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STUDY OF SHALE–FLUID INTERACTIONS USING THERMOGRAVIMETRY

C. C. Corrêa and R. S. V. Nascimento[*]

Instituto de Química – Departamento de Química Orgânica, Universidade Federal do Rio de Janeiro, IQ/UFRJ,
21941-590 Rio de Janeiro, RJ, Brazil

Thermogravimetry was used to study the composition of reactive shale after being submerged into different fluids and submitted to a three-point flexural mechanical test. Using this method, the amount of absorbed water on the surface of the shale was correlated to the chemical nature of the fluid used and the mechanical response obtained, allowing for a better understanding of the mechanisms involved in shale–fluid interactions.

Keywords: *shale, shale–fluid interactions, thermogravimetry*

Introduction

During the drilling of oil and gas wells the preservation of the wellbore stability has fundamental importance. The majority of wellbore walls consists of shales, which are responsible in 90% of the wellbore stability problems [1]. Shales have very low permeability, with a significant amount of clay minerals and other minerals, such as quartz, feldspars and calcite. Some types of shales are very reactive when they contact to water, due to the presence of smectite, and drilling, since they can cause serious problems such as wall instability and formation damage. In the worst situation, partly or even entirely the well can be lost [2]. Several additives can be used in the drilling fluid to prevent degradation of the wellbore walls and to minimize the dispersion of drilled cuttings during their removal from the borehole. The inhibiting additive is any chemical compound which prevents and minimizes the shale hydration. Several types of polymers have been used as reactive shale inhibitors and they can be classified into four basic groups: anionic, cationic, non-ionic and amphoteric polymers. Their stabilizing capacity depends on several factors, although the mechanisms through which they act, are not yet well understood [3]. Wellbore stability has been studied for a long time using mainly two quite different approaches. One of them considers the problem exclusively from the point of view of rock mechanics and the other, from the point of view of the chemical interactions between shale and fluid [4, 5].

In the present study a new test was developed where the rock mechanics and fluid-shale chemical interactions are evaluated simultaneously. A cell for the evaluation of the mechanical properties of the shale while submerged under the fluid was developed. In the test developed, the shale specimen is submitted to a three-point flexural test submerged in the fluid under study. One of the methods used to characterize the composition of the shale before and after the submerged mechanical tests was based on thermogravimetry (TG) [6]. Using this method the influence of the mechanical stress applied and of the nature of the fluid used on the absorption of water on the surface of the shale was possible to characterize.

Experimental

Materials and methods

Shale sample

In this study a reactive shale obtained from a natural outcrop in Calumbi (SE – Brazil) was used. It is classified as a green shale on the Munsel [7] catalogue and has a total clay fraction of 45% [23% illite/smectite (%illite=0–9%), 16% illite, 4% chlorite, 2% kaolinite], determined by XRD. The shale specimens were machined from green-shale rocks with an average initial cross section of 199 mm^2 and submerged in various fluids for the three-point flexural test.

Fluids

The fluids used in this study were: air (blank test), mineral oil, distilled water, aqueous solution (1.0%) of the nearly neutral polyacrylamide (*PAM*) polymer (<2% acrylate groups), aqueous solution (1.0%) of the cationic homopolymer of medium molecular mass

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[*] Athor for correspondence: rsandra@iq.ufrj.br

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

poly(diallyldimethylammonium chloride-MMw) (*PDADMAC-MMw*) and aqueous solution (1.0%) of the cationic copolymer poly(diallyldimethylammonium-co-acrylamide chloride) (*PDADMAC-co-AM*) which contained 13% of cationic groups. All the polymers were supplied by Sigma – Aldrich Company (USA).

Three-point flexural submerged mechanical test

A new three-point flexural submerged mechanical test, where the rock mechanics and fluid–shale chemical interactions are evaluated simultaneously was developed in the present study. A schematic representation of the new test is shown in Fig. 1.

