

EXCESS ELECTRICAL CONDUCTANCE IN CARBONATE ROCKS

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ABSTRACT

Excessive electrical surface conductance is well known in shaly rocks due to the negatively charged surfaces of clay minerals. This conductance is considered to be the main cause for the non-Archie behavior of such rocks, which tend to have a varying formation resistivity factor (i.e., ratio of the electrical conductivity of the brine to the electrical conductivity of the fully brine saturated rock) in contrast to the constant formation factor exhibited by Archie rocks. The clay effect on rock resistivity is determined experimentally in the laboratory through electrical conductivity tests of core samples using multi-salinity brines.

Such multiple-salinity laboratory experiments conducted on carbonate cores from the Middle Eastern reservoirs indicated that formation factor is not constant despite the absence of clay minerals in these samples. In addition to ionic conduction by the dissolved salts in the brine, extra conduction was observed in the samples at low brine concentrations that had caused their formation resistivity factors to decrease rapidly. This excess conductance was observed to be more pronounced in samples having a higher proportion of microporosity that causes higher specific surface area in the rock.

Although the extent of the surplus conductance observed in carbonate rocks was not as high as the one observed in the clay bearing rocks, its role becomes important for the interpretation of carbonates having low-salinity brines. The Archie's cementation factor (m) may measure less than 2.0 in the carbonate reservoirs that have sweet water present in them either in the form of connate water or injected water. In addition to the brine salinity filling up the pore system, the solid rock properties may also affect the overall conductivity of carbonate rocks.

INTRODUCTION

The electrical conductivity of clean (i.e. clay-free) rocks is essentially due to electrolytic (or ionic) conduction through the pore water. The magnitude of the

electrolytic conduction is a function of the pore water resistivity (R_w) and the formation factor (F). The Archie [1] relationship for the rock resistivity can become invalid if any excess conduction is contributed by the reservoir rocks. In such cases the water saturation is overestimated by the lower resistivity values measured by the resistivity logs.

In shaly rocks it was realized that current is transmitted by conductive solids other than the saturation brine [2] and Archie's relationship was modified as:

$$C_o = C_w/F + C_s \quad (1)$$

where C_s is the solid conductivity, C_o is fully brine saturated rock conductivity and C_w is the brine conductivity.

Winsauer and McCardell [3] pointed out the ionic nature of the excess conductivity that mobilizes positively charged cations, or counterions at the clay-brine interface called the double layer, and expressed the total rock conductivity as:

$$C_o = 1/F (C_w + C_z) \quad (2)$$

where C_z is the double layer conductivity.

Jumping hydrated counterions back and forth from the clay surface to the brine is responsible for surface conduction and is called cation exchange capacity (CEC) which is related to counterion concentration on the clay surface. Hill and Milburn [4] conducted CEC measurements on shaly sandstones and limestones and correlated with rock resistivity. Later on Waxman and Smiths [5] developed an empirical model for shaly sand conductivity which accounts for the counterion concentration:

$$C_o = 1/F^* (C_w + BQ_v) \quad (3)$$

where

C_o : Conductivity of rock fully saturated with brine solution (mho/m)

F^* : Formation factor for shaly sandstone

Q_v : Cation exchange capacity per unit pore volume (meq/cc)

C_w : Conductivity of the brine (mho/m)

B : Equivalent conductance of clay exchange cations (or counterion equivalent conductance proportional to ion mobility) (mho cm^2/meq)

The excess conduction along clay mineral-fluid interfaces is called surface conductance, because of being caused by a thin film of material confined to the clay surfaces [6, 7, 8, 9, 10]. When clays are brought in contact with an electrolyte, the negative charges on the clay surfaces attract the positive ions and repulse the negative ions present in it. Generation of an electrical ionic double layer by accumulation of ions near the charged surfaces contributes to the total conductivity of the brine filled

rocks. The type, quantity, distribution and morphology of clays affect the excess conductivity caused by the electric double layers [11, 12].

