

CATION REPLACEMENT STUDIES ON HETEROIONIC BENTONITIC CLAY FRACTIONS USING SPECIFIC ION GLASS ELECTRODES

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Abstract—Centrifuged fractions, ranging in size from 2.0 to 0.05 μ of a Wyoming bentonite, Bentonita de Durango from Mexico, and Helms clay from Texas were studied. The variation in replacement of Na^+ , Ca^{2+} , Mg^{2+} , K^+ , and H^+ from these heteroionic clay systems under specific equilibrium conditions of salt concentrations was measured.

The displacement cation distribution was monitored by using specific ion glass electrodes, such as a sodium ion electrode, a cationic glass electrode, a calcium ion electrode and a Tektite electrode. Some factors affecting the exchange reactions are discussed and application of findings to drilling and production techniques is indicated.

INTRODUCTION AND STATEMENT OF PROBLEM

IN THE development of various types of mud drilling fluids the art of maintaining a mud having the desired rheological properties has changed gradually to a more exact understanding of the fundamental aspects underlying the formulation and treatment of such fluids. Basic to a clearer conception of the mechanism of the behavior observed in different mud fluids is an understanding of the role of the clay particles and the manner by which changes in the electrolyte environment bring about alterations of fluid properties.

The fact that cation exchange takes place, to a varied degree, in most clay suspensions makes this property a most significant one. Monitoring the extent to which cation exchange takes place on a heteroionic clay (of the mud) or a clay or shale contacted in the drilled hole during drilling involves not only a knowledge of the specific cations present in exchange positions on the original clay but also the development of a method for determining the relative change in amount of such individual cations which occurs under equilibrium conditions at known electrolyte concentrations.

The purpose of this investigation was to measure the variation of various individual cation concentrations under specific equilibrium conditions of salt concentrations using specific ion electrodes. Extending the scope of previous work by Fertl and Jessen (1968), five individual cations, namely H^+ , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} were monitored at various exchange conditions taking place on three bentonitic clays of largely varying initial cation populations.

EXPERIMENTAL TECHNIQUES

General

Three natural clay materials from Wyoming, Texas and Mexico were selected for this study. The clay fractions were obtained by Mungan (1962) in previous work of fractionation using a supercentrifuge.

Quantitative studies for cation distribution were carried out by means of special cation sensitive glass electrodes. The results were checked qualitatively by X-ray analysis.

Material description and location

Wyoming Bentonite; Locality: Wyoming; Color: greyish; Impurities: quartz and feldspar. Fraction sizes from 2.0 μ down to 0.05 μ were investigated.

Bentonita de Durango; Locality: Mexico; Color: white; Impurities: crystalite and feldspar. Submicron fractions from 0.4 μ down to 0.05 μ were studied.

Helms; Locality: Texas; Color: white; Impurities: opaline silica. Fractions from 2.0 μ down to 0.2 μ were investigated.

Preparation of samples

The clays were used without any chemical pretreatment. 500 mg of each clay fraction, which had been stored as dry powder, 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, eight samples of the stock suspension each of 10 ml, were removed by pipet and 0.5N CaCl_2 or 0.5N NaCl , respectively, was added in amounts of 0.01 ml, 0.05 ml, 0.10 ml, 0.5 ml, 1.0 ml, 2.0 ml, and

5.0 ml. The total volume was brought to 15 ml by adding demineralized water, then placed into covered polyethylene bottles and shaken for at least 24 hr. Then the clay was separated by filtration and the clear solution investigated.

Electrodes

Ion activity was measured by determining the voltage between a known solution inside the electrode body and the test sample. For both mono- and divalent electrodes, calibration curves were established. Using a semi-logarithmic grid, known normalities of the ion to be determined were plotted against potential in mV obtained from an electrometer output. After each measurement the electrodes were rinsed and dried before immersing them into a different sample. Since response to H^+ may interfere with the specific ions being measured, the operable range in pH was checked. Furthermore, the electrodes were checked against the calibration curves intermittently during the experiments and when necessary the base line reset with one of the calibrating solutions.

