DETERMINATION OF CONNATE WATER SALINITY FROM PRESERVED CORE

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ABSTRACT:

One of the parameters needed to calculate in-situ water saturation from wireline logs is the resistivity of connate water, R_w. It is usually determined by measuring the resistivity and chemical composition of uncontaminated connate water produced from a formation or underline aquifer. If the formation does not produce any connate water, e.g., Deep Basin plays in Western Canada and many tight gas reservoirs, or the produced water is contaminated it is difficult to determine accurate R_w necessary for water saturation calculation. Core-based salinity-determination techniques have been used in practice to determine Rw values in cases of no formation water production and/or variation in salinity of produced water. However, there is no laboratory validation of the techniques. This paper presents the results of a laboratory study of examining the validity of core based salinity determination. Controlled experiments were conducted on core samples, one Berea sandstone core, one tight sandstone core and one tight carbonate core, with the latter two coming from gas producing formations in Alberta. The air permeability of the samples varies from 1 mD to 80 mD. Sandstone brine and carbonate brine of known salinity and compositions were used as the base fluids for comparison in the tests. Several methods, i.e., electrical properties measurement (back calculating R_w), de-ionized water flow through extraction, methanol flow through extraction, and extraction of core salts by leaching ground core, are compared. All of the methods tested in the study provided reasonably good results for the sandstone samples with little soluble minerals but poor results for the carbonate sample due to soluble minerals in the matrix. The effect of dissolution of soluble minerals on extracted salinity and individual ion concentrations are evaluated. The ion that was not affected significantly by dissolution of soluble minerals during extraction was chloride.

INTRODUCTION

One of the parameters needed to calculate in-situ water saturation from wireline logs is the resistivity of connate water, R_w. It is usually determined by measuring the resistivity and chemical composition of uncontaminated connate water produced from a formation or underline aquifer. Log analysis using SP logs and interpretation from porosity and resistivity logs in aquifer are other possible sources of R_w values. If the formation does not produce any connate water, e.g., Deep Basin plays in Western Canada and many tight gas reservoirs, or the produced water is contaminated it is difficult to determine accurate R_w necessary for water saturation calculation. Difficulty also arises if the salinity of connate water in a reservoir is not constant, with vertical and/or areal variation in R_w in the reservoir [1, 2, 3]. In these cases core based salinity measurement provides an alternative and, sometimes, the only method to determine the R_w values.

The validity of core-based salinity measurement is based on the assumption that all of the chemical ions in connate water at reservoir conditions are still contained and remained the same in the core water at ambient conditions at surface. If the formation water is not at or near the solubility limits, i.e., soluble at reservoir temperature and pressure but insoluble at ambient conditions, it is possible to cut cores that retain in-situ formation water compositions by low invasion coring technology and oil-based mud (OBM). Field examples have been documented that properly designed OBM coring procedures do not alter in-situ water content or brine composition of reservoir interval with immobile water saturation [4, 5]. Specifically, McCoy et al. [1], Rathmell et al. [2] and Rathmell et al. [3] have documented core-bases salinity determination in practice, covering both conventional gas and oil reservoirs.

It is more challenging to obtain reliable R_w for tight gas reservoirs than conventional reservoirs as most of them do not produce formation water and usually there is no underline aquifer. Core-based salinity measurement becomes a viable method for R_w determination. Applications of core-based salinity determination in tight gas reservoirs were reported by Nagra et al. [6], who used OBM cores to determine connate water salinity of a Deep Basin tight gas reservoir in Western Canada, and by Newsham and Rashing [7]. Given the limited documentation of successful applications of core-based salinity determination and increased activity in exploitation of tight gas reserve, this technique remains to be recognized as an alternative to more traditional methods.