These accessories were attached to the universal mechanical test apparatus (DL – 10000 EMIC model) with a computer which uses the test program developed by EMIC, which allows the measurement of the maximum tension (MPa), maximum strength (N), deformation (mm), and elastic modulus (MPa).

The shale specimens, with an average initial cross section of 199 mm^2, were submitted to a three-point flexural mechanical test submerged in the fluid under study with the test velocity of 0.05 mm min^{-1}. The average time (min) of the duration test for each shale–fluid system studied was measured with a chronometer.

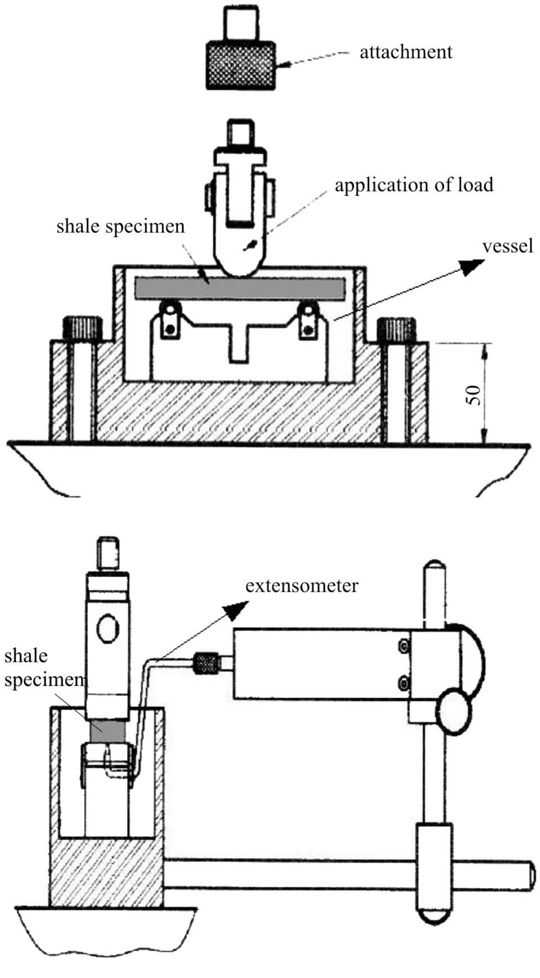

Fig. 1 Schematic representation of the new three-point flexural submerged mechanical test

Thermogravimetry

TG was used to measure the amount of absorbed water (between 30–150°C) on the surface of the green-shale specimen after its submerging in different fluids, submitted to a three-point flexural mechanical test and dried in air at room temperature, for 24 h. The samples were obtained from the upper and lower surfaces at the point where the load was applied, as it is shown in Fig. 2. TG curves were obtained using a Shimadzu TGA-51, under nitrogen atmosphere and at a heating rate of 10 K min^{-1}.

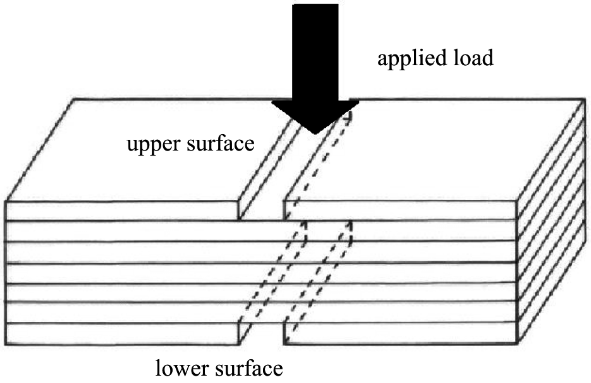

Fig. 2 Schematic representation of the shale sample obtained from the upper and lower surfaces

Results and discussion

Mechanical properties

The results of the mechanical properties of the shale specimens at the maximum tension (MPa), maximum strength (N), deformation (mm) and elastic modulus (MPa) were obtained from the three-point flexural submerged mechanical test in different fluids studied and are shown in Figs 3–5.

