

THE MEASUREMENT OF THE CATION EXCHANGE CAPACITY OF CORE
PLUGS BY A NON-DESTRUCTIVE 'WET' CHEMICAL METHOD

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Abstract A new method for measuring the Cation Exchange Capacity (CEC) of core material has been developed. The technique measures the CEC of solid core plugs and thus circumvents the problem of creating additional cation exchange sites through crushing, which is a feature of the conventional 'wet' chemical method. The new method also offers advantages over other techniques in current use since it is faster (and cheaper) than the multiple salinity (Co/Cw) method and is experimentally less complex than the membrane potential method.

Measurements made to date indicate that results from the proposed technique are reliable. Indeed they produce more convincing and repeatable plots of Q_v (the cation exchange capacity per unit pore volume) versus the reciprocal of porosity, than those from results of conventional 'wet' chemical methods.

The analysis procedure involves passing a series of metal bearing solvent solutions through the sample plug. This is done using an HPLC (High Performance Liquid Chromatography) pump, with the plug mounted in a Hassler tube. The exchangeable cations in the plug (e.g. Na^+ , K^+ , Mg^{2+} , Ca^{2+} , etc.) are first replaced with Ferric Ions (Fe^{3+}). All excess Fe^{3+} ions are removed from the pore spaces within the plug. The plug is then treated with a solvent solution containing Na^+ ions, this enables the Fe^{3+} ions to be stripped from the exchange sites, at which point they are collected in a volumetric flask. The quantity of Fe^{3+} ions recovered after stripping is determined by standard analytical procedures. Finally, the mass and porosity of the plug are measured, and used to calculate the CEC and Q_v values.

INTRODUCTION

There are numerous models available to account for the non-Archie behaviour of rocks. One of the most enduring and widely accepted is that after Waxman and Smits (Waxman and Smits 1968, Waxman and Thomas 1974), where clay conductivity is explained in terms of the clays' cation exchange capacity (CEC). The cations forming part of the clay matrix contribute to the rock's overall conductivity. CEC is often discussed in terms of Q_v which is the CEC per unit total pore volume of a rock sample. The Waxman-Smits model has gained widespread use despite its main weakness, that measurement of a rock's CEC is difficult and can only be made directly on core material. This paper outlines a new method to measure CEC, one which has distinct advantages over those presently in use.

Currently, there are three established methods with which to measure the CEC of a rock. They are (i) the Membrane Potential Method, (ii) the Variable Salinity Method, and (iii) the Wet Chemistry Method.

CONVENTIONAL METHODS

Membrane potential (Thomas 1976)

A core plug saturated with a relatively fresh brine is placed such that one end is exposed to a brine of the same (low) salinity and the other to a solution of higher salinity. The higher salinity brine is forced through the core sample, displacing the fresher brine at a controlled rate. (In the reference, salinities giving 0.1 ohmm and 1.0 ohmm at 23°C were used. For a sample of greater than 10 mD permeability the displacement takes about 20 minutes). Throughout the period of experimentation, the core sample creates an e.m.f. that varies as the more saline brine displaces the fresher brine. In fact it reaches a maximum during the displacement. It is this maximum e.m.f. value which can be used to calculate the Q_v of the core sample.

Variable Salinity Method (Waxman-Smits 1968)

This method was used by Waxman and Smits when they first proposed their equation. A core plug is saturated with a high salinity brine, say 200 000 ppm and the formation resistivity factor (FRF) is measured. The process is repeated a number of times (typically 3 or 4) with successively lower salinity brines.

Each FRF value is plotted on a linear graph of core plug conductivity on the y-axis and brine conductivity on the x-axis. If the rock is an Archie Rock the points lie on a straight line through the origin. However, where there is clay conductivity this will present itself as a negative intercept on the x-axis equal in magnitude to $B.Q_v$ where B is the equivalent conductance of Na⁺ exchange cations. The relevant value for B is that according to laboratory conditions (Keelan 1979). For 25°C and a salinity greater than 70 000 ppm this is 3.9.

Conventional Wet Chemistry Method

This method is frequently used on part of the core plug offcuts from FRF measurements. The samples are crushed and may be passed through a sieve of, say, 500 microns. The cation exchange sites are saturated with sodium ions by immersing the samples in sodium acetate, buffered to a pH of 7, for a long period (say about 15 hours). The excess sodium acetate is removed by washing the samples with an organic solvent such as methanol. The sodium ions are then displaced with either potassium or ammonium ions. The amount of sodium displaced is measured and is directly related to the CEC. This value, in conjunction with the pore volume and weight of the sample prior to disaggregation, is used to derive the Q_v value.

