

Volumes 1 and 2

12TH PANAMERICAN CONFERENCE ON SOIL
MECHANICS AND GEOTECHNICAL ENGINEERING

12AVA CONFERENCIA PANAMERICANA DE MECANICA
DE SUELOS E INGENIERIA GEOTECNICA

39TH U.S. ROCK MECHANICS SYMPOSIUM

Soil
AMERICA
Rock
2003

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EDITORS

Effect of Organic Salts in the Physico-Chemical Properties of Shales Efecto de las Sales Orgánicas en las Propiedades Físico-Químicas de las Lutitas

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Abstract

This paper presents a study of the changes in physico-chemical properties of preserved shale samples when immersed in organic salt solutions. The changes in the immersion fluid are also discussed. An offshore Brazilian shale was used throughout the study. The laboratory tests were conducted with three kinds of formate brines. The obtained results indicated that the samples suffered reductions in water content and increased the pH of rock. Changes were observed in the chemical composition of rock pore fluid and in the cation exchange capacity as a function of the preponderant ions in the organic salt solution. This immersion test shows great potential in understanding the interaction between drilling fluids and shales.

Resumen

El presente trabajo tiene el objetivo de estudiar los cambios en las propiedades físico-químicas de muestras preservadas de las lutitas cuando sumergidas en las soluciones de las sales orgánicas. Una muestra de lutita brasileña de origen offshore se usó para el estudio. Los ensayos de laboratorio se realizaron con tres tipos de soluciones de formiato. Los resultados indican que las muestras sufrieron reducciones del tenor de humedad y aumento de pH de la roca. Se observa cambios en la composición química de el fluido del poro y en la capacidad de intercambio de los cationes como una función de los iones preponderantes en la solución de la sal orgánica. Los resultados muestran la importancia de entender el comportamiento físico-químico de las lutitas en presencia de los fluidos de perforación a base de agua.

1 INTRODUCTION

During the drilling of oil wells, the fluid interacts with the shale layers in the walls of the well, with the cuttings and at the contact drill bit-rock. The physical-chemical interaction between shale and drilling fluid is still not fully understood but many drilling problems are credited to this interaction.

It is assumed in this paper that physico-chemical rock-fluid interactions are consequence of both water and ionic species flow from and into the rock. The main mechanisms of transport in shales considered herein are osmosis, reverse

osmosis, diffusion of ions and hydraulic pressure. This water and ion transport may cause chemical changes in both shale and pore fluid. Chenevert (1969) reports hydration and dehydration of shales exposed to saline solutions and Santarelli and Carminati (1995) discuss shale swelling. Herein, evidences of changes in shale cation exchange capacity are given. Also, ion and fluid transport change pore fluid properties such as suggested by van Oort (1994).

To avoid or to reduce this interaction, new fluids have been developed, forced, mainly by environmental legislations that demand that the drilling fluids be biodegradable. One of the new

types of fluids developed for this purpose are formate brines.

Formate brines were first designed to minimize frictional pressure losses in slim hole drilling because of their temperature stabilizing effect on polymers and their high density (Downs, 1993). According to Howard (1995) these fluids have additional advantages, such as low corrosion potential (good for drilling and completion fluids), are easily recyclable, inhibit gas hydration and bacterial growth, are compatible with salt containing formations and show good potential for shale stabilization. These fluids enhance stability of shales through a combination of reduced hydraulic flow by filtrate viscosity enhancement and stimulation of osmotic backflow of pore water.

2. IMMERSION TESTS

Immersion tests can be used to study the shale-fluid interaction or shale reactivity. A laboratory apparatus was developed in which shale sample is put in contact with fluid, and special sensors measure the electro-chemical properties of the fluid throughout the test. The first version of the equipment, developed at Pontifical Catholic University of Rio de Janeiro (Rabe *et al.*, 2001), allows tests with fluids at atmospheric pressure and at down hole temperature condition. The immersion equipment is presented in Figure 1.

