Evaluation of Reactive Clay in Indian Shale

Shale formations are composed of clays, feldspars, carbonates, and quartz as major ingredients. Among all the constituents, clays are the most important parameter from an application point of view because of their possibly sensitive nature; they are further categorised as migrating (illite, kaolinite, and chlorite) and reactive (smectite and mixed layers) clays. Smectite is always considered as reactive clay, and it appears in shale as an individual phase or as a component of mixed layer clay. This article outlines the laboratory methods used to measure the concentration of reactive clay minerals in shale and their controlling parameters. The process includes analysis of samples by X-ray Diffraction (XRD), Cation Exchange Capacity (CEC), and Capillary Suction Time (CST) tests. The samples used for the study include shale samples from Indian origin. The data obtained from each method are reported, including the effect of brines for inhibiting clay reactivity.

Source rock shale formations have become one of the primary sources for future oil and gas exploration in many parts of the world, including India. However, even though the term shale is often used to describe the unconventional reservoirs that are being exploited today, only a few shales are capable of producing hydrocarbons; productive shale reservoirs would be more accurately defined as organic-rich source rocks, and most of their oil or gas generated has been expulsed over geologic time and trapped in conventional reservoir rocks[1].

Shale formations are defined as a fine-grained, clastic sedimentary rock having low permeability, containing highly diverse mineralogy, ranging from carbonate-rich formations dominated by calcite, dolomite, and siderite to lesser amounts of aluminosilicates. However, many shale formations are rich in silicates, including quartz, feldspar, and clay minerals, as dominant phases, and carbonates are a minor component. Shale formations with rich clay concentrations should be handled systematically because the interaction between the rock materials and water-based fluids (used during well operations) is an important parameter that affects successful production. The presence of reactive (swelling) clays, such as smectite and/or mixed layer clays, causes a formation to be considered water sensitive. Both qualitative and quantitative measures of shale characteristics can be used to informally classify shale as having high, moderate, or low reactivity. The objective of this approach is to determine the type of tests required to anticipate problems likely to be encountered with reactive clays present in shale. The six shale samples considered in this study were derived from producing wells.

X-ray Diffraction (XRD)

XRD can be performed on formation cuttings or cores. Preferably, samples are washed with suitable organic solvent and dried before XRD analysis is conducted. XRD is used for the identification of minerals present in shale samples. The sample is crushed and powdered to pass through a 200-micron screen, loaded in a specially designed sample holder, and placed in the instrument. The sample is scanned from a series of angles by X-ray beam. The crystalline structures of individual minerals present diffract the X-ray beam, resulting in a XRD pattern for each mineral in the sample. Software identifies the minerals present and determines semi-quantitative amounts of each.

Dry sample powder analysis is often supplemented by a clay fraction analysis, which is achieved by separating the clay fraction from the bulk sample. A water dispersion is prepared from the powdered sample. The coarse non-clay portion is allowed to settle, and the clay fraction from the upper layer of the fluid is placed onto a glass slide. The glass slide, along with the clay portion, is dried and analysed by XRD for clay phases. The presence of smectite clays is further enhanced by treating the clay slide with glycol and scanning the slide on the XRD instrument. Because of the limitations of obtaining pure standards and because of the crystalline nature of the samples, XRD provides only semi-quantitative data for the mineralogical composition. The higher the smectite clay content, the more likely the shale will be reactive to swelling. Therefore, XRD data can be used in conjunction

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with other results when determining treatment options for shale formations with high clay content.

Cation Exchange Capacity (CEC)

CEC is a measure of the exchangeable cations present in the shale as clays. These exchangeable cations are positively charged ions that neutralise the negatively charged clay particles. Most of the exchangeable ions in shale samples are from the smectite clay. The CEC measurements are expressed as milliequivalents per 100 g (meq/100 g) of clay. Typically, CEC is measured using the API recommended process Methylene Blue Capacity Test[2]. This test requires one gram of finely ground dried sample be dispersed in water using a small amount of dispersant (diluted sulfuric acid and hydrogen peroxide), which is then boiled gently for few minutes, allowed to cool to room temperature, and titrated with methylene blue solution. The end point is reached when a drop of sample suspension placed on a filter paper results in a faint blue color surrounding the dyed solids. The CEC can be analysed in a laboratory or at the wellsite with a minimum amount of equipment.