COMPARISON OF CONVENTIONAL METHODS

All the conventional methods have drawbacks. The Wet Chemistry Method is technically the worst of the three. In crushing the sample, there is scope for creating cation exchange sites which, while measured in the laboratory, do not contribute to conductivity within the reservoir. At the same time, too little crushing can result in exchange sites not being exposed which really ought to be. Evidence is seen of both occurring in the results discussed later in the paper. Furthermore, the clay orientation in the pore space is not accounted for (Thomas 1976). Yet despite these obvious shortcomings, more CEC data is generated with this method than with any other. The reason is that it is the cheapest available, relatively simple to perform in the laboratory and quick; results can be obtained in two weeks.

The Membrane Potential Method is perhaps technically the best. In determining the e.m.f. across a "salinity membrane" in a core plug the technique measures an electrical property which is directly related to the Q_v of

the rock. Moreover, it is a measurement made on a solid core plug so the clays remain relatively undisturbed. Its advantages have been highlighted quite recently (Yuan and Diederix 1989). However, it is with reluctance that commercial laboratories offer the membrane potential method because it is extremely difficult to perform in the laboratory primarily through its sensitivity to temperature variations (Steward and Burck 1986).

From a technical point of view the variable salinity method has most of the advantages of the membrane potential method. The measurement is made on a core plug without crushing it so the clays remain relatively undisturbed. On the other hand it has two major disadvantages. Firstly, it is very time consuming and expensive. Typically, the analysis take about 4 months to complete. Secondly, there is a dilemma in interpreting the data. At low salinities, below about 70 000 ppm under laboratory conditions, the freshness of the interstitial water causes the clay's own conductivity to be reduced. This is seen mathematically as a decreased value of B in the Waxman-Smits equation and means that such points lie on the curved part of the Co/Cw crossplot. However, in staying above this threshold, the data has to be extrapolated a long way to reach the required intercept adding significantly to the error in the result.

Hence it is clear from the preceding discussion that none of the established methods are entirely satisfactory when considered both in terms of their technical and commercial merits.

THE NEW MEASUREMENT OF CEC

Like the conventional wet chemical method the new technique determines the number of cation exchange sites, present in a formation sample, by an ion exchange process. However, it differs in three important respects from that of the conventional wet chemistry method, i.e.

1. A solid core plug is used for the analysis rather than a crushed sample. This circumvents the problem of creating or exposing additional cation exchange sites, which is the main drawback of the conventional wet chemical method. It also means the measurement may be repeated on the same core plug.
2. The complete analysis is performed using organic solvents (i.e. it is performed under non-aqueous conditions). This minimises clay damage, particularly swelling and the consequential reduction in permeability which would otherwise occur under the conditions required during the cation exchange process.

3. In order to treat the core plug quickly and effectively the reagent solvents are forced through the core plug under pressure.

LABORATORY PROCEDURE

The full analysis procedure (Ganley 1989) is as follows for plugs of one inch diameter and one to one and a half inches in length. For plugs of other sizes, quantities and times mentioned may have to be altered. The procedure described uses Fe^{3+} ions as the exchangeable ions.

The plugs are first cleaned to remove oil and brine. They can either be soxhlet cleaned (ideally cold soxhlet cleaned) with conventional solvents or cleaned using a rapid cleaner.

The plug to be analysed is placed in a core holder fitted with a Hassler tube. A confining pressure of 800 - 1500 psi is applied. For most plugs a confining pressure of 800 - 1000 psi is adequate but for plugs with low permeabilities (below 0.7 mD), higher confining pressures may be required. To ensure that the flow of solvent through the plug is as even as possible (particularly important with horizontal plugs) a back-pressure regulator is used. A back pressure setting of 500 psi is normally adequate.

Using an HPLC pump, a series of solvents and solvent solutions are then passed through the plug. It is advisable to ensure that the solvents are first degassed and that the temperature at which the cation exchange occurs is in the region 18-25°C. Addition rates throughout the analysis are maintained between 1.5 and 2.5 ml/min. In particular an addition rate of 1.5 ml/min should not be exceeded when adding the iron complex. There is evidence to suggest that in general, fragile illitic clays are damaged to a significant degree only when solvent throughput exceeds 4 ml/min.

Table 1 provides an outline of the solvent elution stages used to determine the cation exchange capacity. The most important of these stages is (iii), where iron (Fe^{3+}) is used to displace all the cations from the exchange sites. Stages (iv) and (v) are primarily used to ensure that all the unreacted iron cations are removed from the plug.