Core-Based Salinity-Determination Techniques

Recommended Practices for Core Analysis by American Petroleum Institute [8] has introduced core-based salinity determination in the section of Supplementary Tests. There are two general methods recommended by API. One is direct core water expulsion the other is water extraction of core salts. The first method requires mechanically expelling connate water out of preserved core either using an immiscible fluid flush or by centrifugation. This method is applicable for core samples containing mobile brine saturation, which can be reduced by viscous immiscible fluid flow or centrifugation. In most cases, especially for tight gas reservoir, the method of water extraction of core salts is the only viable choice. This method is also called commutation analysis [7]. A preserved core sample with connate water still in the pore space is first Dean-Starked in toluene to determine the volume of pore water. The sample, with dry salts left in the pore space, is ground in a mortar. A known volume of distilled water is added to the sample and mixed. The salt solution is extracted by filtering and centrifuging the mixture, and saved for salinity determination. The salinity of the extracted water is determined by i) chemical titration of chloride ion, ii) standard water analysis of concentrations of major cations and anions, and iii) resistivity measurement.

The salinity is usually expressed as parts of sodium chloride per million parts of core water. Core water salinity, in terms of sodium chloride concentration, is back calculated by the following equation,

$$Salinity\ of\ core\ water\ \left(mg\,NaCl\,/\,kg\ core\ water\right) = \frac{NaCl\left(mg\right)}{\left[core\ water\left(gm\right) + NaCl\left(gm\right)\right]} \times 1000 \qquad (1)$$

in which *NaCl* weight is determined from measured Cl^- concentration and the volume of the distilled water used for the extraction. Core water weight is determined from Dean Stark analysis.

One potential error of the salt extraction method is that core material containing any sulfide minerals, such as pyrite, may release soluble ion sulfate salts, which may result in overstating the amount of extracted salts. Other soluble minerals, e.g., anhydrite or sodium chloride, in rock matrix not originally in direct contact with pores may become exposed after the core is ground, which will also lead to overstating the amount of extracted salts.

All of the published papers on core based salinity determination are field case studies. No laboratory study has been documented to systematically evaluate the validity of this method. This paper presents the results of a laboratory study of controlled experiments on three core samples, i.e., one Berea sandstone sample, one tight sandstone sample and one tight carbonate sample with the latter two coming from gas producing formations in Alberta. The objectives of the study are i) to examine the validity of core based salinity determination through controlled experiments, ii) to compare several laboratory methods, i.e., electrical properties measurement (back calculating R_w), de-ionized water flow through extraction, methanol flow through extraction, and extraction of core salts by leaching ground core, and iii) to study the contribution of soluble components in rock matrix to the salinity and individual ion concentrations in solution.

EXPERIMENTAL PROCEDURES

The laboratory experiments were designed to investigate whether core water resistivity, R_w, or salinity could be back calculated from either resistivity measurement or various extraction methods except direct expulsion of core water. Core samples with known immobile brine saturation of known salinity were measured for resistivity and extracted using known volume of de-ionized water or methanol. The results of back calculated R_w, total salinity and ion concentrations are compared with the known values, respectively. Details of the experimental procedures and sequence of the tests are given below.

Core Sample and Fluid Preparation

Three core samples were selected for the study, one Berea sandstone sample, one tight sandstone sample and a tight carbonate sample. The samples were cleaned in toluene and methanol to remove any hydrocarbon and salts left in pore space. Standard ambient porosity and air permeability were measured after oven drying and thin sections were made from the end trims of the samples.

Sandstone brine of 124,130 mg/kg salinity was prepared for testing on the two sandstone samples. Carbonate brine of 157,729 mg/kg salinity was made for testing on the carbonate sample. Both brines were prepared from reagent grade chemicals and de-ionized water. The compositions of the brines are presented in Table 1.

Flow Through Extraction Using DI Water

The core samples were vacuum and pressure-saturated with respective brines. Formation resistivity factor, FF, was measured for each sample from which the cementation exponent, m, was calculated. The samples were then desaturated by porous plate in five incremental pressures and resistivity index, RI, at each saturation was measured from which the saturation exponent, n, was determined for each sample. The final water saturation of each sample was determined by Dean Stark using toluene.