The results in Figs 3a and b show differences on the flexural mechanical resistance of the shale under different fluids which are probably due to the occurrence of different chemical interactions between the shale and the studied fluids. The shale specimens submerged in air (without fluid) showed larger mechanical resistance (maximum tension of 6.3 MPa and maximum strength of 1242 N) than the ones in oil based fluid or in water-based fluids, because there was no fluid in contact to produce a less stable condition for the shale. The rupture will occur when the internal energy of the rock reaches to intolerable levels, that is, an energy above the critical limit of the material, determined by the amount of water

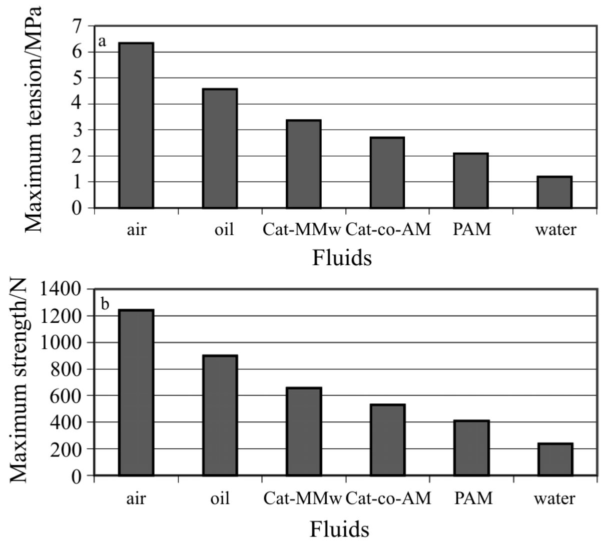

Fig. 3 Comparison of mechanical properties a – maximum tension and b – maximum strength of the shale specimen submerged in different fluids, obtained from the new mechanical test

naturally adsorbed to the shale and by the degree of interaction between the layers [8]. The shale specimens submerged in oil showed higher mechanical resistance (maximum tension of 4.6 MPa and maximum strength of 900 N) than those ones submerged in water-based fluids, probably due to weaker shale–oil interaction. However, the shale–oil interaction produces a less stable condition than that of the natural shale, hence showing lower mechanical resistance.

The shale specimens submerged in distilled water showed the lowest mechanical resistance (maximum tension of 1.2 MPa and maximum strength of 238 N) among all systems studied, probably due to a larger reactivity of the shale towards hydration [9] which produces less stable condition of the shale with weaker interaction between the layers. However, the use of an inhibitive polymer–electrolyte system increases the mechanical resistance of the shale, which is probably due to the stabilization of shale–polymer interactions thus decreasing shale swelling.

The shale specimens submerged in aqueous solution (1.0%) of the nearly neutral polymer polyacrylamide (*PAM*) showed larger mechanical resistance only when compared to water due to the specific interactions between polymer and shale, i.e., hydrogen-bonding between the carbonyl groups of the polyacrylamide and aluminol groups [$AlO_2(OH)$] in the lateral edges of the shale [10]. The shale specimens submerged in aqueous solution (1.0%) of the cationic polymers showed a larger mechanical resistance than the other polymeric systems. It can be attributed to the larger interactions between the cationic groups and the negative sites of the basal face of the shale [11]. However, the cationic homopolymer (*Cat-MMw*) gave better results in terms of mechanical resistance (maximum tension of 3.4 MPa and maximum strength of 657 N) than the cationic copolymer (*Cat-co-AM*) (maximum tension of 2.7 MPa and maximum strength of 530 N). This effect can possibly be due to a better interaction of the homopolymer`s cationic groups with the negative sites of the shale. This effect is not so pronounced for the copolymer since it has less cationic groups in its molecular structure (13%).