The higher the CEC value, the more reactive is the shale. The non-reactive phases (quartz, carbonates, etc.) typically have very low CEC values (≤ 1). Other clays (illite, muscovite, chlorite, and kaolinite) exhibit CEC values better than non-reactive phases but lower than reactive phases. However, reactive clays (smectite and mixed layer) exhibit higher values, depending on their concentration.

Capillary Suction Time (CST) Test

The Institute of Water Pollution Control in the UK originally used the CST device to measure the time required for a slurry filtrate to travel a given distance on a thick porous filter paper3. This technique is adapted to measure the CST of clay or shale slurries. The CST test studies the filtration characteristics of aqueous systems utilising the capillary suction pressure of a porous paper to affect filtration. When a suspension is filtered under the influence of this suction pressure, the rate at which filtrate spreads away from the suspension is controlled predominately by the filterability of the suspension. The CST automatically measures the time (in sec) for the filtrate to advance between radially separated electrodes when a fixed area of special filter paper is exposed to the suspension. A small amount of sample is mixed with the desired quantity of water or brine in a small commercial blender cup, and the mixture is used for the test. Time is measured using a stop watch.

Reactive shale with a high smectite content usually has a high CST value. Therefore, CEC is directly proportional to the CST value. In addition, CST can be used to evaluate the effect of saline water on shale dispersion tendencies for specific shale formations. A study was conducted to measure the effect of deionised (DI) and saline water of different concentrations on the reactive nature of clays.

Samples Taken for Study

Six subterranean shale formation samples from Indian origin were studied for mineralogy by XRD, and the presence of swelling clay characteristics were studied by CEC and CST tests. All samples were taken from producing wells. The results showed a correlation with the presence of swelling (reactive) and non-swelling clays. Samples not containing swelling clays showed small CEC values and a minimum response to CST. All samples were treated and analysed using similar processes to help avoid errors.

Results of XRD Analysis

The samples were scanned for XRD study (Table 1). XRD patterns were generated for six samples, and data were analysed using library data from the International Center for Diffraction Data (ICDD). None of the samples were observed to have an individual smectite phase. However, smectite was observed as a component of the mixed layer clay, along with illite. Carbonate phases were observed in all samples, except Sample 6, which was dominated by aluminosilicates. Moderate carbonate concentrations (< 20%) were observed in Samples 1 and 4, and Samples 2, 3, and 5 were observed to contain high carbonates.

Table 1: XRD Analysis of Shale Samples 1 through 6

Phases	Shale 1	Shale 2	Shale 3	Shale 4	Shale 5	Shale 6
Quartz (%)	39	10	30	43	21	19
Calcite (%)	11	79	11	12	49	—
Dolomite (%)	7	2	21	—	—	—
Na-feldspar (%)	11	4	6	9	8	2
K-feldspar (%)	1	Trace	2	4	4	—
Pyrite (%)	2	Trace	2	—	—	4
Illite (%)	23	4	23	17	8	14
Chlorite (%)	6	1	5	5	3	—
Kaolinite (%)	—	—	—	—	—	46
Illite-Smectite Mixed Layer	—	—	—	10	7	15

Results of CEC Analysis

The samples presented different CEC values (Table 2) in accordance with the concentration of swelling clay in the samples. Samples 1, 2, and 3 displayed very low CEC values because of the absence of swelling (reactive) clays. Samples 4, 5, and 6 were observed with some CEC value because of the presence of smectite as part of the mixed layer clay.