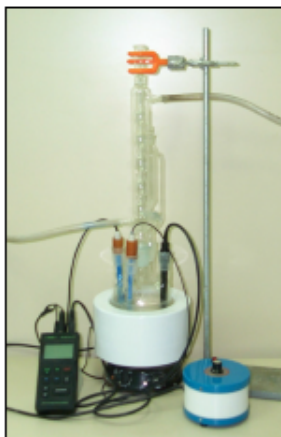


Figure 1 Equipment for immersion tests

The equipment is constituted by one round balloon with five entrance ports: four laterals and one central. The central port is used to place the shale pieces inside the balloon and to house the cooling column. Three lateral ports are used to

house electro-chemical probes and one port is used to collect fluids samples during the tests. The cooling column avoids water losses due to vaporization. A heating blanket, surround the balloon is used to keep the temperature constant during the test.

The electro-chemical instrumentation consists of a conductivity meter, a pH meter and Eh meter. Beside this, the probes monitor the solution temperature. The tests were carried out at 50°C, simulating the shale *in situ* temperature.

3. SHALES AND SOLUTIONS PROPERTIES

The shale tested herein was obtained from wells drilled in Brazilian offshore area. This shale was formed in Tertiary - Cretaceous period (Anjos, 1986) and the core was extracted at 3532m.

Table 1 presents some general characteristics of the tested samples. The specific gravity of grains was determined using a picnometer and the clay fraction was evaluated by sedimentation. The analysis of clay minerals was determined by X-Ray diffraction.

Table 1 General characteristics of the tested shale

Shale properties	Result
Clay fraction	50%
Specific gravity of grains	2.69
Main clay mineralogy	Kaolinite (33.6%) and illite/smectite (22%)

The results indicate a medium clay fraction with low content of expansible clay minerals. Table 2 presents the physical properties of shale sample.

The water content was obtained by oven drying the samples at 105°C for a period of 24 hours. The degree of saturation, void ratio and porosity values were obtained with the use of classical soil mechanics expressions (Lambe and Whitman, 1979).

Table 2 Physical properties of shale samples.

Shale properties	Result
Water content (%)	26.4
Degree of saturation (%)	100
Void ratio	0.67
Porosity (%)	40.2

The shale presents high water content, high degree of saturation, high porosity and low void ratio.

The aqueous solutions used during the tests were prepared with formate brines at different concentrations. Table 3 presents the name,

composition (comp.), water activity (a_w) and concentration (conc.) of aqueous solutions used in tests. Besides these solutions, de-ionized water was used to compare with formate brines.

Table 3 Characteristics of formate brines

Name	Comp.	a_w	Conc. (%)
Sodium formate	NaCOOH	0.935	20%
Potassium formate	KCOOH	0.897	20%
Cesium formate	CsCOOH	0.861	30%
Deionized Water	H ₂ O	1.000	Pure

4. IMMERSION TESTING PROCEDURES

In each test, 3 rock fragments were used, with an approximate weight of 70 g. Before the tests, the samples were handled inside a high humidity room, where the coring was done with the rock immersed in mineral oil and kept immersed until the beginning of the test. This procedure guarantees that the sample is not exposed to air for a long time. Small pieces from cores were used to obtain the original shale water content.

Initially, the fluids are inserted into the balloon and heated to 50°C, and the probes start to monitor the fluid electro-chemical properties. After this, the shale pieces are put into the balloon and the test begins. In the present work, was established the value of 10% (w/w) in the relationship shale sample/fluid.

At the end of test, effluents are collected and sent to chemical analyses to quantify cations and anions present in the solutions. By limitation of space, just the total concentration of ions is presented.

5. ELECTRO-CHEMICAL CHANGES IN IMMERSION FLUIDS

Table 4 presents the initial values of pH, Eh and electric conductivity (EC) of solutions.