After Dean Stark the samples were loaded in core holders and de-ionized water was flowed through each sample against backpressure to facilitate saturation in the sample. The flow was continued until the effluent was salt free or a minimum of 20 pore-volume throughputs. The effluent was collected and analyzed for standard water analysis. Cations were measured by Inductively Coupled Plasma (ICP) and anions by Ion Chromatography (IP). Salinity of the brine or specific ion concentration in each sample can be calculated based on the original water volume in the sample and the extracted salts weight measured from the effluent using the following equation,

$$S_{core}(mg/kg\ of\ corewater) = \frac{W(mg)}{\left[DS\ CoreWater(gm) + ExtractedSalt\ Weight(gm)\right]} x1000 \qquad (2)$$

in which S_{core} is the back calculated salinity in terms of total dissolved solids of the brine or individual cation or anion concentration in mg/kg (ppm); *W* is the total weight of extracted salts or weight of each cation or anion in *mg*, depending on what S_{core} represents; *Extracted Salt Weight* is the total weight of the extracted salts in *gm*.

Back Calculation of R_w from Core Resistivity

After re-saturated with respective brines, the same samples were desaturated in a centrifuge to water saturations close to those obtained by the porous plate. Final water saturation of each sample, S_w, was confirmed by weight after centrifugation. True resistivity, R_t, of each sample was measured and used to back calculate R_w of the brine from the transformed Archie’s equation below,

$$R_w = R_t \phi^m S_w^n \tag{3}$$

in which *m* and *n* are cementation and saturation exponents of each sample measured before. The back-calculated R_w values of the brine in the samples should be close to the known values of the saturating brine.

Flow Through Extraction Using Methanol

After resistivity measurement, and with known volumes of brine still in them, the samples were loaded in core holders and methanol was flowed through each sample. The flow was continued until the effluent was salt free or a minimum of 20 pore-volume throughputs. The effluent was collected and analyzed for water analysis. The salinity and ion concentrations of the brine in the samples were back-calculated using equation (2).

In application methanol extraction is preferred as it can minimize the potential dissolution of minerals that may become soluble in water. But it is effective in mixing with and extracting pore water. Methanol extraction removes both water and salts. The solution is then analyzed for water content and ion concentrations. Dean Stark is not required in this extraction process.

Extraction of Core Salts After Crushing

This is the most common method of core-based salinity determination because i) it is fast, ii) it does not require flow through, and iii) it requires the least amount of equipment. However, it is destructive thus the last one in the sequence of this laboratory study.

After the methanol flow through extraction, the samples were re-saturated with respective brines and desaturated using centrifuge to immobile water saturation. Resistivity of each sample, R_t, was measured again for R_w back calculation. Each sample was then Dean-Starked to determine S_w. After drying the sample was crushed to approximately 16-mesh size and transferred to a flask. Enough de-ionized water was added to just cover the ground sample. The mixture is stirred vigorously for several minutes and left soaking overnight. The solution was extracted by filtration and saved for water analysis. Equation (2) was used to calculate the core brine salinity and ion concentrations.

Sample Properties

The routine properties of porosity, air permeability and grain density of the three core samples are given in Table 2. Archie’s parameters, *m* and *n*, were measured as described before and are included in the table. The parameters were used for R_w back-calculation.

The sandstone and carbonate samples were selected in order to investigate the influence of differences in mineralogy on the effectiveness of core-based salinity determination. Petrographic thin sections were prepared from the samples to identify potential soluble minerals. Thin section photographs of the three samples are shown in Figure 1. The Berea Sandstone is quartzose, consisting dominantly of quartz grains with minor amount of chert and dolomite grains. Ferroan dolomite and siderite are found as cement bounding the quartz grains. Authigenic clay minerals include kaolinite and chlorite. The tight sandstone sample is more argillaceous, containing quartz, glauconite, and chert grains. Illite is the main authigenic clay. There are no visible soluble minerals in the sandstone samples. The carbonate sample is a dolostone dominated by intercrystalline pores with minor mineralized fractures. The cements are mainly anhydrite ($CaSO_4$) and minor calcite ($CaCO_3$), which are potentially soluble in water.