(a) *Glass Electrodes*, such as the *Cationic Glass Electrode* and the *Sodium Ion Glass Electrode*, were used. The following table is valid as an approximation only since detection limits are influenced by interfering ions:

	Sodium electrode	Cationic electrode
Sensitivity	Ag, H, Na, K	H, Ag, K, NH_4 , Li
Detection limit	$1.0-5 \times 10^{-7} N$	$1.0-5 \times 10^{-7} N$
Sample pH-range	7-10 (for Na) 4-8 (for Ag)	7.0-13 (for Na), K 4-10 (for Ag)
Temperature range	0-80°C	0-80°C

The sodium electrode is about 1000 times more sensitive to Na^+ than to K^+ , whereas the cationic electrode responds to K^+ and Na^+ both. Therefore, any possible effect of K^+ -contribution may be evaluated by using both sodium sensitive and cationic sensitive electrodes. The difference in response corresponds to the contribution of K^+ present.

(b) *The Tektite electrode*

A number of these electrodes were constructed and the ones yielding the best response, i.e. stable, reproducible potentials, were used in the experiments. Different electrodes gave different response, generally functioning better when soaked for a period of a few hours in a solution of the ion of interest. Electrode function behavior apparently

decreases with drying, a behavior which seems to be reversible.

Garrels *et al.* (1965) report a pronounced selectivity for the Tektite material to divalent ions such as Ba^{2+} , Sr^{2+} , Ca^{2+} , and Mg^{2+} . Fertl and Jessen (1968) showed the electrode to be selective to the divalent Ca^{2+} and Mg^{2+} ions, and if it is calibrated in solutions similar to the unknown, the effects of other cations or of moderate variations in pH may be neglected.

(c) *The calcium-sensitive electrode*

The Calcium Activity Electrode, Model 92-20, from Orion Research, Inc. (1966) develops a potential across a thin layer of liquid exchanger which is held mechanically rigid by a thin porous inert membrane disc. The liquid ion exchanger is a calcium salt of an organophosphoric acid exhibiting a high specificity for calcium ions. This electrode, unlike other glass electrodes, does not need to be soaked in solution during storage and responds rapidly.

The selectivity is approximately 50 times higher to Ca^{2+} than Mg^{2+} and yet also exhibits a Nernst response to 10^{-3} moles/l. Ca^{2+} in the presence of 1.0 mole/l. Na^+ or K^+ . Furthermore, the electrode gives correct readings over a pH-range of 3.3-11.0 and is not affected by the amount of calcium which is bound by complexing agents such as polyphosphates.

(d) *Reference electrode*

A Beckman Calomel Reference Electrode with a small porous fiber or filter sealed into the immersion tip was used. This electrode is recommended for continuous use from -5 to 80°C.

Electrometer amplifier

A wide-band d.c.-amplifier, Model 603 from Keithley Instruments, Inc., (Catalog 1966-67) with nine voltage ranges from 2.5 to 1000 mV full scale was used. This amplifier has an extremely high input impedance and high voltage and current sensitivity.

X-ray diffraction

The X-ray diffraction patterns were run on a General Electric XRD-3-X-ray diffraction unit with a spectrogoniometer and proportional counter, using Ni-filtered copper $K\alpha$ radiation and operated at 35 KVP and 16 mA.

The suspensions were settled onto standard non-corrosive 1×3 in. microscope slides by use of a dropper. Equal number of drops of suspensions were measured in each case to deposit equal amounts of clay solids on each slide. All X-ray work was done at 50 per cent relative humidity.

RESULTS OF PRESENT INVESTIGATION

(1) X-ray analysis

The 001-peak distinguishes monoionic preparations by relative sharpness and position at a given Bragg angle, and indicates interstratification of mono- and divalent stacking units by its broadness and range of the Bragg angle position 2θ . As the exchangeable cation is changed on a bentonite, the rheological properties change. Investigations have shown Ca^{2+} concentrations at a level of 30–40 per cent of the total exchange capacity as being sufficient to result in behavior as a calcium clay (Mering, 1946).

