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CATION EQUILIBRIA STUDIES ON FRACTIONATED NATURAL CLAYS

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Abstract – Various fractions, ranging in size from 5 to 0·05 μ of natural clays from Mexico and Wyoming, occurring as heterogeneous or multicomponent cationic systems, were studied under specific equilibrium conditions of salt concentrations in the range found in many drilling fluids and formation waters.

Glass electrodes were utilized in this study. A Tektite electrode was found to have specific sensitivity to divalent cations.

INTRODUCTION

THE CONCEPT of cationic exchange reactions on bentonitic clays is fundamental in many aspects related to drilling muds, well logging and formation properties. The basic significance of exchange reactions of montmorillonite in drilling fluids is recognized as an important factor in the rigid requirements of mud properties for drilling deeper and deeper wells.

The purpose of this investigation was to develop a method whereby the exchange cation composition of certain clay fractions could be determined at various equilibrium conditions.

All clay minerals possess a certain exchange capacity, but the capacity varies for different types of clay minerals, such as montmorillonite, illite, kaolinite, etc. Naturally occurring montmorillonites contain as exchangeable cations amounts of Na, Ca, and Mg and lesser amounts of other cations (Grim, 1953; McAtee, 1958). Because the exchange capacity compensates the charge unbalance in the interior of the lattice due to isomorphous substitution, the cation exchange capacity is a measure of the degree of this substitution (Grim, 1953).

Development of an electrode sensitive to divalent cations was recognized as a vital part of the investigation and the scope of the work was broadened to determine the utility of Tektite glass (thin slices of Tektite material) as a divalent sensitive electrode.

Multilayer membrane electrodes (Gregor, 1957) and other methods (Lean, 1934) have been developed which measure divalent cations in the presence of relatively high monovalent ion concentrations, but their application is somewhat troublesome. Garrels (1965) investigated glasses whose composition was nearly the same as insoluble crystalline silicates such as obsidian or tektite. These investigations have shown some encouraging results.

Because heterogeneous clays were investigated, no simple reversible equation expresses the exchange of cations taking place in any one clay fraction. That is, sodium, calcium, magnesium and in small amounts potassium, contribute to different degrees to the exchange.

Because exchange takes place in aqueous solution, H^+ is always available as a competitor for exchange sites, but pH measurements showed this factor to be negligible. Since a complex situation prevails, the explanation of the behavior of the clay samples during the cation exchange is based on the series of replaceability. Such a series, including the theories involved, for cations on a clay surface has been given by Ross (1943) as $Li > Na > NH_4 > K > Mg > Ca$.

EXPERIMENTAL TECHNIQUES

Natural, heterogeneous clays from Mexico (Bentonita Blanca Vetessa, Bentonita Comisa and Bentonita de Durango) and Wyoming (Wyoming Bentonite) were investigated. X-ray analyses showed impurities to consist mainly of talc, feldspar, calcite and quartz. Source of the material was from clay fractions obtained by Mungan (1962) and, as previously reported by this investigator, the exchangeable cations were sodium, calcium, magnesium and potassium, generally ranging for sodium from 22 to 80 meq/100 g clay, for calcium from 23 to 50 meq/100 g clay, for magnesium from 23 to 40 meq/100 g clay and for potassium from 1 to 3 meq/100 g clay.

500 mg of each clay fraction, which had been stored dry, was mixed with 100 ml of demineralized water. These hydrated stock suspensions were allowed to stand for 5 days and were stirred several times a day. After this period, six samples of the stock suspension, each of 10 ml, were removed by pipet and 0·05N calcium chloride or sodium

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chloride, respectively, was added in amounts of 0·01 ml, 0·05 ml, 0·1 ml, 0·5 ml, 1·0 ml and 2·0 ml. The total volume was brought to 15 ml by adding demineralized water. The samples were then placed into covered polyethylene bottles and shaken for several days. The clay was separated by filtration and the clear solution analyzed using glass electrodes.