RESULTS AND DISCUSSION

Back Calculation of R_w From Core Resistivity

The true resistivity values, R_t, of the samples partially saturated with respective brines were measured and, with known water saturation, the R_w of the brine in each sample is calculated using equation (3). To check reproducibility, the measurements were repeated on the same three samples at different stages of the experiments and with different brine saturation each time. The values of the back-calculated R_w are plotted against the measured R_w of the standard brine as shown in Figure 2.

The back-calculated R_w values of the sandstone samples are in good agreement with the measured R_w of the known sandstone brine, indicating that the method is acceptable for the sandstone samples. However, the back-calculated R_w values of the carbonate sample are lower than the measured R_w of the known carbonate brine, implying that the brine in the carbonate sample had higher salinity than the carbonate brine introduced into the sample. The increased salinity of pore water in the carbonate sample was attributed to the soluble anhydrite in it.

In application, as long as a core retains formation brine not contaminated by coring fluid, e.g., OBM core, the resistivity of the formation brine can be back-calculated using the method introduced above. The procedures would be as follow: i) drill a number of small plugs from the center of the core using mineral oil; ii) measure R_t for each sample; iii) Dean Stark to determine S_w for each sample; iv) clean the samples free of salts, measure porosity and Archie's parameters (m and n) using NaCl brine with estimated formation R_w; v) back-calculate R_w from equation (3).

Back Calculation From Extraction Tests

The results of the three different extraction methods are presented in Table 3, comparing the back-calculated salinity in terms of total dissolved solids with the actual brine salinity. The salinities of the extracted brines from both sandstone samples are in good agreement with that of the actual sandstone brine for all of the three methods, which is consistent with the result of the R_w method introduced above. The results of the Berea Sandstone sample are generally better than those of the tight sandstone sample.

On the other hand, the results of the carbonate sample are far from satisfactory. The extracted brine of the carbonate sample had a much higher salinity than the actual carbonate brine. The result from the back-calculated R_w also indicates the brine in the pore space of the carbonate sample was more saline than the carbonate brine (Figure 2), implying that there was dissolution of excessive salts into the brine. An examination of the thin section of the carbonate sample, Figure 1(c), confirms the possibility of dissolution. There is uneven distribution of anhydrite cement ($CaSO_4$) in the pore space, which dissolves in unsaturated solution on contact. Although the carbonate brine had high salinity, it was far from being saturated. It is noted that the salinity of the extracted carbonate brine ranged from a high of 342,004 ppm to 169,457 ppm. This was attributed to the removal of the anhydrite by the de-ionized water and methanol flow through in the steps prior to the last extraction test in which the low salinity was measured.

In addition to total dissolved solids, cation and anion concentrations in the extracted solutions were also measured and then used to back calculate the concentrations in the original core brine. Bicarbonate ion was not measured. The results are presented in Figures 3 to 7.

The flow through extraction of the sandstone samples after Dean Stark produced slightly more cations, i.e., Na^+, K^+, Ca^{+2} and Mg^{+2}, and sulfate anion, SO_4^{-2}, but less chloride, Cl^-, than those in the actual sandstone brine, as shown in Figure 3. The increase is more for the tight sandstone sample than the Berea sample. Being quartzose sandstone, the Berea sample does not contain as many minerals as the tight sandstone sample other than quartz. The much-elevated sulfate reading from the tight sandstone sample strongly indicates that there were sulfide minerals in it which oxidized causing an excess of cations and sulfate anions in extracted solution. The relatively low reading of chloride, however, indicates that the flow through process on the dry samples might not be effective in removing all of the precipitated salts left in pore pace by Dean Stark. De-ionized water removed the salts that came in contact with it but could not do so in pores that were not invaded by the water. Flowing water through a dry sample, even with backpressure, does not saturate all of the pores but bypasses inaccessible ones. Therefore the flow through extraction method is potentially not effective on dry sample unless saturation is easy to achieve, such as in homogeneous and high permeability sample.

