

Effect of Shale Alterations in Oil Recovery. Ionic Treatments.

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INTRODUCTION

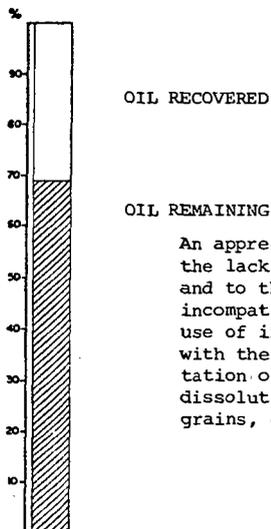
The permeability and porosity of the sedimentary rock in an oil field are responsible for the storage, detection and migration of oil and gas. Previously, it was believed that these properties were not changed even if one or more of the rock components, such as silica clays, reacted with the fluids used during oil recovery. However, we know now that this is not completely valid since the permeability can be affected by the treatment undergone by the porous medium. These problems which originate from alteration phenomena should be investigated mineralogically and chemically in order to understand the physical equilibrium between the oil field shale, the formation water, and the oil. If the chemical reactions which can occur between the liquid used in the treatment and the oil field formation are not known or considered, and if the mineralogical data on the deposit are lacking, a serious waste of time and money can result.

An oil reservoir is generally found in sedimentary rocks such as conglomerates of sand, sandstone, clays, limestone, and dolomites. We will discuss the properties of oil reservoirs of the silicate type, and, among them, the clay types and those consisting of sand mixed with swellable clays known as "sensitive formations" which are found in the surrounding area of an oil field.

I. Oil recovery and chemical-mineralogical parameters, the control of which will allow an increase in oil recovery.

The alteration of silicate rocks by the water of invasion can be avoided or minimized by taking preventive measures aimed at controlling the cause.

Extent of world oil recovery and estimated losses:<sup>1</sup>



An appreciable portion of the oil is not recovered due to the lack of chemical-mineralogical knowledge of the formation and to the damage caused by the use of operational practices incompatible with the impermeable strati of clay such as: use of inadequate fluids that undergo adverse reactions with the formation causing the dispersion of clays, precipitation of salts resulting from chemical reactions, the dissolution or hydration of the cementing materials of the grains, etc.

Table I

## Chemical-Mineralogical Parameters Affecting Oil Recovery

Type of Operation	Chemical-Mineralogical phenomena which can occur
Drilling	Alteration of the underground formation due to migration of mud towards the formation. Reduction of the permeability of the well surroundings.
Electrical Recordings	Electrochemical phenomena effects (membrane potential) and electrokinetics (mud migration) on the inflection of the "Sp" curve renders the detection of hydrocarbons difficult.
Secondary Recovery	During the injection of water, if it is incompatible with the clay or with the water of hydration of the clay, a reduction in alkalinity, and dispersion of the formation can occur; later, the production fluid will cause transport, deposition and blockage of the porous media. If micellar fluids are used, adsorption will bring about failure of the operation. On the other hand, the removed and dispersed clays lead to the production of sand which, in turn, will cause the obstruction of pipes and valves.
Stimulation of the Wells	If the fluids used in the operations of acidification and fracturing are not compatible with the chemical composition of the formation, they can cause unexpected chemical reactions, the products of which reduce the permeability by blocking the porous medium and lead to the failure of the operation.

II. Effect of hydration of the clay lattice.

The water molecule is a dipole with a positive and negative center of charge (see Figure 1). The distance between the center of gravity of the oxygen atom and that of the hydrogen atom in water is  $0.96\text{\AA}$  and the HOH angle is  $104.5^\circ$ . In the crystalline lattice of silicates the molecule of water behaves as if it had two negative charges in the corners of a tetrahedron which bond with metallic ions; on the other side they bond to oxygen atoms<sup>2</sup> (see Figures 1b and 2).