Filtrates obtained from clay suspensions treated with controlled amounts of sodium ions were investigated for calcium and magnesium ions whereas filtrates obtained from clay suspensions treated with known amounts of calcium ions were investigated for the amount of exchanged sodium ions.

Combinations of sodium-Calomel and Tektite-Calomel electrodes were tested with solutions of known concentrations of Ca^{++} ions and Na^{+} ions (Figs. 1 and 2).

After each measurement the electrodes were rinsed in demineralized water to remove adsorbed ions.

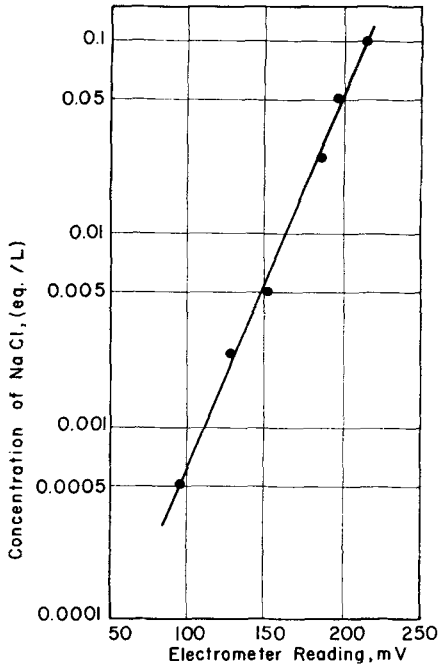


Fig. 1. Calibration curve for sodium-Calomel electrode system.

The Tektite-Calomel arrangement was tested for both sodium and magnesium interference. Addition of sodium seemed to have no appreciable effect on the electrode. Furthermore, any small interference decreased rapidly as cation exchange proceeded since an increasing amount of sodium is needed to replace a higher amount of the more strongly held calcium. The extent of any interference may be

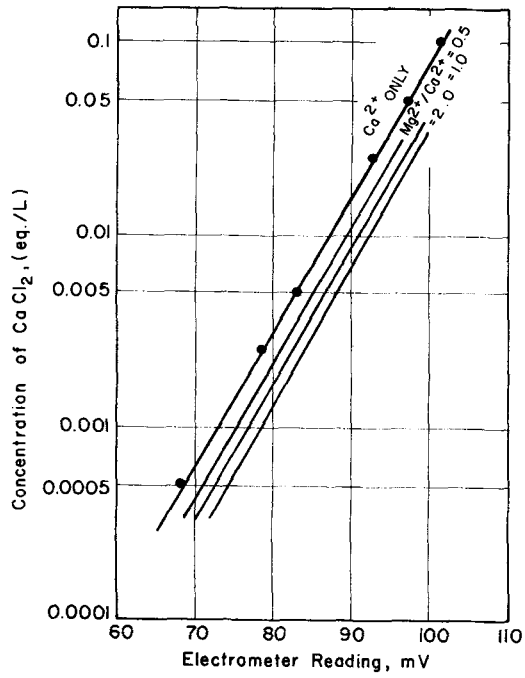


Fig. 2. Calibration curve for Tektite-Calomel electrode system.

observed by carrying out the calibration in solutions with similar ionic background.

The divalent electrodes were prepared using relatively thin sections (0·3–0·4 mm) of Tektite slices (Barnes, 1961). These experimental electrodes are characterized as glass electrodes. Investigation confirmed the findings that each glass (Diamond and Hubbard, 1951) had a characteristic departure thickness, and that beyond this, increasing thickness gave increasing voltage departures. A limitation to the Tektite thickness was due to enclosed air bubbles in most of the specimens.

The sensitive membrane was cemented to the end of a glass tube. Since careful handling was necessary to avoid a break of the thin Tektite membrane, the lower end of the glass tube and the rim of the membrane were coated with a low melting paraffin wax. This was done without affecting the membrane area exposed to the standard solution of calcium chloride. To prevent changes in the concentration of the standard solution due to evaporation, the electrode was sealed. A thin platinum wire was used to complete the electrical component part of the cell.