If there is a mixture of mono- and divalent ions present, the shape and location of the 001-peak can be used to deduce the ratio of mono- to divalent cations. In addition, correlation between the basal distance, type of exchangeable cations and the colloidal properties of bentonites is possible (Williams *et al.*, 1953).

The d -spacings investigated on natural Wyoming bentonite fractions showed broad peaks and varied only slightly in the Bragg angle position, which might be expected because of the very slight increase of monovalent cations present in the smaller size fractions. X-ray diffraction patterns on Bentonita de Durango also indicated layer interstratification, with impurities concentrated in the coarser fractions, whereas X-ray data on Helms clay showed a predominantly calcium clay (Fig. 1).

Clay fractions of various sizes in the range from $40\ \mu$ down to $0.05\ \mu$ were investigated. The coarser fractions, containing such impurities as quartz and feldspar, were discarded before making the exchange cation studies. Despite the fact that sub-micron fractions of Wyoming bentonite were studied, quartz was found in as small a fraction as $0.1\text{--}0.05\ \mu$. Feldspar was found to be present in fractions F, H, and K, in decreasing amount with decreasing fraction size. Fraction M, the finest, apparently was free of feldspar. In addition, some X-ray patterns indicated diffraction effects other than normal integral sequences characteristic of the basal spacing. As example, the peaks at $d = 4.475\ \text{\AA}$, indicate at least some random orientation which results when clay flakes settle on the glass slide in a position other than flat.

(2) Glass electrode measurements

Grim (1953) states that the exchange reaction for kaolinite is almost instantaneous, for montmorillonite somewhat slower while in the case of illites several hours are required to complete the reaction. Thus, for montmorillonite minutes or perhaps a few hours are required for completion of the exchange reaction. Such a time requirement

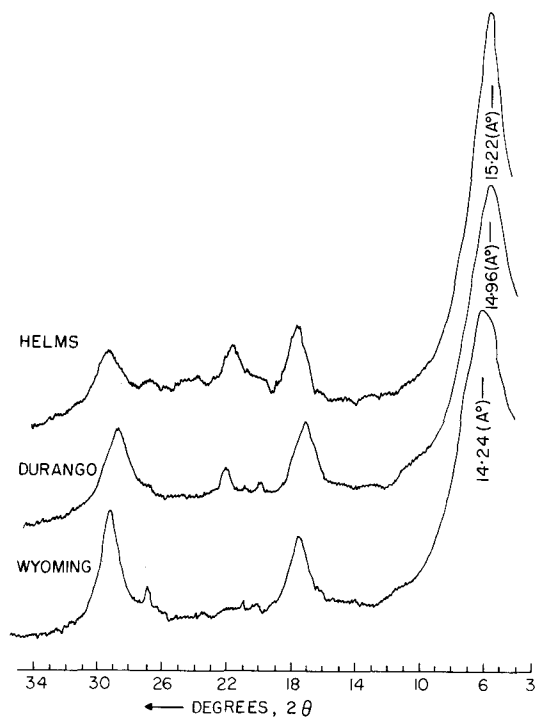


Fig. 1. X-ray diffraction patterns for a Wyoming bentonite, fraction M ($0.1\text{--}0.05\ \mu$), Bentonita de Durango, fraction M ($<0.05\ \mu$) and Helms clay, fraction K ($0.2\text{--}1.0\ \mu$).

was fulfilled in the present experiments, where exchange equilibria measurements were taken at least 24 hr after adding the titration fluid.

The graphical representations in Figs. 2–5 show the results of replacement of Ca^{2+} and Mg^{2+} by sodium chloride and Na^+ and K^+ replaced through cations of the corresponding concentrations of calcium chloride for the original clays. Tables 1, 2, and 3 list replacement cation distributions for all three clays at the highest treatment level, while Tables 1(a), 2(a), and 3(a) show the original cation population determined by Mungan (1962).

