THE EFFECT OF FLUID pH ON CLAYS AND RESULTING FORMATION PERMEABILITY

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INTRODUCTION

Clays are present in a majority of hydrocarbon-bearing formations and their presence can cause many problems in the production of oil and gas. The difficulties that are encountered are complicated by the fact that clay composition and location in the rock can vary extensively. In reality, the presence of clays in any part of the drilled hole can present a variety of problems in all phases of the life of the well. There are shales that show a high degree of deterioration when contacted by the common types of water-base drilling fluids. Fluid loss from cement slurries and certain water-base stimulation fluids are another source of potential damage to permeability.

Clays may be found in all types of rock. Formations made up of such rocks have been called water sensitive and may be defined as formations where a reduction in effective permeability is noted when a foreign water invades the formation. Normally, sandstone formations exhibit the greatest degree of water sensitivity. Clays may also be present in carbonate rocks but are frequently encapsulated in the rock matrix. Thus, they are not in a position to be contacted by the invading fluids. Permeability damage is primarily caused by migration of clays and other fines with fluid flow. High pH fluids, particularly those with low salt content, can cause dispersion of clays which increases their possibility of migrating. Subsequent bridging of particles at flow restrictions in the rock flow channels causes a plugging action which results in a permeability reduction. This overall effect is primarily found during the flow of water.

CLAYS FOUND IN HYDROCARBON-BEARING FORMATIONS

The clays most frequently found in hydrocarbon-producing formations are montmorillonite (bentonite), illite (which can include glauconite and some micas), mixed layer (primarily illite-montmorillonite), kaolinite and chlorite. Their presence in formation samples and approximate concentrations are usually determined by X-ray diffraction analysis. However, the position of clays in the rock matrix and their localized concentration in any area are also very important. This is very difficult to resolve by X-ray techniques but can be quickly determined by the use of dyes. Certain dyes and other chemicals exhibit characteristic colors when they are adsorbed by the different clays. A subsequent examination of the treated rock surface with low power magnification by one experienced in this art can be quite revealing.

DESCRIPTION OF CLAYS

All of the clays noted in this paper are flat crystals. They exist as thin platelets that are normally stacked like a deck of cards or writing paper to form packets. Stacking is not necessarily even as platelets can overlap in the packets. These packets are distributed throughout a sand in many ways. Quite frequently they are concentrated at junctions of sand grains and are more concentrated in the sand near shale lenses. Kaolinite is usually concentrated in isolated spots; montmorillonite in smears throughout the area where it is present; illite in streaks close to shale lenses; mixed layer clay in irregular streaks throughout the sand. Variations of the above will occur which will primarily depend on concentration of the clay in the sand. Detection of the position of these clays in sandstones was accomplished by the use of the dye-staining procedure.

All clays are negatively charged. With montmorillonite, these charges are predominant on faces of the clay crystal while edges of the crystal are positively charged. Density of the negative charges can be measured by determining the number of positive charges required to neutralize the crystal. This is known as the cation exchange capacity (CEC) of the clay and is expressed in milliequivalents (ME) for 100 grams of clay. Table 1 lists the CEC of several clays.

TABLE 1—CATION EXCHANGE CAPACITY OF SELECTED CLAYS AND SAND

Clay	Range of Cation Exchange Capacity
Montmorillonite	80 to 150
Illite	10 to 40
Kaolinite	3 to 15
Chlorite	10 to 40
Sand (2 to 62 microns)	0.6

The replacement of one cation by another on any clay is governed mainly by the law of mass action and the valence of the cation. Generally, where mono- and divalent cations are present in the same concentration, the divalent cation will be preferentially attracted to the clay. If a water solution containing only one cation is brought in contact with a clay, it will tend to replace another cation on the clay, regardless of its valence. Among monovalent cations, it has been found that potassium and ammonium are more effective than sodium in replacing divalent calcium on montmorillonite.

The clays under consideration may be classified as swelling and nonswelling. Montmorillonite is the only clay that swells by adsorbing ordered water layers between clay crystals. Mixed layer clay, which contains montmorillonite, will also swell with water but the illite portion of this clay is relatively non-water swelling. Kaolinite and chlorite, as well as illite, may be classed as non-water swelling clays. They do not build viscosity in water as effectively as montmorillonite since their crystals tend to remain as packets instead of being dispersed as do the montmorillonite crystals. However, we must not ignore the fact that these so-called non-water swelling clays do adsorb some water. Routson, et al [1], reported that some water is adsorbed in illite crystal packets. Aylmore, et al [2], examined kaolinite under a variety of conditions and found that water is associated with this clay and that the cation attracted to the clay and its concentration has little effect on the water content. Thus, all clays do adsorb water with montmorillonite adsorbing the most.

WELL COMPLETION FLUIDS

Fluids currently being used in well completions vary considerably in their chemical compositions and the results of tests discussed in this paper indicate consideration should be given to the pH of these fluids.

Water-base fluids are used in various completion techniques; however, the results presented here are primarily oriented toward hydraulic fracturing. Hydraulic fracturing trends indicate approximately 80% of the treatments are conducted with water-base solutions. Major advances in fracturing fluids in recent years have brought about complex chemical systems which are highly pH dependent. As an example, in the high viscosity, crosslinked, water-base gel systems, the control of pH in very narrow ranges is necessary for the full development of gel viscosity. In many cases, more concern is given to pH control for proper fracturing fluid chemistry than to possible detrimental effects from this required pH on the formation.