According to Garrels (1965) the specific sequence of pronounced selectivity to cations using Tektite slices is given as follows:

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}.$$

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When r.otted on semi-logarithmic paper the calibratic.n curve for Ca^{2+} only is a straight line. Furthermore it was observed that calibration curves of Ca^{2+} plus certain concentration of Mg^{2+} are not only linear but are almost parallel to the calibration curve for Ca^{2+} alone (Fig. 2).

By reading the electrometer output (mV) value and following this point to the intersection of the calibration curve at the given Ca^{2+}/Mg^{2+} ratio, the unaffected Ca^{2+} normality and therefore the meq/100 g for Ca^{2+} exchange may be obtained. By a similar approach Mg^{2+} exchange only can be found. The Mg^{2+}/Ca^{2+} ratio was obtained from Mungan's work (1962) which was based on flame photometer studies. The range of calcium and magnesium investigated may be expected in many raw clays.

Due to the high resistance of the electrodes an Electrometer Amplifier, Model 603, from Keithley Instruments, Inc. (1966) was used for determining the specific changes in ionic concentration. This electrometer amplifier is a wide band, D.C. amplifier with an extremely high input impedance, high voltage and current sensitivity.

Calibration curves were drawn using known salt concentrations of the ion to be determined and plotting the millivolt readings obtained versus concentrations on semi-logarithmic paper.

Both electrodes, monovalent and divalent, were checked from time to time against the standard solutions and calibration curves during the investigation. From the calibration curves all electrometer readings (mV) have been plotted in terms of concentrations, thus simplifying a study of the results.

RESULTS AND DISCUSSION

Tables 1–4 show the amount of ion (meq/100 g clay) exchange from heterogeneous clays at equilibrium conditions of either 0·1N sodium chloride or calcium chloride added.

Of particular interest are data shown in Table 3 and 4. The values determined for the calcium ion alone obtained by the use of a Calcium electrode approximately 50 times more sensitive to calcium than magnesium ion (Orion Research, 1966) may be compared with the values for calcium plus magnesium measured with the Tektite electrode. It appears the magnesium ion contribution increases with decreasing fraction size.

Drying of representative samples 48 hr at 50°C resulted in a weight loss in the range of 20–50 mg. Thus, based on the amount of sample taken for test purpose, a variation of 4–10 per cent in the total amount of cation replacement might be expected. Impurities such as feldspar and quartz shown by X-ray diffraction work to be concentrated in the coarser fractions also contribute to apparent decreases in the magnitude of total replacement.

The general effect of increased concentration of a replacing ion results in a greater exchange reaction

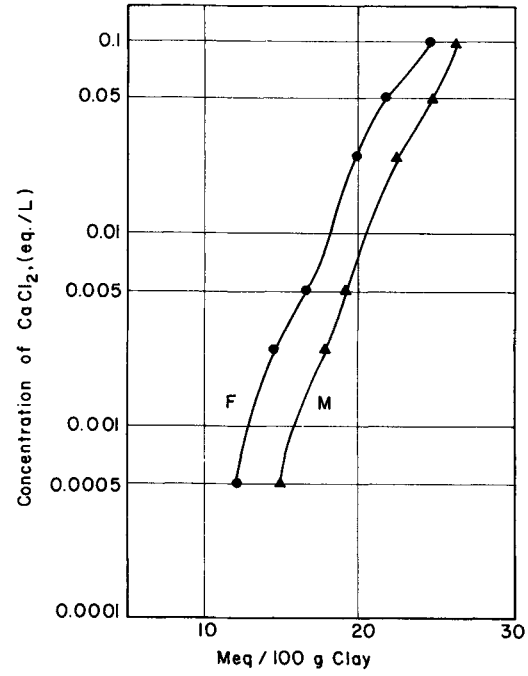


Fig. 3. Replacement of sodium ions by calcium chloride solutions under various equilibrium solutions from fraction F (2–1 μ) and fraction M(0·1–0·05 μ) of Wyoming bentonite.