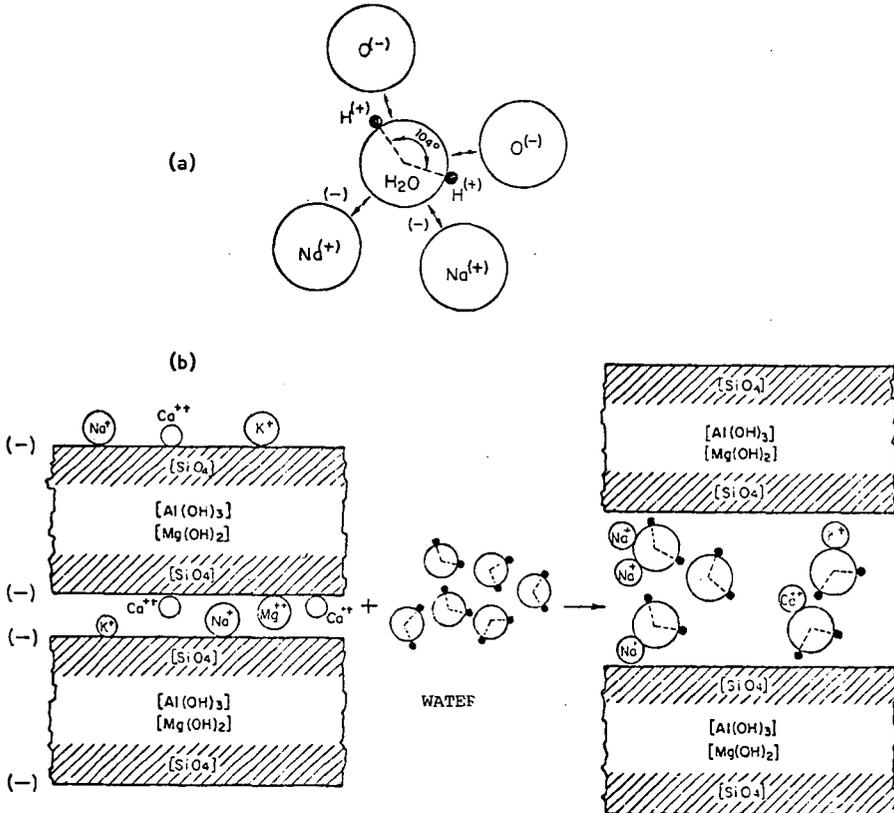


Figure 1. Electrostatic Bond Strength between the clay and the water table.

a) Water dipole. Distribution of electrical charges.

b) Phenomenon of positive ion binding between the layers. Swelling of the clay.

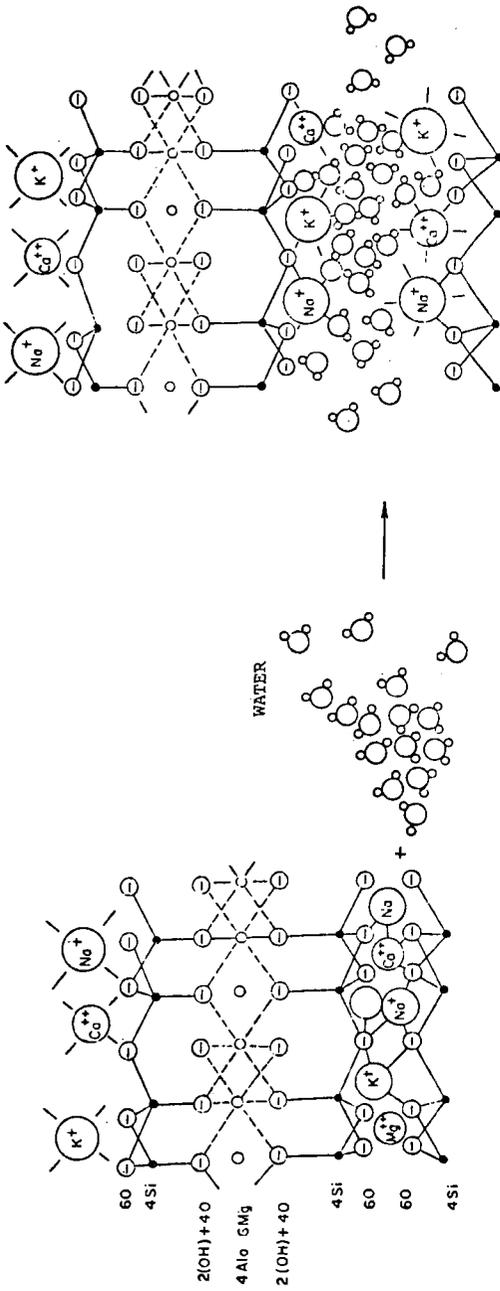


Figure 2. Phenomenon of swelling of clays due to water penetration at the level of the crystallographic unit cell.