DEFINITION OF THE PROBLEM AND OBJECTIVES

During the execution of an experimental study to determine the electrical parameters of samples from a Middle East carbonate reservoir, the cementation factor (m) was observed to vary between 1.195 and 1.509. All values were found to be significantly lower than the expected value of 2 for clean porous carbonates. These were also inconsistent with the ‘ m ’ values obtained in previous studies using high brine salinities for the same carbonates. The only different feature of the experimental setup in the study was the use of low salinity brine.

More carbonate samples saturated with low salinity brine were measured for ‘F’ and ‘ m ’ at both lab and reservoir conditions using two different equipments. Consistently lower values for ‘F’ and ‘ m ’ were obtained for all tested samples (Table 1).

Table 1: Test results for formation and cementation factors conducted on carbonate samples saturated with low salinity brine, at ambient and reservoir conditions.

Sample No	Ambient Conditions		Reservoir Conditions	
	F	m	F	M
1042	4.759	1.190	5.275	1.268
1049	2.768	0.853	4.606	1.280
1120	4.900	1.031	6.311	1.195
1146	5.447	1.191	8.566	1.509
1159	18.518	1.625	13.252	1.439
1187	10.362	1.065	16.080	1.265
Average	7.792	1.159	9.015	1.326

The unexpected test results promoted further research work on determining the reasons for the excessive electrical conductivity issue of carbonate rocks when saturated with low salinity brines. The objective of the new project was to study the effect of low salinity brines on the conductivity of carbonate rocks, to determine and quantify excess electrical conductance, and also to investigate its importance in reservoir evaluation.

EQUIPMENT

In order to make sure that the lower values of Archie parameters were correct and not possibly caused by the faulty equipments, the tests were carried out with four different resistivity meter equipments manufactured by four different vendors; CoreLab, TerraTek, Vinci and DCI Corp.

Schematic of the reservoir conditions test system is illustrated in Figure 1. The setup consists of three major components: 1) Hydrostatic test vessel to simulate elevated temperature and pressure conditions; 2) Fluid circulation setup; and 3) Electronics and data acquisition system. A sample is inserted in an electrode sleeve which contains two embedded ring electrodes 3.81 cm apart in the central portion along the

core plug to read the four-pole conductivity. During the tests, two- and four-pole conductivities were measured while different salinity brines were flooded through the core plugs.

TEST PROCEDURES

Excessive conductivity of reservoir rocks is measured conventionally through multiple salinity tests, also called Co-Cw tests. Generally these tests are conducted to investigate the surface conductivity effect of clay minerals on the electrical resistivity of shaly rocks. In this study similar tests were performed on clay-free carbonate rocks.

Prior to the electrical tests, the core plugs were cleaned in a Soxhlet by circulating toluene and alcohol, and then they were dried at 90°C in a vacuum oven. Alcohol circulation in the Soxhlet continued until removal of entire salts, which was checked by silver nitrate treatment. Porosity, gas permeability, and grain density of plug samples were measured under confining pressure.

Multiple salinity electrical tests were conducted using twelve different concentrations of NaCl brines. Tests were started by mounting the core plugs in the hydrostatic cell at a confining pressure of 2,000 to 3500 psi and an elevated temperature of 65 to 75°C. Following the stabilization of the confining pressure and temperature, a brine of 250 kppm salinity was circulated through the sample. The salinity of the circulated brine was systematically decreased in steps until it was completely replaced by the distilled water in the last stage. In order to investigate the possibility of salt entrapment during flooding, some samples were saturated with distilled water and tests were initiated with the increasing salinity cycle. After reaching the maximum salinity of 250 kppm, the trend of measurements was reversed from high to low salinity in steps. Circulation at each salinity step continued until 15 to 20 pore volumes of brine had circulated through the core samples and their conductance had stabilized. The resistivity of the effluent brines was monitored to assure the removal of the previous brine with the new brine. The equilibrium of core plugs' conductance (almost constant reading) took 1 to 3 hours but brine circulation at each step continued for 6 to 24 hours to ensure that the previous brine was completely removed from the pores.

Two- and four-pole resistivities of core plugs were monitored and measured continuously. A typical resistivity versus elapsed time plot for the plug B-23 in Figure 2, is showing the brine resistivity and the total plug resistivities (2 and 4 electrodes) for the cases of decreasing and increasing brine salinities in steps.