Potassium chloride has been successfully used[3] in water-base fracturing fluids for several years to minimize permeability damage due to clay migration. The success obtained in this area then led to the use[4] of potassium chloride in drilling fluids. Since potassium chloride has been proven over a wide variety of field conditions, it was used as the base fluid in the flow tests reported here.

It has long been known that a high pH, along with a minimum amount of salts, will effectively disperse clays. Data[5] has been reported on the effect of pH on the permeability of Berea cores. Damage at high pH was observed in these flow tests.

It was the purpose of the tests detailed here to investigate the effect of pH on the permeability of cores containing clays where a 2% potassium chloride solution was used. The effects of methyl alcohol in the 2% potassium chloride was also investigated.

TEST PROCEDURE — DATE GATHERING

Two series of tests were conducted, the first using Bandera formation core samples and the second using Morrow formation core samples from the Anadarko Basin. The X-ray diffraction analyses of these samples are given in Table 2.

Twenty core plugs, one inch diameter and one inch in length, were used for each test series. All the core plugs were saturated in 2% potassium chloride water having a specified pH.

TABLE 2—X-RAY DIFFRACTION ANALYSIS OF TEST CORES

	Bandera Core	Morrow Core	
Quartz	67%	91%	83%
Feldspar	19%	-	-
Dolomite	4%	-	-
Illite	5%	-	-
Kaolinite	7%	5%	11%
Chlorite	2%	2%	4%
Montmorillonite Mixed Layer Clay	2%	2%	2%

Following saturation, initial flow rate data was recorded while using the saturating fluid for flow. This flow data was the base data against which later flow data could be compared.

The next step was to obtain flow rate data with 2% potassium chloride solutions having a pH of 3, 5, 7, 9, or 11 and flowing in the reverse direction of the initial flow. Only one solution pH was used with each core in this step.

With this procedure, each core was subjected to only two fluids, the initial base fluid and the test fluid. For each test series, 20 cores and 10 test fluids were used with each fluid being tested on two cores.

In the first test series the evaluated flow period was 15 minutes for both initial and reverse flow. Flow rates (ml/min) were recorded at 0-1, 7-8 and 14-15 minute intervals. In the second test series, the flow period was 30 minutes for both initial and reverse flow. Flow rates (ml/min) were recorded at 0-1, 7-8, 14-15, 22-23, and 29-30 minute intervals.

Average values for initial and reverse flow were then used in calculating percent flow regained. Since two cores were used for each fluid, the average percent flow regained for the two cores was calculated for each fluid.

In the first test series (Bandera Core), the average number of pore volumes flowed was approximately 30 for the initial flow and reverse flow. In the second test series (Morrow Core), the average number of pore volumes flowed was approximately 100 for the initial and reverse flow.

The results of these tests are shown in Tables 3 and 4.

TABLE 3—FIRST TEST SERIES

Bandera Core
Average Permeability: 23 md. (air)
Average Porosity: 19.3%
Test Temperature: 70°F
Test Pressure: 100 psig
Saturating Fluid: 2% KCl water (pH 7.0)

Initial Fluid Flow Rates taken with 2% KCl Water (pH 7.0)

Reverse Flow Fluid	Percent Flow Regained*
2% KCl Water, pH 3.0	101.0
2% KCl Water, pH 5.0	99.0
2% KCl Water, pH 7.0	100.0
2% KCl Water, pH 9.0	68.5
2% KCl Water, pH 11.0	74.6
Mixture**, pH 3.0	92.0
Mixture**, pH 5.0	88.0
Mixture**, pH 7.0	87.0
Mixture**, pH 9.0	81.5
Mixture**, pH 11.0	88.0

* Based upon the average flow rate for two cores (Average Reverse Flow Rate/Average Initial Flow Rate) x 100. These percentages were normalized such that 2% KCl water - pH 7.0 would show 100% flow regained and tests with the other fluids are relative to this.

** Mixture: 70%-2% KCl water and 30% methyl alcohol.

TABLE 4—SECOND TEST SERIES

Morrow Formation Core
Average Permeability: 27 md. (air)
Average Porosity: 12.3% (Helium Compression)
Test Temperature: 70°F
Test Pressure: 25 psig
Saturating Fluid: 2% KCl water (pH 5.0)

Initial Fluid Flow Rates taken with 2% KCl Water (pH 5.0)

Reverse Flow Fluid	Percent Flow Regained*
2% KCl Water, pH 3.0	131.0
2% KCl Water, pH 5.0	100.0
2% KCl Water, pH 7.0	91.5
2% KCl Water, pH 9.0	82.5
2% KCl Water, pH 11.0	56.5
Mixture**, pH 3.0	133.5
Mixture**, pH 5.0	132.0
Mixture**, pH 7.0	105.0
Mixture**, pH 9.0	97.0
Mixture**, pH 11.0	131.0

* Based upon the average flow rate for two cores (Average Reverse Flow Rate/Average Initial Flow Rate) x 100. These percentages were normalized such that 2% KCl water - pH 5.0 would show 100% flow regained and tests with the other fluids are relative to this.

** Mixture: 70%-2% KCl water and 30% methyl alcohol.

CONCLUSIONS

Although these tests results are not meant to be conclusive for all formations, the results presented here indicate that even though a clay control material such as potassium chloride is used in a water-base fluid, the pH of this fluid should be considered.

The results of these tests indicate 2% potassium chloride water with a pH in the range of 3.0 to 7.0 would be more compatible with formations containing clays than the same fluid with a pH greater than 7.0. The results also indicate that methyl alcohol will reduce the detrimental effects from high pH fluids on formations containing clays.

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