### III. Clay differentiation.

Most of the silicates of the so-called "layer" type are characterized by structural similarities. The crystals belong to the same symmetry group and show the same type of geometric distribution of the structural elements such as, for example, the unit cell, which has the same symmetry and the same relation of axes<sup>2</sup>. From the crystallographic point of view, the silicates of the layer type have the same number of ions and the same relation for the radii of cations and anions.

The difference in the sensitivity towards alteration or hydration is caused by the pressure due to ions of isomorphic interchange placed in the exterior of the crystal lattice. These ions act as a cement, binding the structural units by electrostatic forces, and are directly responsible for the structural compactness and hardness of the rock.

Clays of sedimentary origin, previously situated in marine waters, are formed of various types mixed in different proportions. The most sensitive components of the clays are montmorillonite, illite and their mixtures. They constitute up to 80% of the total weight of the clay rock and often cause serious problems during the operation of the oil field. Due to the presence of monovalent ions, these minerals easily absorb water, the base of the conventional operating fluids, and as a result they hydrate and disperse. The first step in the colloidal dispersion of clays consists of a reduction in the bond strength between hydrated structural layers, and in the second step they are separated and the rock is dispersed. This dispersion is not the same for every type of clay.

Generally, the expandable clays are present in relatively small amounts and the problems of structural expansion, the so-called "swelling", are not so alarming as people tend to believe.

Colloidal dispersion and the migration of particles, however, can be much more damaging because serious problems can be caused by very small quantities of clay. These particles of clay dispersed in the flux channels are eventually deposited in a porous constriction, producing a collapse.

Lately, research has focussed on mixed operational fluids consisting of polymer and brine, which react only slightly with the rock. This fluid should be selected for the particular conditions of the oil field such as:

- 1) chemical composition of the formation;
- 2) chemical content of the formation water;
- 3) pH of the water of formation;
- 4) temperature and pressure of the oil field;
- 5) the unpredictable reactions "in situ";
- 6) the erosive action of the fluids;
- 7) the residence time in the "sensitive" region.

Recently it has been found<sup>3</sup> that pressure and high temperature accelerate the effects of the colloidal dispersion of clays (see Figure 3). Unfortunately it is rare for geochemical laboratories to consider these parameters and to simulate the conditions of the oil field.

Table 2 shows the differentiation of clays by the presence of the isomorphic interchange ion, and Table 3 shows the physical characteristics of clay formations when there is an invasion of fresh water. Until recently this differentiation and classification which are encountered in practice have not been considered<sup>4,5</sup>.

Table II

## Differentiation of Clays

Type of Clay	Ions of the Isomorphic Exchange Structural Components	Effect Produced By Water of Invasion	Remarks
Montmorillonite	$(H_3O, Na, K, Ca) - (Al, Mg, Fe, Ni, Zn, Cr)_{2-3} / (Si, Al)_4 O_{10} (OH)_2 \cdot nH_2O$	Easy hydration and elimination of alkaline ions with swelling and colloidal dispersion.	The predominance of Na ions which are easily interchanged by the ambient water.
Illite	$(H_3O, K) Al / (Si, Al)_4 O_{10} (OH)_2$	Easy penetration of water between layers but it hydrates with more difficulty. It has less tendency to disperse.	The only clay type of material which contains a lot of radioactive K* which can be detected by gamma ray profile. Potassium is predominant.
Chlorite	$Mg_2 Al (Mg, Al)_3 / (Si, Al)_4 O_{10} (OH)_6$	Difficult penetration of water between layers because of the presence of polyvalent Mg and Al ions.	
Kaolinite	$Al_4 (Si_4 O_{10}) (OH)_8$	It contains structural water which weakens the cohesion of the layers so that it is easily dispersed.	It is the most pure clay. It does not contain ions of interchange, and does not swell.
Mica	$K (Mg, Fe)_3 (AlSi_3 O_{10}) (OH, F)_2$	The invasion of water produces swelling more easily than dispersion due to the elimination of interchangeable ions (OH and F).	The interchange of the anion $F^-$ by $OH^-$ or the reverse takes place which destabilizes the structure and the electrostatic charges.
Isomorphic Mixture	Kaolinite/Illite Illite/Montmorillonite Kaolinite/Chlorite Montmorillonite/Chlorite/Kaolinite	Isomorphic mixtures of clays are present in nature. The physico-chemical properties of the mixture depend on the relative amounts of each clay.	