DISCUSSION OF RESULTS

The electrode measurements on heteroionic Wyoming bentonite indicate a slight increase in the amount of exchangeable Na^+ and Mg^{2+} with decreasing particle size, whereas the reverse trend is observed for the Ca^{2+} (Table 1). Furthermore, taking impurities into account, the total amount of exchange appears not to be affected by particle size. The results of cation exchange versus electrolyte concentration when plotted on a semilogarithmic grid show a S-shaped equilibrium trend (Fig. 2). Both Ca^{2+} and Mg^{2+} replacement patterns look alike, with Mg^{2+} indicating an increased rate of removal relative to Ca^{2+} at all

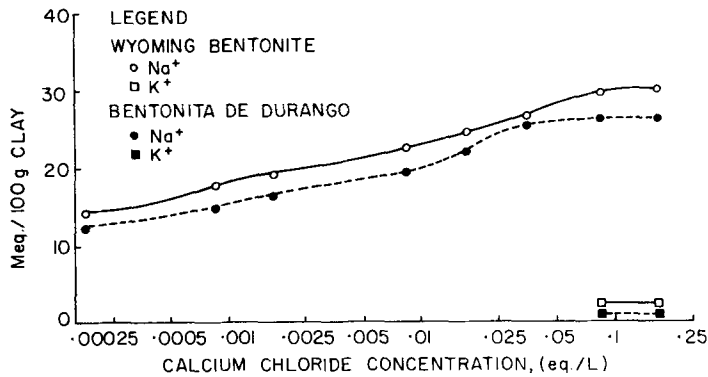


Fig. 2. Displacement cation distribution on Wyoming bentonite, fraction M (0.1–0.05 μ) and on Bentonita de Durango, fraction (< 0.05 μ).

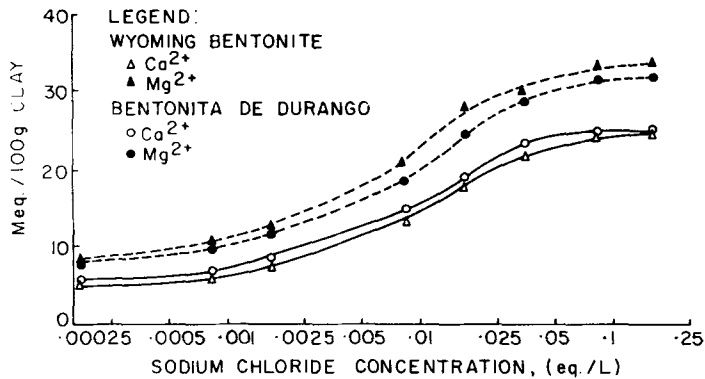


Fig. 3. Displacement cation distribution on Wyoming bentonite, fraction M (0.1–0.5 μ), and on Bentonita de Durango, fraction M (< 0.05 μ).

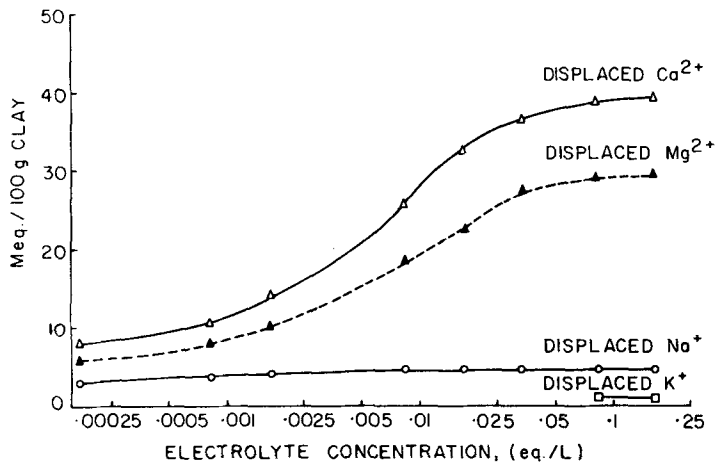


Fig. 4. Displacement cation distribution on Helms clay, fraction H (0.3–0.2 μ).