The solvent quantities which are recommended should be adequate to remove all the excess iron reagent, however, it is best to confirm this by adding acetylacetone to the eluted solvent. If the solvent turns yellow, orange or red, then further elution will be necessary but stage (vi) may be commenced if it remains colourless. During stage (vi) and

TABLE 1 CEC determination - solvent elution stages

STAGE	SOLVENT	VOLUME OF SOLVENT
(i) Preconditioning	Methanol	40 ml
(ii) Preconditioning	50/50 (vol/vol) mixture of methanol and dichloromethane	40 ml
(iii) Removal of the indigenous 'exchange' cations and their simultaneous replacement with Fe ³⁺	Iron (III) di(2-ethylhexyl) phosphate in 50/50 methanol/dichloromethane	160 ml
(iv) Elution (removal) of the excess iron reagent	50/50 (vol/vol) mixture of methanol in dichloromethane	120 ml
(v) Further elution to remove the remaining (unreacted) iron reagent from the interstitial pore spaces	Dichloromethane	200 ml
(vi) Re-extraction of the iron (with the sodium ions) from the clays cation exchange sites.	Sodium di (2-ethyl hexyl) phosphate dissolved in dichloromethane	120 ml
(vii) Continued re-extraction of iron.	Dichloromethane	40 ml
(viii) Continued re-extraction of iron.	50/50 (vol/vol) mixture of methanol in dichloromethane	30 ml

to a lesser degree stages (vii) and (viii) iron is released from the cation exchange sites. This iron should be collected in a 250 ml volumetric flask, containing 2 ml of acetylacetone.

Upon completing the final addition stage (viii), the contents of the volumetric flask are made up to a total volume of 250ml with methanol, this solution is referred to as Solution A. Using a pipette, 10ml of Solution A together with 4ml of acetylacetone are added to a 50ml volumetric flask and then made up to volume with a 50/50 (vol/vol) mixture of methanol and dichloromethane, this is Solution B. The absorption of Solution B is then determined, in a 1 cm cell, at the maximum absorption occurring in the region of 435-438 nanometres. The concentration of iron present can then be calculated from a calibration curve prepared using standard solutions (Figure 1).

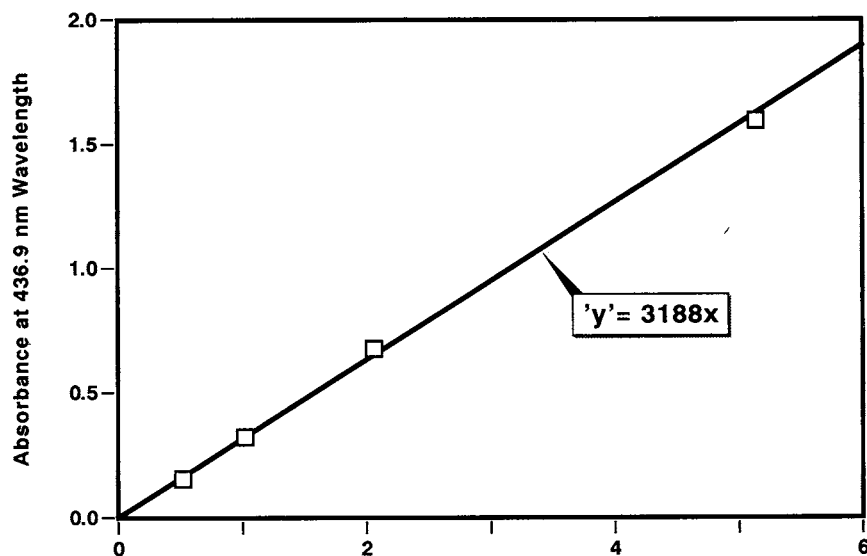


Figure 1 Master calibration for the new CEC measurement

The plug is further cleaned to remove all traces of sodium di(2-ethylhexyl) phosphate and is then dried at 105°C for 24 hours prior to determining its mass and helium total porosity. Finally, the cation exchange capacity and Q_v values are determined.

DISCUSSION OF LABORATORY PROCEDURE

Use of Ferric Ions

The laboratory method previously described could in theory make use of cations other than ferric (Fe^{3+}) and sodium (Na^+), although in the case of Fe^{3+} there are several good reasons why it is favoured:

- Unlike a number of other metals, the iron (III) complex of di(2-ethyl hexyl) phosphoric acid does not react with the stainless steel used in the construction of the core holder and pressure tubing.
- The course of the analysis can be observed visually. This is particularly useful during stage (v) when it is important to remove all the unreacted iron reagent from the plug.
- Purity and ease of preparation. These are important considerations since metal salts of di(2-ethyl hexyl) phosphoric acid are not available commercially. The purity factor is especially important during stage (iii), and in this respect the iron (III) salt is favoured over most mono-valent ions, Na^+ included.
- Iron (III) forms a very intensely coloured complex with acetylacetone. This fact has allowed a simple, yet accurate analysis procedure to be devised.

Time Required for Analysis

The time which it takes to perform a CEC analysis, on a core plug, depends on the size and permeability of the plug. For example, a 1" diameter by 1-1½" long plug, with a permeability greater than 0.7 mD, can be analysed within a day. For permeabilities in the range 0.4 to 0.7 mD, the cation exchange generally takes from 2 to 5 days. It is possible to analyse plugs down to permeabilities of about 0.2 mD, though under these circumstances the plug can best be analysed if it is trimmed to about ½" in length.