Table 4 Electro-chemical characteristics of formate brines at 50°C

Solution	pH	Eh (Volts)	EC (mS/cm)
20% NaCOOH	8.25	-0.369	209
20% KCOOH	8.75	-0.295	347
30% CsCOOH	9.80	-0.245	366
H ₂ O	6.94	0.211	0.005

The results presented in Table 4 indicate that the formate solutions are alkaline and oxidants and have high electric conductivity. The de-

ionized water is acid and reductant and non conductive.

Figures 2, 3 and 4 present, respectively, the results of pH, Eh, and the variation in electric conductivity of the immersion fluid as a function of time.

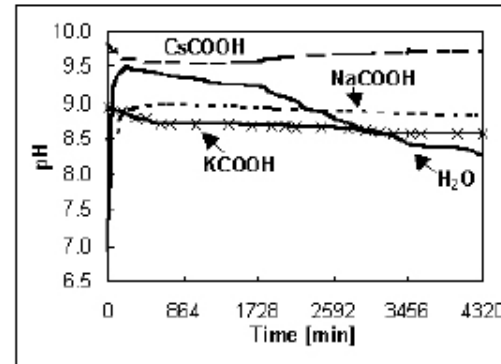


Figure 2 PH during the immersion tests

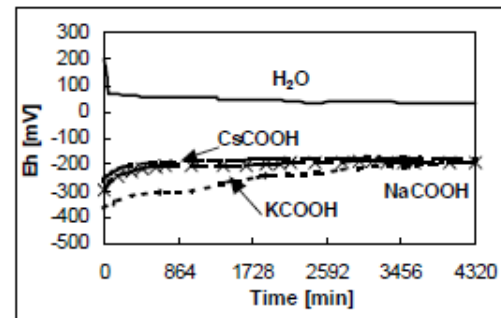


Figure 3 Eh during the immersion tests

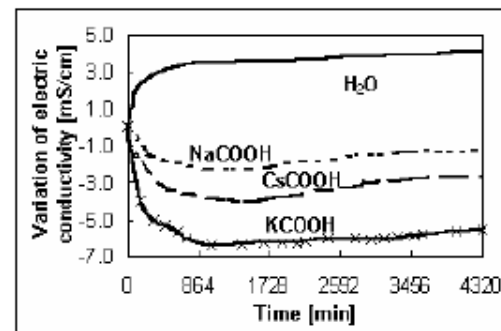


Figure 4 Variation in electric conductivity during the immersion tests

During the immersion tests, the variation in pH e Eh of de-ionized water was intense. These positive variations can be explained by the low pH

of water, which contributes to the solubilization of certain elements, like calcium carbonate (that represent 19,2% of composition of rock) and calcium sulfate. The variations were more intense during the first day of immersion. After the first day, the pH decreased with the increase of concentration of neutral salts in solutions.

PH plays a very important role in the behavior of clay suspensions. At low pH, the clay minerals in liquid solutions can often lead to a flocculation. Stable suspensions or dispersions of clay particles often require high pH.

The pH and Eh of formate solutions almost did not change during the immersion tests, indicating a buffer behavior of solutions.

The positive variation of electric conductivity showed a migration of ions from the rock to water by ionic diffusion. The opposite happened with formate solutions, in which the ions migrated from fluids to the rock, indicated by negative variation. The results also show that the reactions were more intense during the first day of immersion, like pH and Eh.

Table 5 presents the results of chemical analysis of fluids. These results indicate a reduction of total concentration of ions in organic salts and an increase of ions in de-ionized water that are consistent with the changes in electric conductivity.

Table 5 Variation of concentration of immersion solutions (% in mg/l)

Solution	Original value (%)	Variation after immersion tests (%)
H ₂ O	0	+0.034
NaCOOH	20	-0.0108
KCOOH	20	-0.0134
CsCOOH	30	-0.0440

The results indicated that the more intense diffusion of caesium could be explained by the high of concentration of solution. The opposite happened with the water, in which the concentration of ions in water increased, by the high concentration of ions in the shale sample.