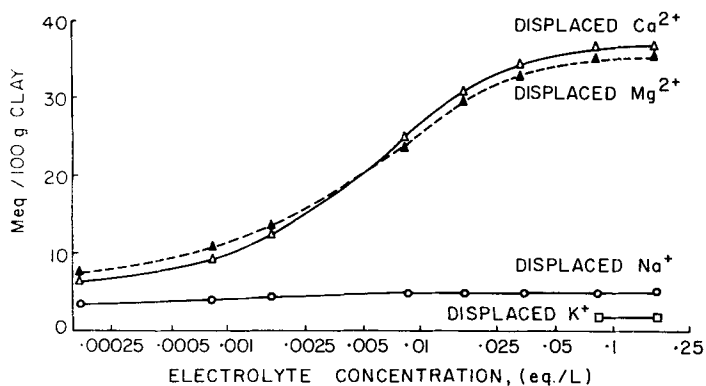


Fig. 5. Displacement cation distribution on Helms clay, fraction K (0.2-0.1 μ).

Table 1. Replacement cation distribution on Wyoming bentonite treated with 0.5 N sodium chloride or 0.5 N calcium chloride solutions

Fraction	Size (μ)	pH	Meq/100 g clay				Total
			Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	
F	0.4-0.3	6.8-7.2	25	3	27	24	79
H	0.3-0.2	7.0-7.1	26	2	25	35	88
K	0.2-0.1	6.8-7.3	28	2	26	34	90
M	0.1-0.05	6.7-7.3	30	2	25	34	91

Table 1(a)*. Exchange capacity, flame photometer

Fraction	Size (μ)	pH	Meq/100 g clay					Total exchange (Kjehldahl)
			Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Total	
As rec'd	—	7.0	78	1	19	12	109	82
F	0.4-0.3	7.0-7.2	45	1	24	12	82	
H	0.3-0.2	7.0-7.2	49	1	22	15	87	
K	0.2-0.1	7.0-7.2	49	2	20	20	91	
M	0.1-0.05	7.0-7.2	60	2	15	21	98	100

*From Mungan and Jessen (1962).

Table 2. Replacement cation distribution on Bentonita De Durango treated with 0.5 N sodium chloride or 0.5 N calcium chloride solutions

Fraction	Size (μ)	pH	Meq/100 g clay				Total
			Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	
G	0.4-0.3	7.0-7.1	24	1	24	23	72
L	0.15-0.05	7.1-7.2	24	1	25	26	76
M	-0.05	7.1	26	1	26	30	83

Table 2(a)*. Exchange capacity, flame photometer

Fraction	Size (μ)	pH	Meq/100 g Clay				Total	Total exchange (Kjehldahl)
			Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺		
As rec'd	—	7.0-7.2	42	0	17	12	70	70
G	0.4-0.3	7.0-7.1	27	1	21	30	79	
L	0.15-0.05	7.0-7.1	29	1	27	39	95	
M	-0.05	7.0-7.1	28	1	32	44	106	75

*Mungan, N. (January, 1962) Gel Strength Studies in Fractionated Clay Suspensions, Dissertation, The University of Texas.

Table 3. Replacement cation distribution on Helms clay treated with 0.5 N sodium chloride or 0.5 N calcium chloride solutions

Fraction	Size (μ)	pH	Meq/100 g clay				Total
			Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	
F	0.4-0.3	7.1-7.2	5.0	1	40	26	72
H	0.3-0.2	7.0	5.0	1	39	29	74
K	0.2-0.1	7.1	5.0	1	36	35	77

Table 3(a)*. Exchange capacity, flame photometer

Fraction	Size (μ)	pH	Meq/100 g clay				Total	Total exchange (Kjehldahl)
			Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺		
As rec'd	—	7.0-7.1	8	0	45	19	72	75
F	0.4-0.3	7.0-7.1	6	0	45	32	83	
H	0.3-0.2	7.0-7.1	5	0	44	34	83	
K	0.2-0.1	7.0-7.1	6	1	47	33	86	

*From Mungan and Jessen (1962).

higher electrolyte concentrations. The main displacement of the Na⁺, Ca²⁺, and Mg²⁺ takes place in the range of higher treatment levels.