SAMPLE PROPERTIES

The carbonate samples used in the study were obtained from four different oilfields (marked as A, B, C, and D in Table 2) of the Middle East. One outcrop sample from the Indiana Limestone of the USA (E) was also tested. The samples had varying

carbonate-mud contents and particle sizes; nine of them were grainstones, three were packstones, one was dolomitic mudstone and one was dolomite.

Porosity values ranged from 17.48 to 32.29 percent and permeability values ranged from 3.47 to 1067 mD. All the core plugs were 3.81 cm (1.5 inch) in diameter. In addition to the plugs, two whole core samples of 6.65 cm (2.62 inch) diameter were also tested. The main purpose of testing whole cores was to avoid any possible noise in the electrical measurements caused by the smaller size of the core plugs. Basic core properties of samples used in this study are shown in Table 2.

Table 2: Basic core properties of carbonate samples used in the multi-salinity tests.

Field	Sample No.	Lithology Type	Length (cm)	Dia. (cm)	Dry Wt. (g)	Gr. Dens. (g/cc)	Pore Vol (cc)	He Por. (%)	Perm. (mD)
A	1037	Foram grst	4.673	3.762	101.326	2.695	51.94	26.62	1067
	1120	Dol. pkst	4.642	3.760	109.200	2.702	51.54	21.41	6.38
	1140	Skeletal grst	4.464	3.760	101.558	2.701	49.57	23.29	481.4
	1157	Dol pkst	4.818	3.733	115.030	2.708	52.73	19.21	3.47
B	18/67	Skl pel grst	7.119	3.770	168.800	2.700	16.96	21.58	51.74
	18/68	Dol mdst	7.115	3.766	162.518	2.741	19.41	24.67	4.32
	4/96	Dol skl pel grst	7.044	3.758	141.466	2.696	25.02	32.29	449.2
	13/96	Skl pel grst	7.041	3.762	153.970	2.707	20.32	26.33	139.5
	22/96	Skl pel grst	6.590	3.762	144.870	2.733	19.31	26.71	23.46
	25/96	Dolomite	6.918	3.775	164.950	2.818	18.30	23.82	275.5
	12/96	Skl pel grst	5.185	3.742	122.579	2.704	11.69	20.5	900
C	W-1	Fine grst	10.087	6.538	712.210	2.653	70.19	20.73	4
	W-3	Fine grst	10.018	6.514	725.420	2.700	65.28	19.55	6
D	B-23	Pkst	5.050	3.763	92.190	2.710	11.04	25.01	4.13
E	L-1	Ool skl grst	6.142	3.801	154.728	2.700	12.17	17.48	7.22

Dia: Diameter, Wt: Weight, Gr Dens: Grain density, Vol: Volume, He Por: Helium porosity, Perm: Permeability, grst: Grainstone, pkst: Packstone, mdst: Mudstone, ool: Oolitic, skl: Skeletal, pel: Peloidal, Dol: Dolomitic.

MULTIPLE SALINITY ELECTRICAL TEST RESULTS

The tests on the carbonate samples were made at different times and stages that span over several years. The observations and findings in each stage are discussed below:

Stage 1 - Tests on Samples from Field-A

Low values of formation and cementation factors were first realized while testing the electrical properties of samples from Field-A. Multiple salinity tests were performed on these four samples at 3000 psi confining pressure and 70°C temperature using an electrical system fabricated by TerraTek. A brine of 250 kppm was used for the tests in the beginning, which was followed by tests with decreasing brine salinity in steps. Systematically decreasing values of formation factor were observed with the decreasing salinity of brines in all four samples (Table 3). Accordingly the similar decreasing trend for the cementation factor (m) was achieved. A plot of normalized

cementation factor (m/m_{max}) versus brine conductivity in Figure 3 shows 5 percent decrease in cementation factor when brine salinity drops from 250 kppm to 8 kppm. Below this salinity, the drop in the values of cementation factor is larger. At 1.5 kppm brine salinity, the cementation factor decrease is 25 percent.

Table 3 demonstrates a general decreasing formation factor with decreasing salinity. A local increase and then decrease of formation factor in 15 to 25 kppm salinity range is observed in many samples. Although such a hump could be due to erroneously high brine conductivity, here it is related with rock conductivity but its origin is unknown.