The results of methanol flow through extraction of the sandstone samples are better as shown in Figure 4. The chloride readings of both samples are close to the known chloride concentration in the sandstone brine. Although still higher than the original values, the concentrations of the extracted cations (except Na^+) and sulfate ions are lower than those of the dry extraction.

The back calculated ion concentrations of the flow through extraction of the carbonate sample are much higher than the original values of the carbonate brine, especially the Ca^{+2} and SO_4^{-2} ions, as shown in Figure 5. There was little calcium in the original carbonate brine. However, the back-calculated concentration of calcium was 1000 times higher in the extracted brine from the DI water extraction of the dry sample and 2000 times higher from the methanol extraction of the same sample partially saturated with the carbonate brine. Similarly as much as twice the amount of sulfate was measured from the methanol flow through extraction compared to the original sulfate content in the carbonate brine. It is certain that the anhydrite mineral in the matrix framework was dissolving and extracted by the flow through processes. The methanol flow through extraction on the sample with brine still in its pore space yielded higher ion concentration than the DI water extraction of the dry sample for the same reason that water did not have access to some tight spots with anhydrite in the dry sample, whereas those spots became accessible in the sample partially saturated with the brine.

Core salt extraction from ground sample is the most common and economic method for core based salinity determination. It was included in this laboratory study as the last method investigated since it is destructive. The results of the sandstone samples are presented in Figure 6 and that of the carbonate in Figure 7. The extracted ion concentrations of both sandstone samples are in good agreement with the values of the sandstone brine. The apparently good match indicates the extraction was successful. The most significant change happened in the carbonate sample. Although the calcium reading was still a little high, the sulfate concentration dropped remarkably close to the standard value. The improvement might be attributed to the sample having been flow through cleaned twice before this step. A large amount of soluble components, one of them being anhydrite, had already been removed in the previous steps, leaving minor volumes of soluble minerals for further dissolution. The same improvement was also evident in the result of the tight sandstone.

Dissolution of solid minerals in rock matrix can be divided into two types. One is direct dissolution at large water/rock ratio such as anhydrite, as we have demonstrated in this study. The other is oxidation dissolution, which applies to those minerals insoluble in an anaerobic environment, but soluble after oxidation. Sulfide minerals such as pyrite belong to this group. The oxidation of pyrite releases sulfate salts, which not only elevate the sulfate level, but increase concentrations of cations such as sodium, calcium and magnesium, due to an acidic environment created by the release of sulfate ions [2]. Chloride, however, is not affected by this mechanism. A comparison of the chloride concentrations of the sandstone samples from different extraction methods is given in Figure 8. Except in flow through extraction of the dry samples, the chloride concentrations from the other two methods are very close to that of the sandstone brine, confirming the validity of using chloride as the least affected ion in an extraction process.

In summary, all of the methods tested in the study provided reasonably good results from the sandstone samples, which have little soluble minerals, but a poor match for the carbonate sample, due to soluble minerals in the framework of the sample. There is no clear winner among the methods tested in this study. The good results obtained from the extraction of core salts from the ground samples were influenced positively by the flow through cleaning steps prior to the test. The best practice is not relying on just one method, but using a combination of two tests to check reproducibility. For example, instead of just using the method of core salt extraction from ground sample one may choose to use it together with the flow through extraction method or back-calculation of R_w from core resistivity measurement.

CONCLUSIONS

1. Core based salinity determination is valid as long as the core does not have significant volumes of soluble minerals.
2. All four methods, i.e., back-calculation of R_w from core resistivity measurement, water flow through extraction, methanol flow through extraction and extraction of core salts from ground sample, provided reasonably good results for the sandstone samples which have little soluble minerals, but poor results for the carbonate sample, due to the presence of soluble minerals.
3. Soluble minerals affecting the extraction results included anhydrite and sulfide minerals such as pyrite. As a result of mineral dissolution/oxidation, concentrations of sodium, potassium, calcium, magnesium and sulfate were overstated.
4. Chloride concentration was consistent and not significantly affected by different extraction methods and dissolution of soluble minerals encountered in this study.