6. PHYSICO-CHEMICAL PROPERTIES OF SHALE SAMPLES AFTER IMMERSION TESTS

At the end of the immersions tests, the equipment was dismantled and the samples were used to carry out physico-chemical tests.

6.1 Shale water content

The water content of shale samples was obtained by oven drying at 105°C for 24 hours as recommended by the International Society of Rock Mechanics.

The results of water content are presented in Table 6. These results show that the shales in contact with the water suffer a significant hydration (almost 23%). When in contact with the organic salts, the samples showed an intense dehydration that reached 20% in the caesium formate. The high salt concentration used in the immersion fluids is responsible for such a high dehydration effect.

Table 6 Water content of shale samples

Solution	Original value (%)	3 days (%)	Variation (%)
H ₂ O	25.86	31.71	+22.62
NaCOOH	26.67	24.93	-6.52
KCOOH	25.44	23.03	-9.46
CsCOOH	25.04	20.00	-20.13

6.2 Pore fluid composition

The composition of shale interstitial fluid is an important element during the analysis of mass transfer mechanisms between the drilling fluid and shale. The fluid extraction technique developed by Schmidt (1973) was followed during the experiments, where the sample was dried and the salts removed by washing.

The results of the concentration of ions dissolved in the pore fluid are indicated in Table 7. The original shale pore fluid is constituted basically by chlorites and sulfates of sodium, magnesium, calcium and potassium. This is similar to the seawater composition, which confirms the submarine origin of the shale.

The immersion tests indicated an intensive diffusion of ions from the saline fluid to the shale pore fluid. When immersed in water, the ions suffered an ionic diffusion from the shale pore fluid to the water. The content of caesium was not determined, due to limitation of the atomic absorption equipment.

Table 7 Ions dissolved in the pore fluid (mg/l)

Sol.	Na ⁺	K ⁺	Ca ⁺²	Mg ⁺²	Cl ⁻	SO ₄ ⁻²
Nat	23,496	367	325	234	26,734	14,137
H ₂ O	23,379	356	324	235	26,576	14,122
Na(*)	23,919	306	264	226	26,342	13,977
K(*)	23,720	611	276	229	26,486	13,943
Cs(*)	23,358	323	322	227	26,428	13,943

Note: Nat = Natural, (*) = COOH and SW = Sea water

6.3 Cation exchange capacity (CEC)

Table 8 presents the results of cation exchange capacity of shale before and after the immersion tests. The ammonium acetate method was used to obtain the CEC properties of the samples. This testing methodology allows the evaluation of the individual cations that are being interchanged and has been described by Brower et al. (1952). Each test was carried out using 4g from the coarse fraction of the shales.

In this method, the original cations are displaced by the ion Na^+ during the treatment with a solution 1N of sodium acetate at a pH of 7.0, to determinate potassium, calcium and magnesium in solution. Next, the Na^+ ion is displaced by the ion NH_4^+ through the treatment with a solution 1N of ammonium acetate, to determinate the tenor of sodium. The CEC is the sum of all of the interchanged cations and the individual cation concentration was obtained analytically through atomic absorption. The results indicated that the studied shale has a medium CEC value, and the main interchangeable cation is Na^+ .

Table 8 Cation exchange capacity (CEC) and interchangeable cations (meq/100g)

Sol.	CEC	Na^+	K^+	Ca^{2+}	Mg^{2+}
Nat	38.2	22.4	3.6	10.4	1.8
H_2O	37.9	22.3	3.6	10.3	1.7
Na^*	34.1	24.3	2.9	8.3	0.6
K^*	33.5	18.7	5.1	6.7	2.0
Cs^*	36.0	21.1	3.1	10.4	1.4

Note: Nat = Natural, (*) = COOH

The immersion in water almost did not affect the CEC of shale. Reductions in total CEC were observed for the samples immersed in the formate solutions. Largest change occurred with the potassium formate solution. The results also show that ions of one type were adsorbed and replaced by ions of another type. In NaCOOH, the Na^+ of solution was adsorbed by clay minerals and replaced by K^+ , Ca^{2+} and Mg^{2+} . The same behavior happened with the solution of KCOOH, where, the K^{2+} of solution was adsorbed by clay minerals and replaced by Na^+ , Ca^{2+} and Mg^{2+} that suffered a reduction of its values.