Temperature Sensitivity

In contrast to the membrane potential method, the ion exchange analysis has not been found to be sensitive to temperature and can be performed over the normal room temperature range of 18 to 25°C. This finding is not surprising since the analysis simply measures the number of permanent cation exchange sites present on a plug.

Repeatability of Results

If required the new CEC measurement technique can be repeated on the same core plug. The quality assurance opportunities which this provides are self evident.

In order to gauge how reproducible the method is, two 1" by 1" diameter core plugs (F1 and F2) have been analysed six times. The results are given in Table 2. These results indicate that the analysis is repeatable with Qv varying from 0.202 to 0.227 for F1 and from 0.160 to 0.184 for F2.

TABLE 2 Results of Repeat Measurements

Number of repeats	Core Plug No.	CEC (Meq/100g)	Qv (Meq/ml)
1	F1	1.133	0.217
2	F1	1.152	0.221
3	F1	1.186	0.227
4	F1	1.053	0.202
5	F1	1.088	0.208
6	F1	1.125	0.215
1	F2	1.308	0.176
2	F2	1.365	0.184
3	F2	1.195	0.161
4	F2	1.220	0.164
5	F2	1.228	0.165
6	F2	1.187	0.160

INITIAL RESULTS

Three studies have been made using core plugs from the North Sea; one with Permian (Rotliegend), a second with Jurassic and a third with Triassic sandstones. In each study, the CEC was measured on all the plugs with the new method and control measurements were carried out by a different commercial laboratory using the conventional wet chemistry method, blind from the test results. Most of the measurements of CEC with the new method were made with Ferric ions although Cobalt ions were used in some cases. Table 3 gives a complete breakdown.

TABLE 3 CEC data measured with the new method

Well	Formation/ Age	No. of Samples	Exchangeable Ion Used	Control
R1	Rotliegend	5	Fe ³⁺	Wet Chemistry
R2	Rotliegend	11	Co ²⁺	
R3	Rotliegend	17	Co ²⁺	
R4	Rotliegend	14	Fe ³⁺	
J1	Jurassic	6	Fe ³⁺	Wet Chemistry
J2	Jurassic	5	Fe ³⁺	
J3	Jurassic	3	Fe ³⁺	
J4	Jurassic	5	Fe ³⁺	
T1	Triassic	32	Fe ³⁺	Wet Chemistry

The first study involved forty-seven Permian Rotliegend core plugs from four wells in the Southern North Sea all from one field. Results are in Table 4. The conventional wet chemistry results provide no correlation between Q_v and the reciprocal of porosity whereas the new method provides a plausible relationship that is consistent between the four wells in the study (Figure 2 and Figure 3). A direct crossplot of the two sets of results is not possible because the two sets of measurements were made on samples from different depths.

The second study involved nineteen core plugs from numerous Jurassic formations. The samples used in the control measurements were offcuts of the core plugs used for the CEC's measured with the new method. A direct comparison of the results is shown in Table 5 and Figure 4. At the lower end, there is excellent agreement. In five cases at the higher end however the control CEC's are significantly greater than those from the new method. It may well be that these five samples were crushed too heavily during the control, exposing cation exchange sites.

The third study involved thirty two core plugs from five Triassic formations in one well. A direct comparison of the results is shown in Table 6 and Figure 5. At the lower end the new method generally gives slightly higher CEC values than those from the conventional method. This is somewhat surprising and could have been caused by undercrushing of the samples in the conventional procedure. It may also be that the organic solutions in the new procedure act more efficiently in exchanging their ions and this has only shown up in the study on the Triassic samples.