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Table 1. Composition of brines used in the tests

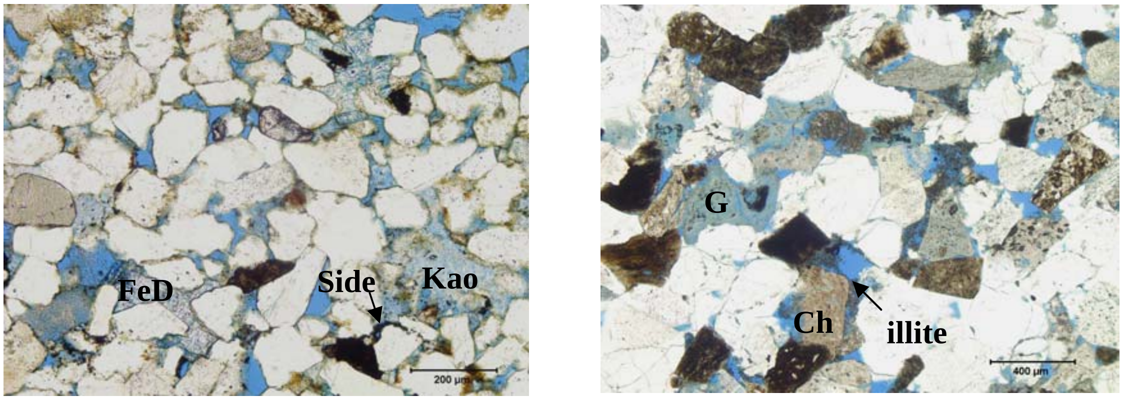
Ion	Sandstone Brine, meq/L	Carbonate Brine, meq/L
Na^+	1238	2165
K^+	325	0.0
Ca^{++}	420	28
Mg^{++}	0.0	1.3
Cl^-	2100	6.8
SO_4^{--}	4.0	2140

Table 2 Properties of the core samples and brines used

Sample	Porosity %	Air permeability mD	Grain density kg/m^3	Cementation Exponent, m	Saturation Exponent, n	Brine
Berea sandstone	18.6	76.8	2680	1.76	1.47	Sandstone brine
Tight sandstone	11.4	1.34	2650	1.90	2.43	Sandstone brine
Tight carbonate	17.5	1.80	2820	1.92	1.79	Carbonate brine

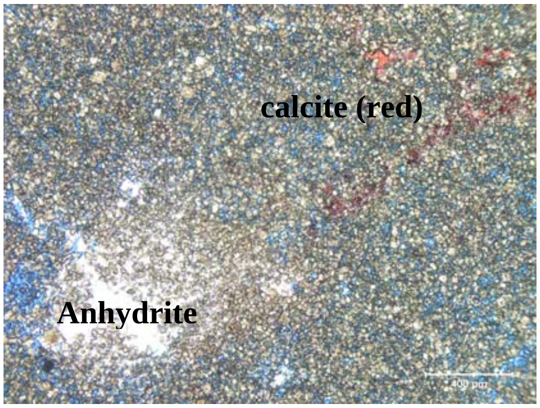
Table 3. Results of back calculated salinity in terms of total dissolved salts from various extraction tests

Extraction Method	Sandstone Samples, mg/kg			Carbonate Sample, mg/kg	
	Sandstone Brine	Berea SS	Tight sandstone	Carbonate Brine	Tight carbonate
DI Water Flow Extraction	124,130	121,712	172,199	157,729	264,592
Methanol Flow Extraction	124,130	136,229	140,727	157,729	342,004
Extraction of Core Salts	124,130	122,620	122,355	157,729	169,457