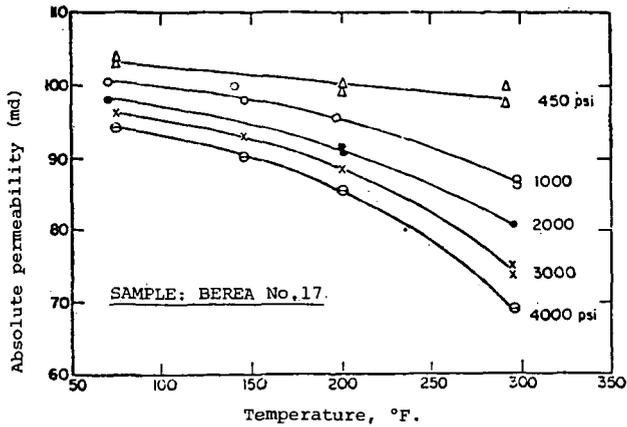


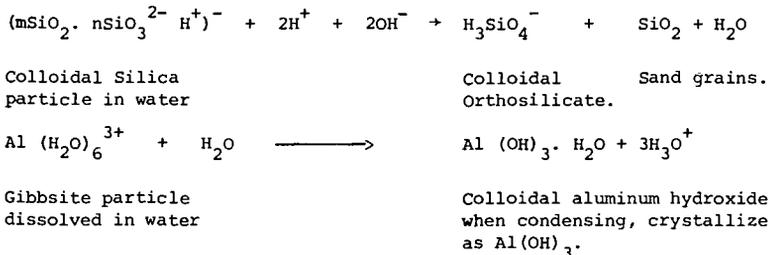
Figure 3. Effect of pressure and temperature on the permeability of the oil field (affected by clays).

Table III

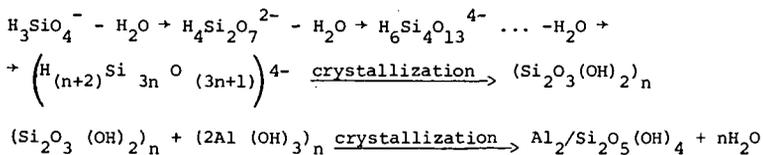
Class	Characteristics	Clay Contents
1	Soft rock. It is easily dispersed in a colloid state.	High concentration of montmorillonite. Low concentration illite.
2	Soft rock. It is relatively easily dispersed in a colloidal state.	Medium concentration montmorillonite. High concentration of illite.
3	Medium-soft rock. It is moderately dispersed. Strong swelling.	High concentrations of illite and chlorite.
4	Medium-hard rock. Little colloidal dispersion. Medium swelling.	Medium concentration of illite and chlorite.
5	Hard rock. No colloidal dispersion, little swelling.	High concentration of illite. Medium concentration of chlorite.

IV. Chemical reactions of clays altered by the water of invasion.

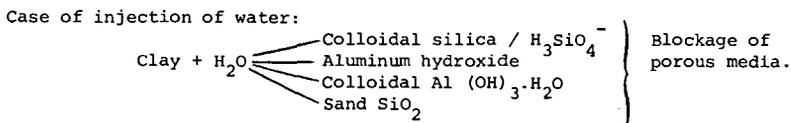
IV.1. Colloidal dispersion and appearance of sand:



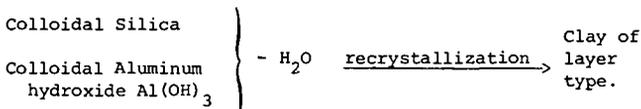
IV.2. Recrystallization of colloids by extracted water.



IV.3. Effect of the water of injection on the clay.



Case of extraction or transformation of water of injection (sedimentation of colloid, condensation).



V. Ionic treatment.

This type of treatment consists of forcing an ionic interchange between monovalent ions and bivalent or trivalent ions in order to assure better coherence and resistance of the clay layers.

We shall discuss the interchange between  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ions making use of the isomorphic substitution phenomenon since both belong to the same isomorphic row in the periodic table and have similar electronegativities and coordination numbers from 6 to 8.

