay bound water in these plugs was on average 12% of the Dean-Stark water volume. After making clay bound corrections the average Dean Stark crush and leach salinity was within 2.8% of the original makeup brine.

Core Ultra-Centrifuge

The ultra centrifugation of preserved state core plugs has been used in other fields to recover formation brine samples for measurement of major ionic species and Rw. Centrifugal capillary pressure must be greater than reservoir capillary pressure if additional water is to be expelled for analysis. Two key elements associated with this process are; preservation of the water volume from the well site to the laboratory and accurate determination of Rw when recovered volumes are significantly less than one milliliter. The volume of brine produced using the ultra centrifuge system on core plugs at irreducible water saturations is generally very small (<0.5 ml). Two measurements are generally conducted on these small brine volumes; measurement of Rw and full chemical analysis. Clinch et al. [5] provide detailed methodology used for ultra centrifugal brine recovery and procedures for chemical analysis of very small water samples.

Before results of this procedure are used in reservoir evaluation, the procedure must be validated on rocks similar to the reservoir in question. The ultimate goal of this procedure is to recovery a representative formation brine sample from preserved core plug at irreducible water saturation. Laboratory tests results of this technique following protocol similar to that provided for the initial portion of the Dean-Stark crush and leachate expect that after step 5 samples are ultra centrifuged and the make-up brine was slightly different.

The composition of brine produced during the high speed centrifugation process, Table 4, should be more representative than Dean Stark crush and leach, because: less oxidation of pyrite, original water is being produced, less dissolution of minerals, and clay bound water will not be produced. These high speed centrifuge extracted brine samples have elevated sulfate, barium and strontium levels. The source of the sulfate is oxidation of pyrite during the core plug cleaning and drying stages before the plug is saturated with brine. Some pyrite oxidation is likely to occur during the high speed centrifugation process, Table 4 compared to Table 3 indicates much less pyrite oxidation occurs during the centrifuging technique.

CONCLUSIONS

Two laboratory methods were evaluated to determine formation brine salinity in the oil leg, Dean Stark crush and leach, and ultra centrifugation. Multiple core plugs should be tested over the full hydrocarbon column. This will help remove statistical error and ensure salinity trends can be identified.

There are two major sources of error in the Dean Stark crush and leach protocol. Oxidation of trace amounts of pyrite results in elevated concentrations of sulfates and bicarbonates which can significantly overstate the original salinity (0 to 20%). Clay bound water is driven off during the Dean Stark extraction which overstates the amount of pore water and thus can significantly understate the original salinity (0 to 30%). For the rock samples evaluated in the tests reported here these two errors are about equal and would cancel each other if no corrections were made. However this would not always be true being rock dependent. The salinity of the brine expel from the core by ultra centrifugation was less effected by elevated concentrations of bicarbonate and sulfate.

Formation water salinity in the reservoir does not just impact original oil-in-place, it also has an impact on hydrate formation and facilities design. Core testing must be conducted early in the field appraisal cycle to ensure the reservoir is fully appraised before development, allowing mitigation plans to be put in place.

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Table 1: Dean-Stark Extraction - Crush & Leach					
Sample Number	Dean Stark Water Weight, gm	Humidity - Vacuum Difference, gm	clay bounc water corrected	Extract Water, gm	Dry Sample Weight, gm
#1	3.26	0.37	2.89	146.0	93.8
#2	3.09	0.34	2.74	145.4	93.9
#3	1.96	0.26	1.70	140.1	92.1
#4	2.54	0.27	2.27	138.1	90.9
#5	2.23	0.29	1.94	137.5	89.1

Table 2: Chemical Analysis of Leachates					
	Extract Analyses, mg/Kg				
Analyte	#1	#2	#3	#4	#5
Chloride	1,657	1,515	1,055	1,175	1,357
Sulfate	26.4	27.4	62.5	101.4	26.9
Thiosulphate	0.8	1.1	16.7	21.1	0.8
Bicarbonate	140	147	168	162	136
Bromide	4.4	4.3	3.2	3.4	4.1
Sodium	1084	1003	741	825	903
Potassium	26.0	25.0	24.0	26.0	23.0
Calcium	17.0	17.0	19.0	26.0	14.0
Magnesium	2.8	2.5	3.5	4.8	2.1
Barium	0.9	1.0	0.5	0.3	0.8
Strontium	2.1	1.9	1.6	2.1	1.6
Silica	6.4	5.7	10.0	6.6	6.7
TDS	2,968	2,751	2,105	2,354	2,476

Table 3: Comparison of makeup brine and corrected Dean Stark crush and leach compositions				
	ave. conc. for five samples			
	Makeup brine	no correction	TDS correction	TDS & free H2O correction
Analyte	mg/kg			
Chloride	70,407	64,839	65,748	71,770
Sulfate	11	2,485	2,529	2,721
Thiosulphate	0	436	445	470
bicarbonate	32	7,455	7,569	8,191
Bromide	223	187	190	207
Sodium	42,600	43,858	44,480	48,510
Potassium	625	1,212	1,230	1,336
Calcium	1,866	915	929	1,007
Magnesium	216	156	158	171
Barium	391	33	34	37
Strontium	434	90	91	99
Silica	14	359	365	392
TDS	116,435	122,033	123,776	134,920
TDS from Cl			109,339	119,353
diff. from makeup brine (%)		**4.8**	**-6.1**	**2.5**

Table 4: Comparison of makeup brine and ultra centrifuge extracted brines				
Analyte (mg/kg)	**Makeup Brine**	**Samples**		
		Plug 1	**Plug 2**	**Plug 3**
sample wt (mg)		**131**	**139**	**707**
Chloride	78,268	81,986	83,844	78,880
Sulfate	1.9	2111	2045	2087
Thiosulphate	<2	135	265	305
bicarbonate	6	57	<30	<30
Bromide	7.6	9.9	9.5	11.1
Sodium	40,547	43,588	45,003	42,852
Potassium	3,469	2,172	1,627	1,627
Calcium	4,627	5,433	5,538	4,623
Magnesium	1,645	1,744	1,850	1,806
Barium	-	<4	<4	<2
Strontium	1.3	92	114	101
TDS	128,573	138,210	141,800	133,405