Stage 2 - Tests on Samples from Field-B

In this stage six core plugs from Field-B were tested using Vinci electrical test system at a confining pressure of 3500 psi and an elevated temperature of 75°C. The results obtained in Stage 2 were used in quantifying the excess conductivity based on Co versus Cw plots as shown in Figure 4. The trend of decreasing formation factor with decreasing brine salinity shows a deflection point where the formation factor decreases rapidly for fresher salinities. The critical brine salinity corresponding to the deflection points for all the samples ranged between 8 and 15 kppm with an average of 10 kppm.

Table 3: Test results of all core plugs, used in the project, showing variation in formation factor with changing brine salinity.

Salinity (kppm)	Cw@80°C (mho/m)	Stage-1 Samples				Stage-2 Samples						Stage-3 Samples				
		1037	1120	1140	1157	18/67	18/68	4/96	13/96	22/96	25/96	W1	W3	B-23	12/96	L1
0												6.19	4.79	4.01	4.25	36.86
0.5	0.226		16.49	13.71	6.90	18.45	3.97	15.55	15.88	11.95	15.48	12.18	10.67	7.29	14.13	32.80
1	0.437	9.37	16.83	16.04	10.91	20.41	6.44	18.37	16.81	12.92	16.07	15.53	13.45	9.37	15.66	31.88
2	0.843	12.91	17.53	17.67	14.33	21.90	9.92	18.84	19.87	13.74	17.70	17.70	15.08	11.52	17.23	31.90
4	1.578	14.09	18.00	20.47	17.80	22.84	13.82	19.95	20.09	13.39	18.21	19.65	16.84	13.05	17.52	33.11
8	3.057	16.40	18.52	20.72	19.34	24.51	21.78	21.14	22.10	15.05	19.06	21.68	18.72	14.66	19.07	35.21
15	5.559	17.59	20.38	23.48	21.45	25.62	23.23	21.69	22.47	15.77	19.47	22.71	19.57	16.06	20.28	36.73
25	9.058	17.82	20.80	22.90	23.04	25.58	26.04	21.98	22.47	15.59	18.96	23.36	20.12	16.73	21.15	36.91
50	16.638	17.23	22.30	22.06	23.79	25.44	26.92	21.81	20.95	16.16	18.89	24.62	21.28	16.89	20.75	36.14
100	30.195	16.73	24.59	20.95	23.88	27.62	28.70	22.40	21.79	16.69	18.71	25.20	21.84	15.96	21.67	37.43
150	40.763	16.58	25.46	21.03	25.12	27.76	29.40	23.22	21.40	17.34	19.47	25.61	22.14	17.39	21.65	37.29
250	54.351	16.58	26.00	20.84	24.91	27.93	29.76	23.52	20.76	17.54	18.75	25.83	22.17	17.45	21.26	36.97
150	40.763											25.57	22.22	17.58	22.14	37.54
100	30.195											25.37	21.31	16.31	22.10	36.26
50	16.638											24.85	18.19	16.97	21.30	36.55
25	9.058											24.03	14.78	16.91	21.43	35.25
15	5.559											23.54	11.92	16.06	21.00	33.04
8	3.057											22.19	8.55	14.66	20.13	30.68
4	1.578											20.15	5.34	13.17	18.77	29.06
2	0.843											17.97	3.13	11.52	18.23	26.33
1	0.437											14.67	1.71	9.16	16.57	25.29
0.5	0.226											10.82	0.89	6.38	15.86	2.75
0												4.44	0.19	2.76		

The Co - Cw relations of Samples 13/96 and 25/96 showed that a straight line fitted all data points and passed through the origin, where brine and rock conductivities both were zero. Such behavior indicates absence of excessive conductivity effect and the total conductivity of the rock is controlled by the conductivity of the brine saturating it. Other samples showed a linear fit for high salinity points but the fit concaved downward to indicate abrupt drop in Co for the Cw values less than 15.8 mho/m,

which correspond to brine salinity of 50 kppm. At high concentrations of equilibrating electrolyte solution the rock's conductivity increases linearly with increasing solution conductivity because the exchange-cation mobility reaches its maximum value and remains constant [13]. The abrupt drop in the conductivities of rocks (C_o) at very low brine salinities (C_w), is attributed to an abrupt drop in exchange-cation mobility [5].