The substitution of  $\text{Na}^+$  ions by  $\text{Ca}^{2+}$  ions is desirable not only because of the better electrostatic interaction between the  $\text{Ca}^{2+}$  ions and the clay layers but also because of its chemical reactivity with respect to the swelling phenomenon and its reaction enthalpy in aqueous solutions.

The  $\text{Na}^+$  ions, present because of the isomorphous changes at the crystalline aluminum-silicate lattice level, are easily dissolved in fresh water. If there is an isomorphous substitution of the type  $2\text{Na}^+ + \text{Ca}^{2+}$ , the  $\text{Ca}^{2+}$  ions act as a new binding agent between the clay layers, and its reactions with water will be altered. Let us compare the dissolution of different oxides in 100 ml of fresh water at 20°C (see Table 4).

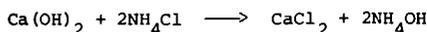
Table IV  
Solubility of oxides in 100 ml water at 20°C

Type of Oxide	$\text{SiO}_2$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{CaO}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$
Solubility in mg.	insol.	65,700	76,700	151	0.89	insol.

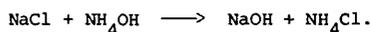
The low solubility of  $\text{CaO}$  (151 mg  $\text{CaO}$  compared to 65,700 mg  $\text{Na}_2\text{O}$ <sup>2,6</sup>) causes an increase in the electrostatic coherence between the clay layers and ensures that the elements of electrostatic coherence are maintained in the crystal lattice.

The technology of the proposed interchange will consist of injection of calcium hydroxide  $\text{Ca}(\text{OH})_2$  and, since reactions giving products of lower enthalpy are favoured,  $\text{CaCl}_2$  can be precipitated while at the same time the sodium that exists between the clay layers is dissolved<sup>2</sup>. The reactions which take place during this injection are the following:

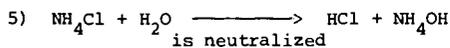
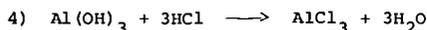
- 1) Injection in the oil field of the solution



- 2) Spontaneous dissolution of sodium salts in ammonium hydroxide and substitution for  $\text{Ca}^{2+}$



If colloids of the silicate acid type are present, the reactions can be a function of pH and enthalpy as follows:



If reactions 1) and 2) take place in aqueous solution,  $\text{NaCl}$  is substituted by the precipitated  $\text{CaCl}_2$  and  $\text{NaCl}$  diffuses into the ammonium hydroxide. The reaction sequence is determined by the reaction enthalpy (see Table 5)<sup>6</sup>. Thus of the two salts  $\text{CaCl}_2$  and  $\text{NaCl}$ , the preference for forming hydroxides with  $\text{NH}_4\text{OH}$  depends on the value of  $\Delta H^\circ_{298}$  which is greater for  $\text{NaOH}$ .

Table V  
Enthalpies of Ionic Reactions

Type of Salt	$\Delta H^{\circ}_{298}$ kcal/mol
Ca <sup>2+</sup> Cl <sub>2</sub> <sup>-</sup>	190.60
Na <sup>+</sup> Cl <sup>-</sup>	98.82
Ca <sup>2+</sup> (OH) <sup>-</sup>	235.60
Na <sup>+</sup> (OH) <sub>2</sub> <sup>-</sup>	101.96
H <sub>2</sub> <sup>+</sup> SiO <sub>3</sub> <sup>2-</sup>	267.80
H <sub>2</sub> <sup>+</sup> SiO <sub>4</sub> <sup>4-</sup>	340.60

### Conclusion

In the commercial development of an oil field a chemical-mineralogical study should precede the engineering study. One of the problems encountered in oil field operations such as drilling, completion, and reconditioning is the damage to the oil producing formation due to the reduction of the permeability of the surroundings. This damage can impede the detection of some hydrocarbons in an exploratory well, or diminish the productivity of a functioning well. Furthermore, the extent of damage will often affect the viability of secondary recovery operations.

The permeability and porosity of the oil field rocks are responsible for the storage and migration of oil and gas. The explanation of field problems should be searched for by chemical and mineralogical studies because it is easier to take preventive measures than to reestablish a damaged permeability by chemical treatment.

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