a) Berea Sandstone

b) Tight Sandstone



c) Tight Carbonate

Figure 1. Thin Section Photographs of the Core Samples

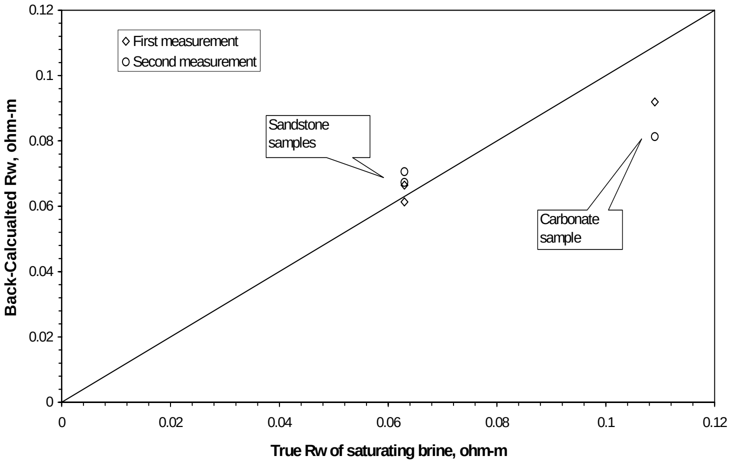


Figure 2. Comparison of the back-calculated R_w and the true R_w of the saturating brines

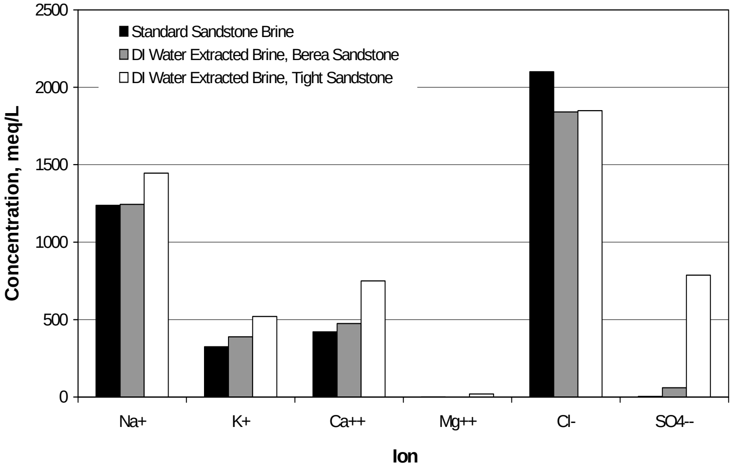


Figure 3. Ion concentrations from DI water flow through extraction of the sandstone samples after Dean Stark and drying

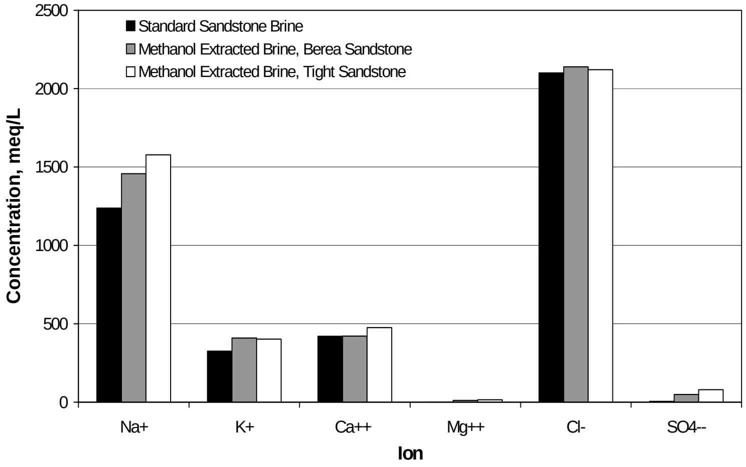


Figure 4. Ion concentrations from methanol flow through extraction of the sandstone samples with known brine saturation