The $C_o - C_w$ relationships obtained from the linear regression analyses were used to determine the formation factor (F^* , referred to as the shaly sand formation factor in shaly rocks) and the values of shaliness term (BQ_v). As shown in Figure 4, F^* is calculated as the reciprocal of the slope of the linearly fitted C_o-C_w curve, and the shaliness term (BQ_v) is equal to the value of C_w when C_o is zero. In clay-free carbonates, the shaliness term appears to have maintained its existence possibly due to cation exchange caused by non-clay constituents. The following representative relationship between C_o and C_w was obtained for the tested samples.

$$C_o = 0.044 C_w + 0.059 \quad (4)$$

The values of the term (BQ_v) for the tested samples varied between 0.0004 and 0.0253 mho/cm with an average of 0.0144 mho/cm.

Table 4: Measured and estimated parameters that are used for quantification of excess conductivity in carbonate rocks.

Sample No	Slope	Intercept	F^* (1/Slope)	BQ_v (mho/cm)	Q_v (meq/cc)	BQ_v/C_w	$C_w =$ $BQ_v/0.1$ (mho/m)	Salinity (kppm)
18/67	0.0348	0.0495	28.74	0.0142	0.110	0.0284	14.224	50
18/68	0.032	0.0809	31.25	0.0253	0.195	0.0506	25.281	80
4/96	0.0409	0.0893	24.45	0.0218	0.168	0.0437	21.834	65
13/96	0.0483	0.0353	20.70	0.0073	0.056	0.0146	7.308	22
22/96	0.0554	0.0969	18.05	0.0175	0.135	0.0350	17.491	55
25/96	0.0528	0.0019	18.94	0.0004	0.003	0.0007	0.360	1
Avg	0.0440	0.0590	23.69	0.0144	0.111	0.0288	14.416	45

The parameter B is the factor relating the cation exchange capacity to excess conductivity in shaly rocks [5]. In another term it is introduced as the equivalent conductance of the counterions as a function of solution resistivity (R_w) and temperature (t) in Celsius, and can be calculated by the following expression [14]:

$$B = (-1.28 + 0.225t - 0.0004059t^2) / (1 + R_w^{1.23} (0.045t - 0.27)) \quad (5)$$

Assuming this empirical method is applicable to carbonates; B was calculated to be 0.130 mho cm^2/meq for 250 kppm brine concentration at 75°C test temperature. Knowing B , the cation exchange capacities for the six samples were calculated that ranged between 0.003 and 0.195 meq/cc with the average value of 0.111 meq/cc.

Hoyer and Spann [15] used the term BQ_v/C_w to interpret the significance of the excess conductivity effect on water or oil saturation calculations. For BQ_v/C_w values smaller than 0.1, the shaliness effect will be less than 10 percent and tolerable for the considered salinity. An average of 2.88 percent BQ_v/C_w for 250 kppm formation brine indicates insignificant excess conductivity for undisturbed reservoir but its significance increases if formation salinity is disturbed during drilling or water injection. From the term $BQ_v/0.1$, a critical salinity [16] of 45 kppm is calculated.

Stage 3 - Tests on Whole Cores from Field-C and Plugs from Different Sources

The objective of this stage was to examine excess conductivity with a different equipment, investigate effect of sample size on measurements, and investigate if the water from the preceding steps is trapped in some pore spaces. Keeping in view the objectives, a new electrical system fabricated by DCI Corporation was used for the measurements. The carbonate core samples were comprised of two whole cores from Field-C, one core plug from Field-B, one core plug from a Cretaceous reservoir in the Middle East and one core plug from the Illinois Limestone outcrop. All the core samples were cleaned to remove all possible salts present in them. Tests in this stage mostly started with distilled water and then systematically increased in steps up to very high salinities. Moreover some tests started with high salinity which systematically decreased in steps to low salinity.