Bentonite de Durango is a bentonitic clay with almost equal amounts of Na⁺, Ca²⁺ and Mg²⁺ in exchange positions (Table 2). At low electrolyte concentrations Na⁺ shows the largest amount of replacement followed by Mg²⁺, whereas Ca²⁺ is the most difficult to replace from the clay surfaces (Fig. 3).

Helms clay is a predominately Ca-Mg-clay with the amount of exchangeable Mg²⁺ increasing with decreasing particle size (Figs. 4 and 5). In all fractions investigated Ca²⁺ was replaced more easily than Mg²⁺. The same relative rate of removal was noted for both Ca²⁺ and Mg²⁺ up to 0.025 N sodium chloride. At higher electrolyte concen-

trations Ca²⁺ is replaced faster than Mg²⁺, except as shown in Fig. 5, where for the finest fraction, K, an almost equal population of Ca²⁺ and Mg²⁺ was observed. The marked increase in replacement of Ca²⁺ on the Helms clay is explained by the fact that all fractions of the Helms clay showed a higher Ca²⁺ population. The low Na⁺ contribution is fairly constant for all clay fractions investigated (Table 3). Replacement of the small Na⁺ population appears to be completed at low electrolyte concentrations, since no marked change in the amount of replacement with higher electrolyte concentrations was observed.

Numerous tests using the different clay fractions with the specific electrodes employed showed excellent reproducibility of results.

Various investigators (Jessen and Mungan,

1962; McAtee, 1958) report a concentration of Ca^{2+} in the coarser fractions of natural heteroionic montmorillonite. The monitored cation distribution obtained from glass electrode measurements confirms these previously reported values. It may be assumed that the greater concentration of Ca^{2+} in coarser clay fractions does not depend on an ionic preference with size but rather on the tendency of polyvalent cations to coagulate more effectively, i.e. to form clumps of clay flakes in a suspension.

Investigations by Weiss (1958), show cation-exchange at near neutral pH values to be associated exclusively with the planar surfaces. Jackson (1967) considers a 5 per cent contribution by broken edges to the total exchange capacity to be about the maximum to be expected from such sources.

The pH-data of the present study revealed a similar proportion in all suspensions investigated, namely almost exclusively planar surface contribution to exchange reactions. In the pH range prevailing in the samples studied, namely from 6.7 to 7.3, not more than 5 per cent variation in the total amount of exchange cases would be introduced.

The general effect of increased concentration of a replacing cation will result in a greater exchange action by that cation. In heteroionic systems at equal electrolyte concentrations and near initial cation composition the Ca^{2+} displaces a larger fraction of Na^+ than Na^+ will replace Ca^{2+} . Mg^{2+} is bound stronger than Na^+ but shows a somewhat larger reproducibility than Ca^{2+} , a behavior apparently related to the small ionic radius of 0.78 \AA for Ca^{2+} (Pauling, 1948).

Measurable K^+ replacement took place only at the highest treatment level 0.167 N calcium chloride. The low K^+ population was found to be in agreement with Mungan's (1962) determinations by flamephotometer measurements.

The steep slope of the equilibrium curves is directly related to an increase in the basal spacing and to a rapid decrease in the electrophoretic mobility since pure Na-Wyoming bentonite has approximately twice as large electrophoretic mobility as pure Ca-Wyoming bentonite. These mobilities reflect the lessened tendency of calcium to ionize and in turn explain the larger sensitivity of Na-Wyoming bentonite to environmental changes.

The practical aspect of such behavior is found in "dirty" reservoir sands, since fluids containing mainly Ca^{2+} moving through a formation containing a bentonitic clay having Na^+ in the exchangeable position would exchange the monovalent by the divalent cation. It has been shown that a fluid

having an excess of 3500 ppm Ca^{2+} will provide maximum inhibition of bentonitic clay swelling (Monaghan, 1958).

Investigations by von Engelhard and Tunn (1954) showed that montmorillonite could hold a greater amount of bound or fixed water as the salt concentration is decreased. In other words, the less saline the water, the greater the decrease of permeability due to swelling. Therefore, it is poor practice to inject sodium chloride solutions into a well into which fresh water may later be introduced.