Table 1. Replacement cation distribution on Bentonita Blanca Vetessa (Mexico) with 0·1N sodium chloride and calcium chloride and calcium chloride solutions

Fraction size (μ)		Na^+	Ca^{2+} plus Mg^{2+} (meq/100 g clay)	Total cation exchange 0·1N
F	1·0–0·4	13·8	51·0	64·8
G	0·4–0·3	13·8	39·0	52·8
M	0·1–0·05	45·0	33·0	78·0

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Table 2. Replacement cation distribution on Bentonita de Durango (Mexico) with 0·1N sodium chloride and calcium chloride solutions

Fraction size (μ)		Na^+	Ca^{2+} plus Mg^{2+} (meq/100 g clay)		Total cation exchange 0·1N
E	5·0–1·0	40·5	14·8	11·6	66·9
F	1·0–0·4	48·0	10·2	16·2	74·4
G	0·4–0·3	33·0	15·2	14·8	63·0
M	0·1–0·05	14·4	22·4	34·6	71·4

Table 3. Replacement of sodium ions by calcium chloride solutions under equilibrium conditions from various tractions of Wyoming bentonite

Electrode	Sodium Na^+ (meq/100 g clay)			
Fraction	F	H	L	M
Concentration of ion added (eq/L)				
0·0005	12·0	12·6	13·2	14·7
0·0025	14·7	14·4	14·7	17·7
0·005	16·5	15·6	15·6	19·2
0·025	19·8	19·2	18·3	22·5
0·05	21·9	22·2	22·2	24·9
0·10	24·6	24·9	26·9	26·9

Table 4. Replacement of calcium and magnesium ions by sodium chloride solutions under equilibrium conditions from various fractions of Wyoming bentonite

Electrode	Calcium Ca^{2+} (meq/100 g clay)				Tektite Ca^{2+} plus Mg^{2+} (meq/100 g clay)			
Fraction	F	H	L	M	F	H	L	M
Concentration of ion added (eq/L)								
0·0005	5·4	5·7	5·7	5·1	10·8	12·3	12·0	13·5
0·0025	6·0	6·9	6·15	6·15	12·3	15·0	13·65	16·2
0·005	7·35	7·8	7·35	7·5	14·85	19·2	16·95	20·4
0·025	18·3	14·4	15·0	13·5	33·00	32·4	31·80	34·65
0·05	22·8	18·0	20·4	18·0	41·55	43·5	45·0	45·75
0·10	26·4	23·4	22·8	21·9	47·00	55·8	52·2	51·60

by that ion. A rapid increase in the amount of sodium ion replacement taking place at lower concentration ranges of calcium chloride added tends to flatten out, probably indicating a near total replacement. Equilibrium curves for both divalent cations at 0·1N sodium chloride treatment levels still show considerable slope, indicating incomplete replacement. This agrees with the well known fact that as the percentage of exchangeable cations becomes smaller, the more difficult is the replacement of the calcium ion by sodium, whereas the replacement of sodium by calcium shows the reverse relationship.

Because most reservoir sands contain some clay,

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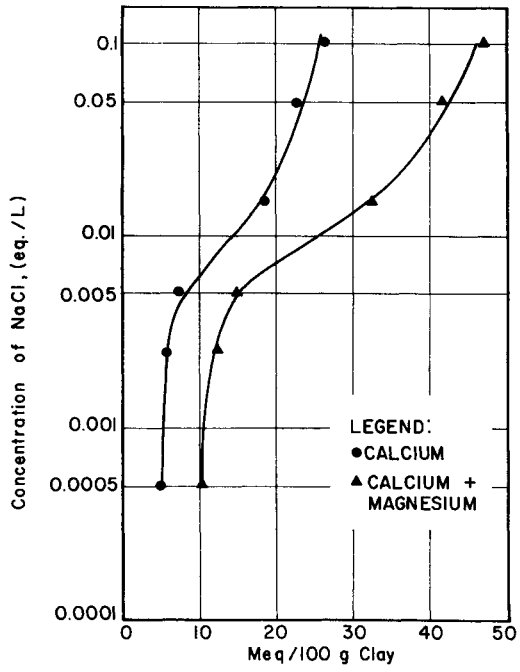


Fig. 4. Replacement of calcium and magnesium ions by sodium chloride solutions under equilibrium conditions from fraction F (2–1 μ) of Wyoming bentonite.