The tests on the whole cores and the plug from the Cretaceous carbonates confirmed the existence of excess conductivity as observed in the tests conducted at Stages 1 and 2. However, $C_o - C_w$ plots for the tests on Samples 12/96 from Field B and Sample L1 from Illinois Limestone, did not show the same behavior. The excess conductivity term (BQ_v) for both of these samples was small but the formation factor was not constant for varying brine salinities.

Discussion of Results

In order to understand the origin of the excess electrical conductance in the clay-free carbonate rocks, possible causes were investigated through laboratory experiments. These investigations are summarized below:

1. Consistent experimental results using different test systems confirmed that low resistivity readings cannot be considered as instrumental error.
2. The BQ_v values were found to be systematically negative. Therefore, excess conductivity is not a random error. Tests on the whole cores reliably confirmed that the excess conductance is not an erroneous reading due to small sample size
3. The brine resistivity measurements were not erroneous as they were repeated at with different instruments and also compared with the published tables.
4. When excess conductance was realized first time, salt entrapment in the pores was interpreted to be responsible of it. Subsequent experiments were conducted using plug samples which thoroughly cleaning was ensured with silver nitrate treatment. It was further assumed that salt entrapment might take place when tests are initiated with high salinity brine and followed by lower salinity brines. To prevent

salt entrapment, 15 to 20 pore volumes of lower salinity brines were circulated through samples. Moreover the brine salinity order was reversed (mainly in the Stage-3 tests), whereby carbonate samples were saturated with the distilled water at the start and the brine salinity was increased gradually in the subsequent steps. Having taken all these precautions into consideration, excess conductance was still observed in carbonate samples.

CONCLUSIONS

The excess electrical conductance in the clay-free carbonates has been verified with several multiple salinity tests. Probably surface electrical conductance is the cause for excess conductance in carbonate rocks. When excess conductance exists, formation and cementation factors are not solely dependent on the rock property rather it also depends on the rock-brine interaction.

The excess conductance becomes more pronounced in carbonates that are in abundance of micrite (micro crystalline calcite) [17] which is known to increase microporosity and the active surface area (Figure 5). Very low and indistinguishable excess conductance in Samples 13/96, 25/96, 12/96, and L1 is due to absence of micrite and micropores, and dominance of macro pores (Figure 6). Photomicrographs of Samples 1120 and L1 are shown in Figures 7 and 8, respectively. As known fines can act as a surface active mineral even if they are comprised principally of quartz [18]. Such behavior has been reported in some sweet water (20,000 to 1500 ppm) bearing clay-free reservoirs consist of silt size particles. In carbonate reservoirs micro calcite crystals' surfaces probably behave like silt particles. Interaction of water with calcite is a complicated process that releases CO₂ molecules and other ions [19, 20]. The cations that are attached to the surfaces of calcite crystals possibly create surface conductance in carbonates but of lower strength than that of clay minerals.

The significant variation in cementation factor occurs when brine salinity drops below 10 kppm. The change in 'm' varies from 5% at 10 kppm brine salinity to about 25% at 1.5 kppm salinity. Evaluation of carbonates having variable amount of sweet water would overestimate water saturation when it is computed by setting m=2 in the Archie equation. Therefore a care must be taken when computing saturations for sweet water bearing reservoirs.

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NOMENCLATURE

Co: Conductivity of rock fully saturated with brine solution (mho/m)

Cw: Conductivity of the brine (mho/m)
 F: Formation resistivity factor
 F*: Formation factor for shaly sandstone
 Qv: Cation exchange capacity per unit pore volume (meq/cc)
 B: Equivalent conductance of clay exchange cations (mho cm²/meq)
 BQv: Shaliness effect on conductivity (mho/cm)
 m: Cementation factor