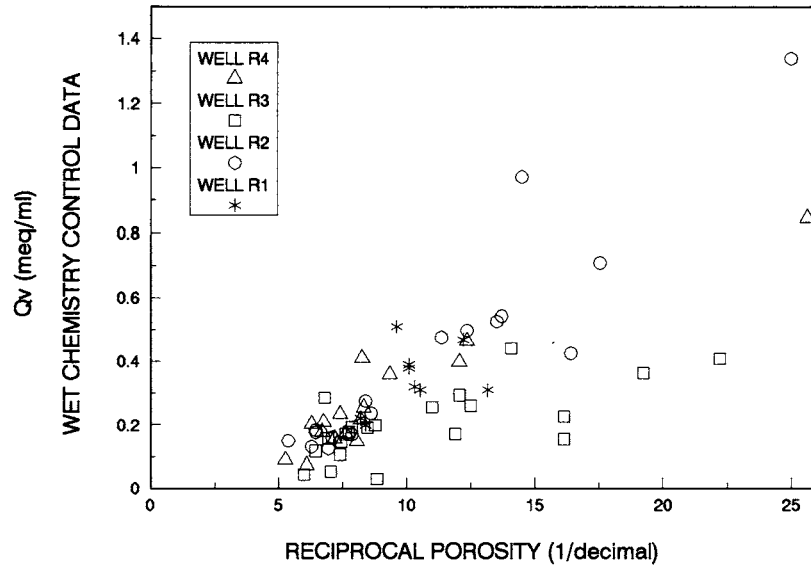


Figure 2 Qv vs reciprocal porosity from the Rotliegend formation: control data

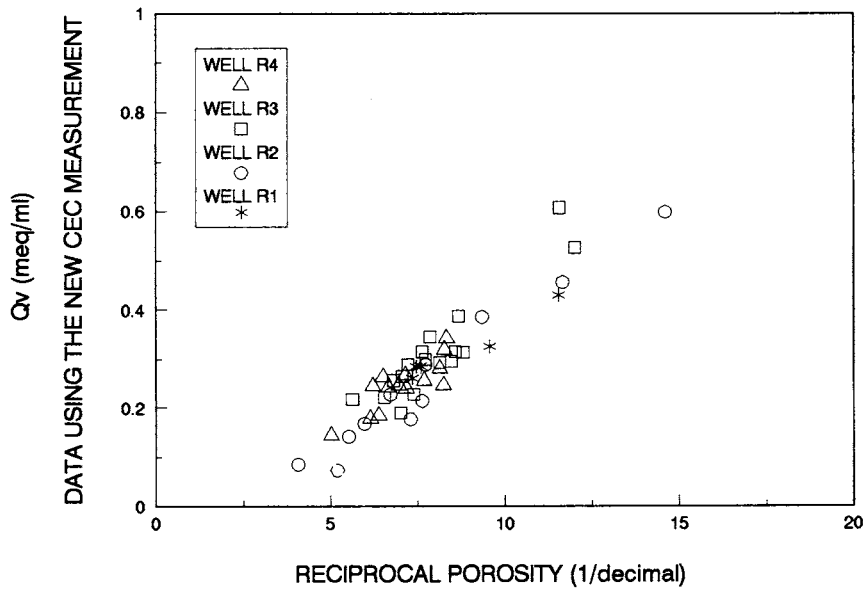


Figure 3 Qv vs reciprocal porosity from the Rotliegend formation: data from the new CEC method