The ease of replacement depends mainly on the valence, relative abundance of the different ion types, and ion size. The caesium of CsCOOH solution almost was not adsorbed by the clay minerals due to its low replacing power.

6.4 pH of rock

The rock pH was obtained both before (natural) and after the immersion tests. The tests were conducted with 10 grams of pulverized samples and 25ml of water with neutral pH (1:2.5 ratio of rock to water). Table 9 presents the results.

Table 9 Values of pH of shale samples

Solution	pH of rock
Before immersion	7.11
H_2O	5.12
20% NaCOOH	7.54
20% KCOOH	7.67
30% CsCOOH	7.72

The shale sample immersed in water presented a large reduction in pH due mainly by the loss of salts present in the shale pore fluid, leading to an acidification of rock. On the other hand, the shale samples immersed into formate solutions showed an increase in pH in response to both dehydration and cation movement from the shale pore fluid to the immersion fluid.

7 CONCLUSIONS

The results show that immersion of shale samples in salt solutions reduce, when compared with de-ionized water, the changes in chemical and electrochemical properties of solutions, like the ionic composition, pH, Eh, electric conductivity.

When immersed, the formates reduce the rock water content, the changes in the rock pH, interstitial water, in the cation exchange capacity, in the changes in chemical composition of interstitial water.

These reductions in the physico-chemical properties of shale samples indicate that the formate brines avoid or reduce the potential of instability of well, being a good inhibitor of interaction shale-fluid.

ACKNOWLEDGMENTS

The authors wish to thank ANP and CNPq for the scholarship support. Special thanks go to Petrobras, for proving the cores and Cabot Corporation, for proving the organic salts.

REFERENCES

- Anjos, S. M. C., (1986). "Absence of clay diagenesis in cretaceous-tertiary marine shales, Campos Basin, Brazil", Clay and Clay minerals, v. 34, 424-434.

- Brower, C. N., Reitmeir, R. F., Fireman, M., (1952). "Exchangeable cation analysis of saline and alkaline soil", *Soil Science*, s.1, 251-261.
- Chenevert, M. E., (1969). "Shale hydration mechanics", Society of Petroleum Engineers, SPE Paper 2401, 284-296.
- Downs, J. D., (1993). "Formate brines: novel drilling and completion fluids for demanding environments", Society of petroleum Engineers, SPE paper 25177, 267-279.
- Howard, S. K., (1995). "Formate brines for drilling and completion: state of the art", Society of petroleum Engineers, SPE paper 30498, 483-498.
- Lambe, T. W., Whitman, R. V., (1979). "Soil Mechanics", New York, John Wiley and Sons.
- Rabe, C., Fontoura, S. A. B., Antunes, F. S., (2001). "Experimental study of interaction shale-fluid through immersion tests", *Thermal Engineering, Special Edition*, 2 (1), 22-28.
- Santarelli, F. J., Carminati, S., (1995). "Do shales swell? A critical review of available evidence", Society of Petroleum Engineers, SPE Paper 29421, 741-756.
- Schmidt, G. W., (1973). "Interstitial water composition and geochemistry of deep Gulf Coast Shales and Sandstones". *The American Association of Petroleum Geologists Bulletin*, Tulsa, 57 (2), 321-337.
- van Oorth, E., (1994). "A novel technique for the investigation of drilling fluid induced borehole instability in shales", Society of Petroleum Engineers, SPE Paper 29421, 29-32.