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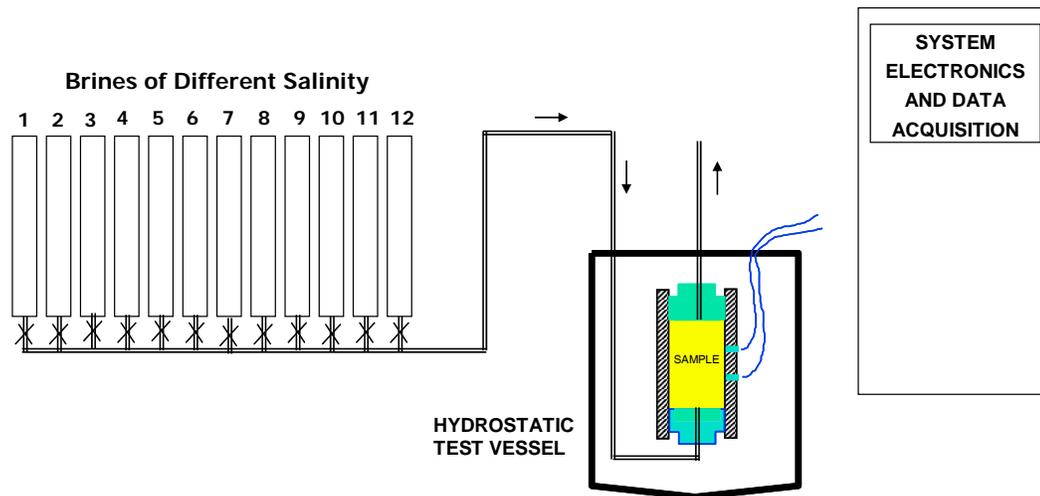


Figure 1. Schematic of the reservoir conditions multiple salinity tests equipment.

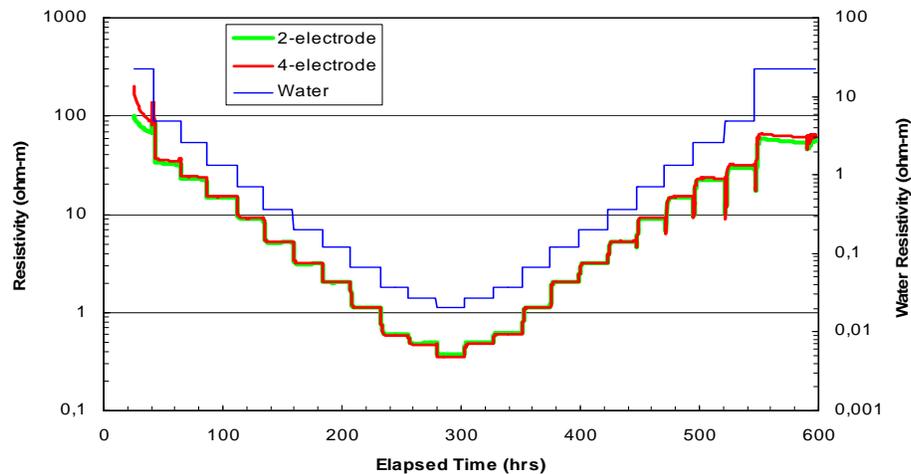


Figure 2. Brine saturated carbonate core plug's (Sample B-23) 2- and 4-electrode resistivity profiles for decreasing and increasing brine salinity cycles

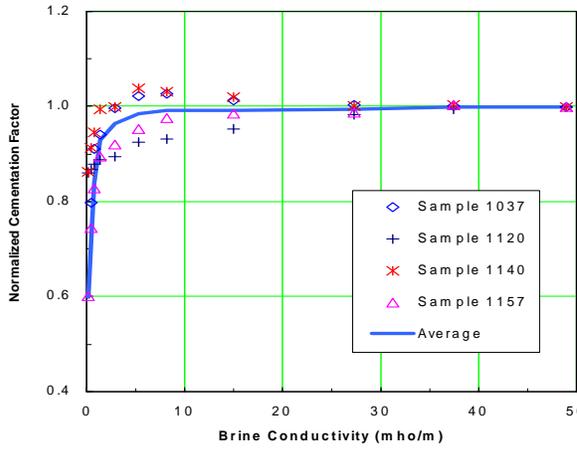


Figure 3. Normalized cementation factor versus brine conductivity plot for samples tested in Stage 1