TABLE 4 CEC data from the Rotliegend formation

	EXPERIMENT: NEW CEC METHOD					CONTROL: WET CHEMISTRY CEC METHOD				
	Sample No.	Depth (ft)	Qv (meq/ml)	Por.	(1/Por)	Sample No.	Depth (ft)	Qv (meq/ml)	Por.	(1/Por)
WELL R1	A92	9327.00	0.326	0.105	9.57	1A	9326.60	0.470	0.082	12.20
	A95	9360.83	0.430	0.087	11.55	4C	9361.40	0.320	0.097	10.31
	A96	9366.40	0.262	0.136	7.35	5B	9366.80	0.510	0.104	9.62
	A98	9381.00	0.285	0.134	7.47	7A	9381.30	0.200	0.119	8.40
	A99	9389.75	0.286	0.132	7.60	8C	9390.30	0.220	0.122	8.20
WELL R2	D167	10371.83	0.598	0.069	14.60	16A	10371.80	0.527	0.074	13.51
	D170	10394.08	0.168	0.167	5.98	19A	10394.50	0.132	0.159	6.29
	D171	10406.50	0.215	0.131	7.63	20A	10406.65	0.183	0.155	6.45
	D172	10415.33	0.228	0.149	6.72	21A	10415.50	0.161	0.141	7.09
	D173	10424.50	0.456	0.086	11.66	22A	10424.60	0.453	0.900	1.11
	D175	10448.17	0.177	0.137	7.30	24A	10448.35	0.276	0.119	8.40
	D176	10456.00	0.289	0.129	7.73	25A	10456.20	0.236	0.116	8.62
	D177	10463.25	0.085	0.246	4.07	26A	10463.45	0.126	0.144	6.94
	D178	10473.58	0.142	0.181	5.53	27A	10473.80	0.150	0.186	5.38
	D179	10482.92	0.386	0.107	9.35	28A	10483.10	0.170	0.127	7.87
D180	10492.75	0.073	0.192	5.20	29A	10492.95	0.177	0.155	6.45	
WELL R3	G268	8699.08	0.607	0.087	11.56	31A	8699.30	0.294	0.083	12.05
	G269	8709.08	0.526	0.083	12.02	32A	8709.25	0.256	0.091	10.99
	G270	8719.00	0.346	0.127	7.86	33A	8719.20	0.106	0.135	7.41
	G271	8731.92	0.315	0.117	8.58	34A	8731.40	0.172	0.084	11.90
	G272	8748.08	0.388	0.115	8.68	35A	8748.35	0.199	0.114	8.77
	G273	8757.00	0.293	0.123	8.13	36A	8757.25	0.029	0.113	8.85
	G276	8800.08	0.289	0.138	7.23	39A	8800.30	0.146	0.134	7.46
	G277	8811.83	0.314	0.114	8.80	40A	8811.30	0.193	0.127	7.87
	G278	8822.08	0.300	0.129	7.73	41A	8822.30	0.157	0.144	6.94
	G279	8835.92	0.296	0.118	8.47	42A	8836.30	0.442	0.071	14.08
	G280	8840.92	0.218	0.178	5.63	43A	8841.15	0.043	0.167	5.99
	G282	8863.25	0.222	0.153	6.55	45A	8863.50	0.118	0.155	6.45
	G283	8875.08	0.229	0.135	7.39	46A	8875.25	0.192	0.118	8.47
	G284	8886.50	0.190	0.143	7.02	47A	8886.75	0.286	0.147	6.80
	G285	8903.00	0.315	0.131	7.63	48A	8903.20	0.178	0.129	7.75
G286	8916.83	0.257	0.147	6.82	49A	8917.00	0.171	0.131	7.63	
G287	8929.17	0.266	0.142	7.06	50A	8929.35	0.053	0.142	7.04	
WELL R4	M216V	8423.00	0.243	0.150	6.66	2A	8410.90	0.843	0.039	6.76
	M217V	8431.00	0.281	0.123	8.14	3A	8430.00	0.465	0.081	12.35
	M218V	8445.17	0.268	0.140	7.15	4A	8446.10	0.255	0.120	8.33
	M219V	8460.00	0.247	0.121	8.24	5A	8459.90	0.217	0.122	8.20
	M220V	8575.67	0.247	0.144	6.96	6A	8475.30	0.157	0.139	7.19
	M221V	8495.67	0.246	0.161	6.22	7A	8495.45	0.073	0.164	6.10
	M222V	8501.00	0.178	0.163	6.15	8A	8500.35	0.203	0.159	6.29
	M223V	8518.25	0.320	0.121	8.27	9A	8518.80	0.148	0.124	8.06
	M224V	8536.42	0.257	0.130	7.69	10A	8536.60	0.172	0.131	7.63
	M225V	8554.83	0.185	0.157	6.39	11A	8554.00	0.178	0.149	6.71
	M226V	8571.00	0.240	0.139	7.18	12A	8571.90	0.234	0.135	7.41
	M227V	8588.17	0.144	0.199	5.02	13A	8588.30	0.089	0.190	5.26
	M228V	8599.67	0.264	0.154	6.51	14A	8599.00	0.359	0.107	9.35
	M229	8614.75	0.343	0.120	8.33	15A	8613.90	0.411	0.121	8.26