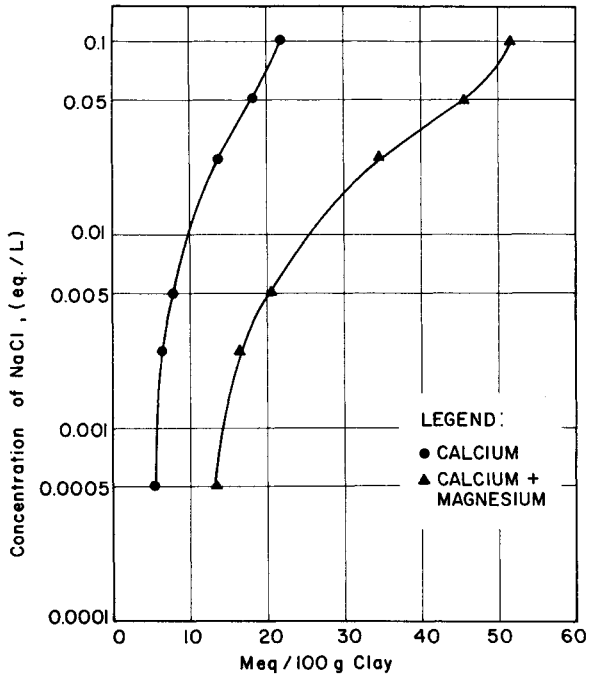


Fig. 5. Replacement of calcium and magnesium ions by sodium chloride solutions under equilibrium conditions from fraction M (0·1–0·05 μ) of Wyoming bentonite.

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cation exchange processes are of great importance in both drilling and production operations. It is important that neither invading mud filtrate nor injection waters upset the natural existing equilibria because bentonitic clay minerals respond to such environmental variations by base exchange reactions, the replacement mainly depending on the type and saturation of exchangeable cations on the clay. Increased volume of expanding bentonitic clays and transportation of dispersed clay flakes may result and both restrict fluids flow in a reservoir sand, affecting formation permeability and productivity or injectivity indices.

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Résumé—Un certain nombre de fractions, de 5 μ à 0.05 μ de grandeur, d'argiles naturelles du Mexique et de Wyoming, trouvés sous forme de systèmes cationiques hétérogènes ou multicomposés, ont fait l'objet d'études sous des conditions d'équilibre spécifique de concentrations de sel telles qu'on en trouve dans plusieurs fluides de forage et eaux de formation.

On a utilisé des électrodes en verre pour cette étude. Il s'est avéré qu'une électrode Tektite avait une sensibilité spécifique pour les cations bivalents.

Kurzreferat—Natürliche Tonfraktionen mit Korngrössen von 5 μ bis zu 0,05 μ aus Mexiko und Wyoming, die als kationische Heterogenoder Mehrbestandteilsysteme auftreten, wurden unter den spezifischen Gleichgewichtsbedingungen von in vielen Bohrflüssigkeiten und Formationswassern festgestellten Salzkonzentrationen untersucht.

In dieser Untersuchung wurden Glaselektroden verwendet, und es wurde festgestellt, dass eine Tektit Elektrode besondere Empfindlichkeit für zweiwertige Kationen aufweist.

Резюме—Различные фракции естественной глины от Мексики и штата Вайоминг, размером от 5 до 0,05 μ, встречаемые как однородные или многокомпонентные катионные системы, исследовались в условиях равновесия концентраций солей в пределах, встречаемых во многих глинистых растворах и месторожэениях.

В настоящем исследовании пользовались стеклянным электродом. Установлено, что электроды из тектита (природного стекла) особо чувствительны на эвухвалентные катионы.

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