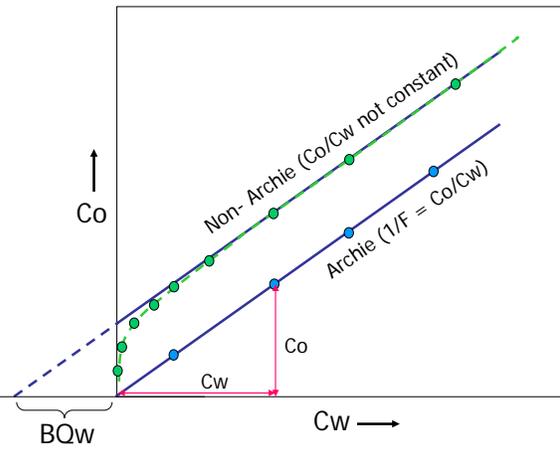


Figure 4. Schematic showing Archie and non-Archie data points in a Co-Cw plot.

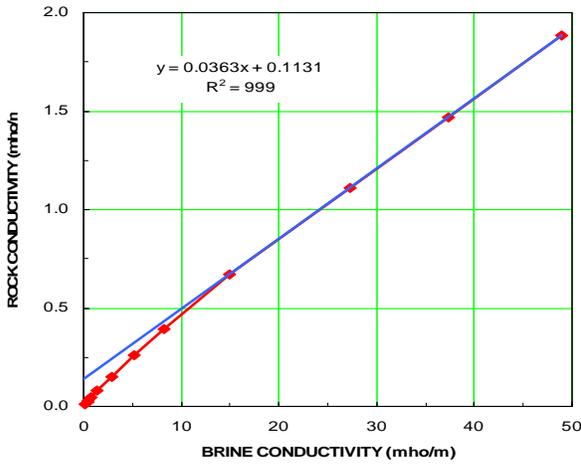


Figure 5. Co-Cw plot of Sample 1120 showing distinct excess conductance.

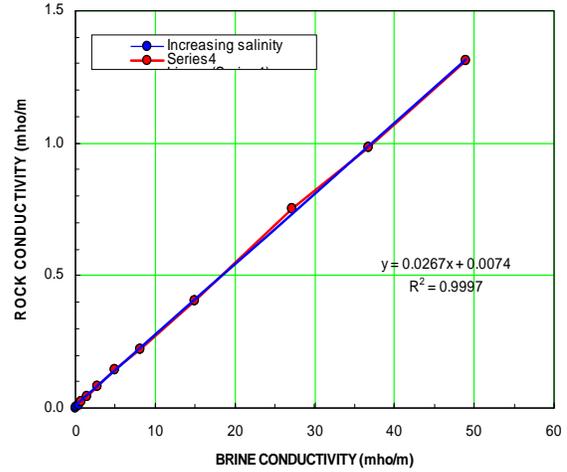


Figure 6. Co-Cw plot of Sample L-1 showing too low excess conductance..

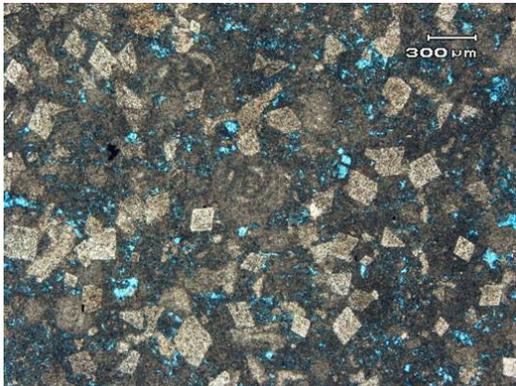


Figure 7. Photomicrograph of Sample 1120 showing presence of muddy matrix.

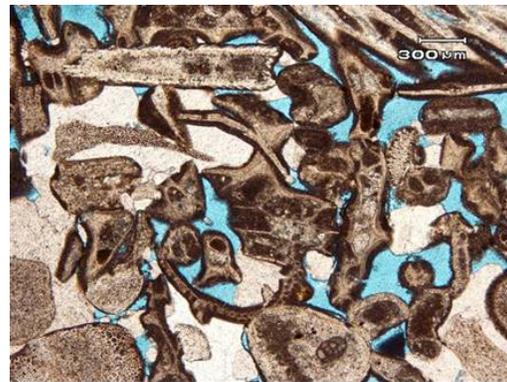


Figure 8. Photomicrograph of Sample L-1 showing grains but no mud content.