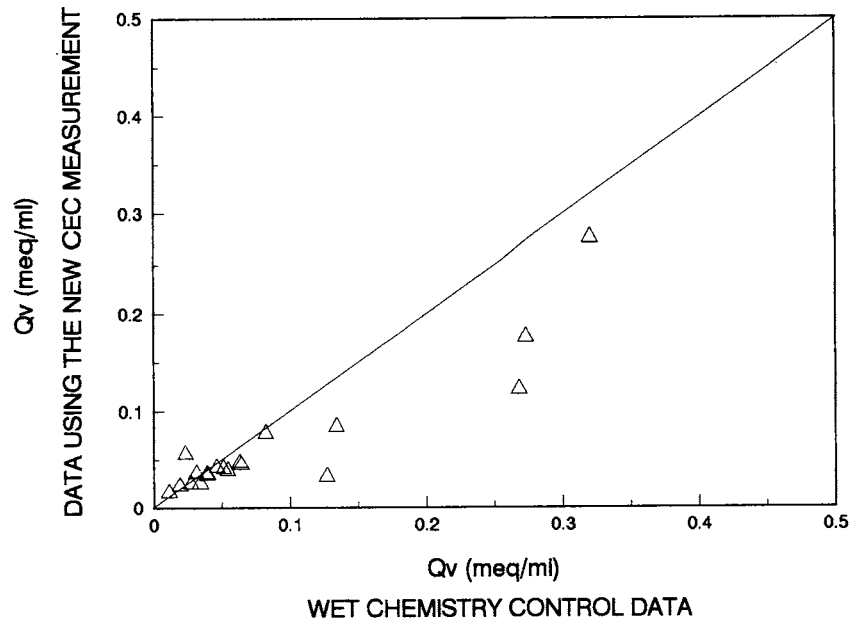


Figure 4 Comparison of Qv data from Jurassic Formations

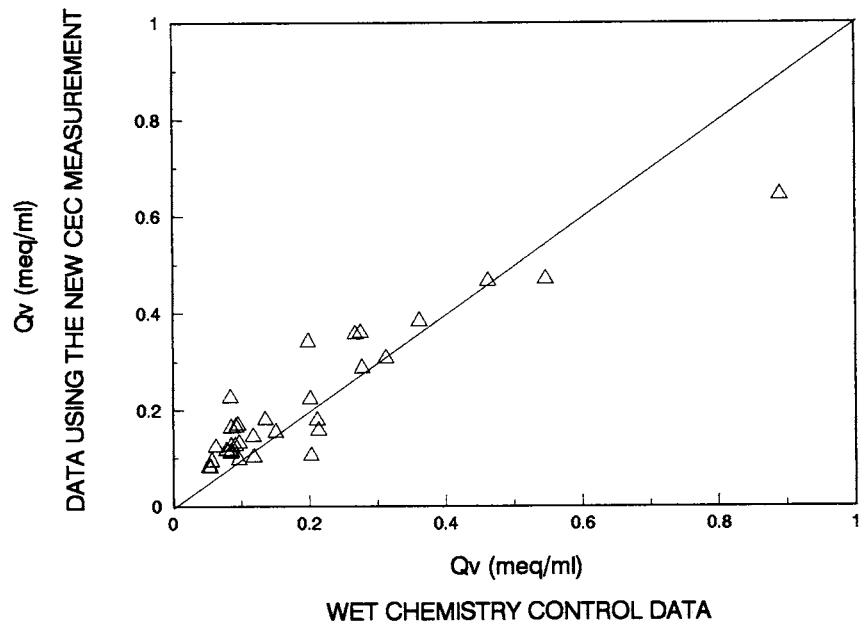


Figure 5 Comparison of Qv data from Triassic formations

TABLE 5 CEC data from Jurassic formations

EXPERIMENT: NEW CEC METHOD						CONTROL: WET CHEMISTRY CEC METHOD					
Sample No.	Depth (ft)	Formation	Qv (meq/ml)	Por. (1/100)	Por. (1/100)	Sample No.	Depth (ft)	Formation	Qv (meq/ml)	Por. (1/100)	Por. (1/100)
32A	11752.50	JF1	0.047	0.201	4.99	32A	11752.50	JF1	0.063	0.200	5.00
1A	14467.20	JF1	0.045	0.200	4.99	1A	14467.20	JF1	0.064	0.199	5.03
20A	14289.20	JF1	0.056	0.109	9.19	20A	14289.20	JF1	0.023	0.107	9.35
16A	14165.30	JF1	0.023	0.221	4.53	16A	14165.30	JF1	0.019	0.221	4.52
5A	14591.85	JF2	0.036	0.201	4.98	5A	14591.85	JF2	0.031	0.201	4.98
27A	14434.30	JF2	0.016	0.198	5.05	27A	14434.30	JF2	0.011	0.201	4.98
41A	11950.90	JF3	0.025	0.237	4.23	41A	11950.90	JF3	0.034	0.240	4.17
37A	11866.70	JF3	0.025	0.222	4.51	37A	11866.70	JF3	0.027	0.225	4.44
15B	14828.25	JF3	0.176	0.122	8.18	15B	14828.25	JF3	0.273	0.120	8.33
14A	14810.10	JF3	0.042	0.194	5.16	14A	14810.10	JF3	0.046	0.197	5.08
8A	14680.20	JF3	0.041	0.205	4.88	8A	14680.20	JF3	0.051	0.205	4.88
45A	12098.60	JF4	0.035	0.205	4.87	45A	12098.60	JF4	0.039	0.213	4.69
48A	12153.30	JF5	0.039	0.161	6.23	48A	12153.30	JF5	0.054	0.163	6.13
50A	12207.00	JF5	0.032	0.218	4.58	50A	12207.00	JF5	0.127	0.226	4.42
60A	13507.35	JF6	0.275	0.168	5.95	60A	13507.35	JF6	0.320	0.172	5.81
62A	13536.50	JF6	0.084	0.200	4.99	62A	13536.50	JF6	0.134	0.204	4.90
63A	13555.50	JF6	0.122	0.136	7.37	63A	13555.50	JF6	0.268	0.137	7.30
69A	14182.35	JF7	0.077	0.180	5.55	69A	14182.35	JF7	0.082	0.186	5.38
72A	14251.75	JF8	0.034	0.118	8.51	72A	14251.75	JF8	0.039	0.119	8.40