Feature

The integrated study of different parameters can reveal the nature of reactive clay in shale samples so that the proper assessment and treatment of a shale formation can be determined, enabling the use of drilling or fracturing processes.

Table 2: CEC Values of Shale Samples 1 through 6

Parameter	Shale 1	Shale 2	Shale 3	Shale 4	Shale 5	Shale 6
CEC (meq/100 g)	2	1	2	5	4	6

Results of CST Analysis

The samples with the presence of reactive clay were observed to have higher CST values when treated with DI water (Table 3). Results were also tabulated for change (decrease) in CST values when the samples were treated with various saline solutions (Figure 1). The study showed that (among the solutions tested) the best control in CST values was obtained with a 3% potassium chloride (KCl) solution. The KCl solution at a 7% concentration also helped to further decrease the CST values; however, from a commercial feasibility viewpoint, the 3% KCl solution was more acceptable for field application. The CST values in Table 3 were determined as an average of three readings. Samples 1, 2, and 3 were not observed to contain any smectite or mixed layer phase, but some CST values were observed in the samples. This might be a result of the presence of illite, which was also determined to be controlled by the salt solutions.

Table 3: CST Values (in sec) of Shale Samples 1 through 6

Parameter	Shale 1	Shale 2	Shale 3	Shale 4	Shale 5	Shale 6
CST in DI Water	40.2	31.5	39.4	113.0	66.8	144.6
CST in 3% KCl	28.3	28.1	27.6	31.2	29.2	34.0
CST in 7% KCl	27.6	27.4	26.8	30.6	28.4	33.8
CST in 5% NH4Cl	31.2	30.6	28.4	31.5	29.6	34.3
CST in 3% NaCl	36.7	30.9	33.4	39.3	37.6	40.7
CST in 1.5% KCl + 1.5% NaCl	32.7	29.4	31.6	35.5	34.8	35.1
CST in 2% KCl + 1% NaCl	29.7	28.8	28.3	32.0	30.4	34.1

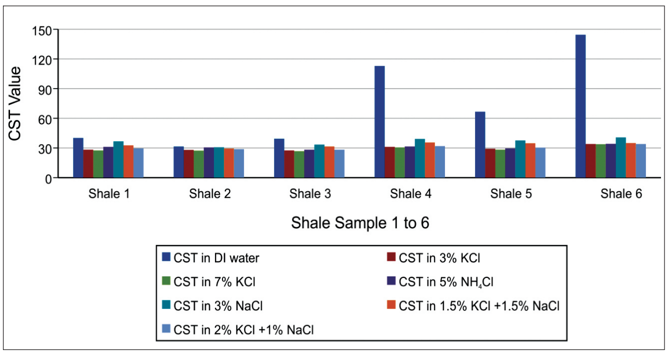

Figure 1: Change in CST values (in sec) before and after treatment with salt solutions.

Conclusion

The integrated study of different parameters can reveal the nature of reactive clay in shale samples so that the proper assessment and treatment of a shale formation can be determined, enabling the use of drilling or fracturing processes. The quantitative and semi-quantitative methods recommended in this study can be used in combination to interpret and understand the chemistry of a shale formation, and proper classification can be used to categorize the reactivity and anticipate the potential instability mechanism with fluids. The study infers the following:

- The reactive nature of clay samples can be measured by CEC and CST tests. These are simple tests and can be performed at any location.
- CEC and CST tests are directly proportional parameters to the reactive clay (smectite or mixed layer) concentration in shale, and this can be controlled using saline water.
- Migrating clays (illite, kaolinite, and chlorite) show some sensitivity toward CST values, which also can be regulated using saline water.
- A KCl (3 and 7%) solution in water was determined to be the most suitable for controlling reactive clay, though other types of saline waters or saline waters with mixtures of salts also can be used, depending on commercial and technical parameters.
- A minor development in CST value was observed with the 7% KCl solution compared to the 3% solution. From a commercial viewpoint, 3% KCl brine was recommended.

References:

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