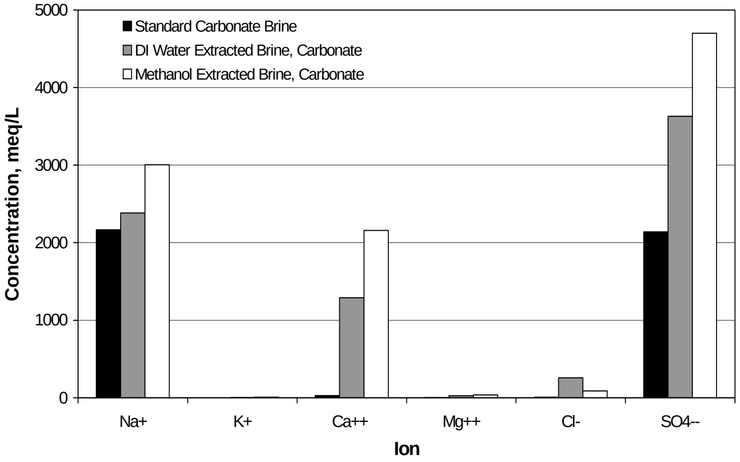


Figure 5. Ion concentrations from flow through extraction of the carbonate sample, both after Dean-Stark/drying and with known brine saturation

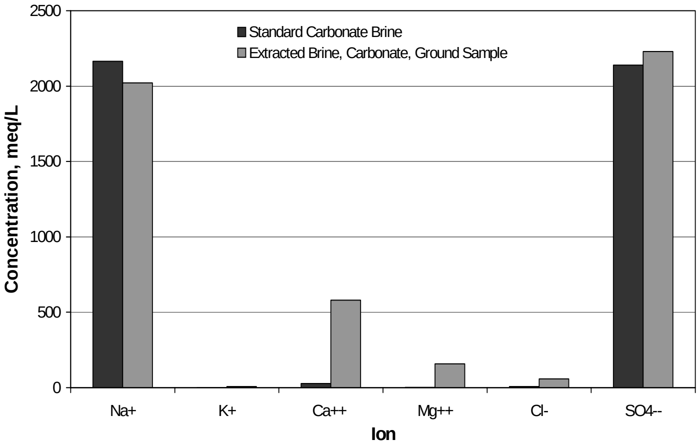


Figure 6. Ion concentrations from extraction of core salts of the ground sandstone samples after Dean Stark and drying

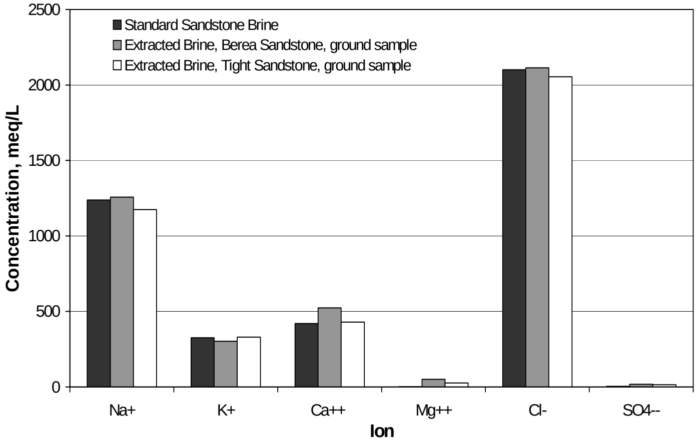


Figure 7. Ion concentrations from extraction of core salts of the ground carbonate sample after Dean Stark and drying

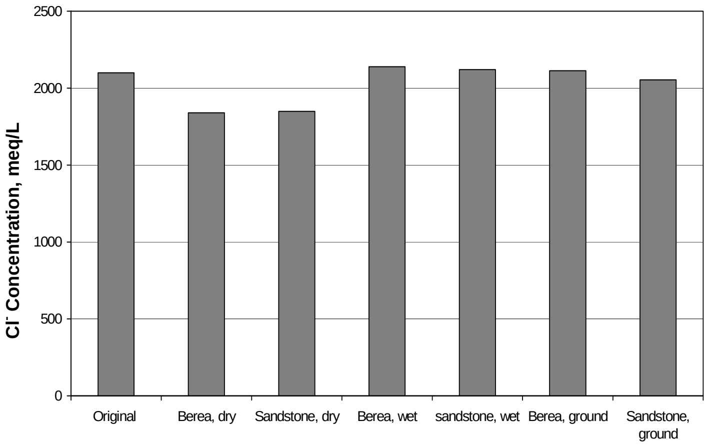


Figure 8. Chloride concentrations of the sandstone samples from all three tests