The least reduction in permeability can be expected when formation brines most closely approximate the interstitial water composition or as long as the electrolyte composition of the clay and the water are compatible.

CONCLUSIONS

1. Through the use of specific glass electrodes sensitive to individual cations, the change in such cations upon replacement with either Na^+ or Ca^{2+} was determined. Results of replacement cation distribution are reproducible.

2. Coarser fraction sizes of Wyoming bentonite were found to have a larger Ca^{2+} population, whereas the Na^+ concentration increases with decreasing particle size.

3. Bentonita de Durango of Mexico has almost equal amounts of Na^+ , Ca^{2+} and Mg^{2+} in the exchange positions whereas Helms clay of Texas is a predominantly $\text{Ca}^{2+} - \text{Mg}^{2+}$ in which the amount of exchangeable Mg^{2+} increases with decreasing particle size.

4. Wyoming bentonite indicates an increased rate of Mg^{2+} removal relative to Ca^{2+} at all higher electrolyte concentrations, whereas for Bentonita de Durango both Ca^{2+} and Mg^{2+} exchange patterns indicate a similar rate of exchange.

5. Helms clay showed Ca^{2+} replacement predominant to Mg^{2+} , the only exception being the finest fraction wherein an almost equal population of Ca^{2+} and Mg^{2+} exists, and where an almost identical rate of exchange occurs.

6. For all three clays investigated a small K^+ contribution was observed at only the highest electrolyte concentrations.

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Résumé— On a étudié des fractions centrifugées, à dimensions allant de 2,0 à 0,05 μ , d'un bentonite du Wyoming, d'un bentonite de Durango en provenance du Mexique et d'une argile Helms du Texas. On a mesuré la variation du remplacement du Na^+ , Ca^{2+} , Mg^{2+} , K^+ at H^+ à partir de ces système d'argile hétéroioniques dans des conditions d'équilibre spécifiques des concentrations du sel.

On a contrôlé la distribution des cations de déplacement en utilisant des électrodes en verre à ion spécifique, p.e. une électrode à ion de sodium, une électrode de verre cationique, une électrode à ion de calcium et une électrode Tektite. On discute certains facteurs relatifs aux réactions d'échange et on indique l'applicabilité des résultats aux techniques de forage et de production.

Kurzreferat— Es wurden zentrifugierte Fraktionen mit einem Grössenbereich von 2,0 bis 0,05 μ eines Wyoming Bentonits, Bentonite de Durango aus Mexiko, sowie von Helms Ton aus Texas untersucht. Die Variationen beim Austausch von Na^+ , Ca^{2+} , Mg^{2+} , K^+ , und H^+ aus diesen hetero-ionischen Tonsystemen wurde unter spezifischen Gleichgewichtsbedingungen der Salzkonzentrationen gemessen.

Die Verdrängungskationenverteilung wurde unter Verwendung spezifischer Ionenglaselktroden, wie z.B. einer Natriumionenelktrode, einer kationischen Glaselektrode, einer Kalziumionenelektrode und einer Tektitelektrode überprüft. Einige der die Austauschreaktionen beeinflussenden Faktoren werden gemeinsam mit der Anwendung der Ergebnisse auf Bohr- und Fördermethoden erörtert.

Резюме— Изучены фракции от 2,0 до 0,06 мк вайомингского бентонита, «бентонита де-Дуранго» (Мексика) и глины из Хелмса (Техас). Установлены вариации замещений Na^+ , Ca^{2+} , Mg^{2+} , K^+ и H^+ в этих гетероионных глинистых системах при определенных равновесных концентрациях солей. Изменение распределения катионов контролировалось с помощью специальных ионных стеклянных электродов, а именно натриевым ионным электродом, катионным стеклянным электродом, кальциевым ионным электродом и электродом Тектайт. Рассматриваются некоторые факторы, оказывающие воздействие на реакции обмена; отмечено значение результатов для техники бурения и технологии.