TABLE 6 CEC data from Triassic formations

EXPERIMENT: NEW CEC METHOD						CONTROL: WET CHEMISTRY CEC METHOD					
Sample	Depth (ft)	Formation	Qv (meq/ml)	Por. (1/100)	Por. (1/100)	Sample	Depth (ft)	Formation	Qv (meq/ml)	Por. (1/100)	Por. (1/100)
1A	9106.30	TF1	0.225	0.107	9.35	1A	9106.30	TF1	0.085	0.111	9.01
2A	9120.35	TF1	0.158	0.201	4.97	2A	9120.35	TF1	0.214	0.200	5.00
6A	9153.10	TF1	0.131	0.173	5.77	6A	9153.10	TF1	0.098	0.179	5.59
7A	9179.95	TF2	0.384	0.194	5.15	7A	9179.95	TF2	0.362	0.194	5.15
9A	9206.20	TF2	0.466	0.172	5.81	9A	9206.20	TF2	0.463	0.169	5.92
10A	9209.75	TF2	0.116	0.235	4.25	10A	9209.75	TF2	0.079	0.234	4.27
11A	9230.00	TF3	0.642	0.113	8.85	11A	9230.00	TF3	0.891	0.113	8.85
13A	9236.90	TF3	0.180	0.238	4.21	13A	9236.90	TF3	0.136	0.238	4.20
14A	9243.55	TF3	0.471	0.172	5.83	14A	9243.55	TF3	0.547	0.156	6.41
15A	9260.95	TF3	0.357	0.189	5.30	15A	9260.95	TF3	0.268	0.178	5.62
17A	9285.35	TF3	0.307	0.166	6.04	17A	9285.35	TF3	0.313	0.168	5.95
18A	9298.70	TF3	0.080	0.247	4.05	18A	9298.70	TF3	0.055	0.251	3.98
19A	9305.00	TF3	0.093	0.212	4.73	19A	9305.00	TF3	0.057	0.219	4.57
21A	9323.20	TF3	0.154	0.204	4.91	21A	9323.20	TF3	0.151	0.208	4.81
22A	9333.95	TF3	0.287	0.209	4.78	22A	9333.95	TF3	0.278	0.212	4.72
24A	9372.95	TF3	0.123	0.221	4.53	24A	9372.95	TF3	0.063	0.227	4.41
26A	9390.00	TF3	0.165	0.143	6.98	26A	9390.00	TF3	0.093	0.146	6.85
27A	9407.00	TF3	0.102	0.233	4.29	27A	9407.00	TF3	0.119	0.238	4.20
28A	9415.50	TF3	0.105	0.185	5.40	28A	9415.50	TF3	0.203	0.175	5.71
30A	9442.90	TF4	0.163	0.206	4.85	30A	9442.90	TF4	0.086	0.198	5.05
31A	9443.80	TF4	0.125	0.222	4.50	31A	9443.80	TF4	0.086	0.217	4.61
32A	9456.95	TF4	0.223	0.202	4.95	32A	9456.95	TF4	0.202	0.207	4.83
33A	9471.00	TF4	0.341	0.199	5.04	33A	9471.00	TF4	0.199	0.201	4.98
36A	9504.75	TF5	0.360	0.206	4.85	36A	9504.75	TF5	0.276	0.205	4.88
37A	9524.20	TF5	0.126	0.236	4.24	37A	9524.20	TF5	0.092	0.240	4.17
38A	9534.05	TF5	0.113	0.260	3.84	38A	9534.05	TF5	0.086	0.252	3.97
39A	9541.10	TF5	0.145	0.229	4.37	39A	9541.10	TF5	0.118	0.226	4.42
40A	9547.20	TF5	0.169	0.235	4.26	40A	9547.20	TF5	0.096	0.233	4.29
41A	9557.55	TF5	0.111	0.248	4.03	41A	9557.55	TF5	0.085	0.238	4.20
42A	9571.45	TF5	0.097	0.256	3.91	42A	9571.45	TF5	0.097	0.246	4.07
44A	9587.60	TF5	0.082	0.233	4.30	44A	9587.60	TF5	0.053	0.230	4.35
46A	9610.55	TF5	0.178	0.245	4.08	46A	9610.55	TF5	0.212	0.237	4.22

CONCLUSION

A new method has been developed which measures the cation exchange capacity of core material. The analytical principle behind the new technique is similar to that used in the conventional wet chemistry method, in that it measures the number of cation exchange sites present in the core sample by an exchange process. However, the new analysis differs by using a solid core plug, thus circumventing the problem of creating or exposing additional exchange sites. Work has demonstrated that the analyses can be repeated with a reasonable degree of accuracy.

Preliminary results indicate a marked improvement on the conventional wet chemistry method. The higher precision of the new method was particularly apparent in work conducted on the Rotliegend formation, in which a convincing relationship was discernible between Q_v and the reciprocal of porosity.

Further work could usefully be directed towards a comparative study on the Q_v results generated by the new method with that of the membrane potential and variable salinity methods.

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