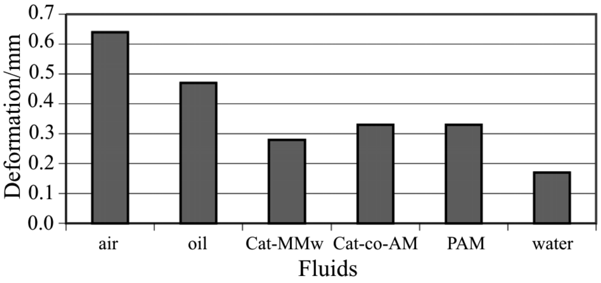

Fig. 4 Comparison of the deformation of the shale specimens submerged in different fluids, obtained from the new mechanical test

The results presented in Fig. 4 indicate the differences in the samples' deformation, probably due to the different chemical interactions occurring between shale and the studied fluids. The shales immersed in fluids are less susceptible to hydration (air and oil) and showed larger deformation than those which were immersed in more reactive fluids (water and aqueous polymeric solutions). The shale specimens submerged in the cationic homopolymer (*Cat-MMw*) showed the lowest deformation (0.28 mm) among all samples immersed in aqueous polymeric solutions. It can be explained by the extent of interaction between the cationic groups and the negative sites of the shale surface. Despite the differences in the mechanical resistance, the cationic copolymer (*Cat-co-AM*) and the polyacrylamide (*PAM*) showed the same deformation (0.33 mm). These identical deformations could possibly be attributed to the very small number of cationic groups of the copolymer interacting with the shale, while the larger mechanical resistance is attributed to the joint action of the cationic and the non-ionic groups.

The results in Fig. 5 show that the shale specimens submerged in air and oil have larger rigidity and mechanical resistance compared to the ones submerged in water and in polymeric solutions of either *Cat-co-AM* or *PAM*. The shale specimens submerged in the *Cat-MMw* polymeric solution exhibited the largest rigidity (409 MPa) among all the studied systems, although it was less resistant to flexion than the shale specimens submerged in less reactive fluids (air and

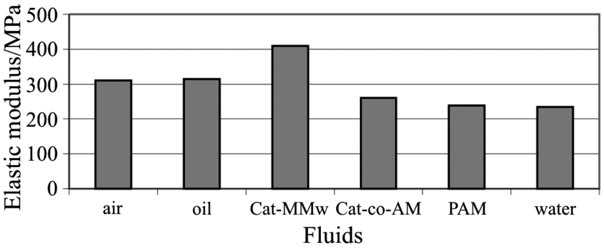

Fig. 5 Comparison of the elastic modulus of the shale specimens submerged in different fluids, obtained from the new mechanical test

oil) and more resistant to flexion than the ones that were immersed in water and polymeric solutions of *Cat-co-AM* and of *PAM*.

Thermogravimetry

Figure 6 shows the results obtained for absorbed water (between 30–150°C) on the surface of the green-shale specimen after submersion in different fluids and submitted to mechanical testing.

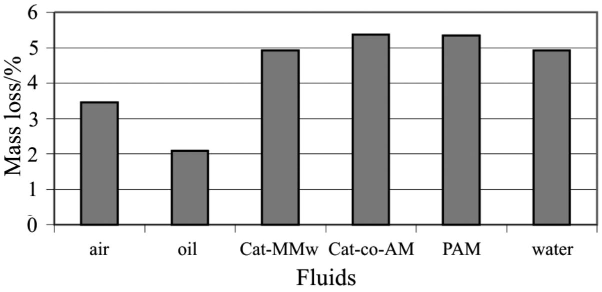

Fig. 6 Comparison of the amount of absorbed water (between 30–150°C) on the surface of the green-shale specimens after being submerged in different fluids and submitted to mechanical testing

The results in Fig. 6 show that the shale specimens submerged in air contained 3.5% water which is equal to the water content of the natural shale. This amount is altered when the specimens were in contact with any of the studied fluids, since smaller mass losses were observed (2.1%) for less reactive fluid (oil) and larger mass losses (~5.0%) were obtained for more reactive fluids (water, *Cat-MMw*, *Cat-co-AM* and *PAM*).

The shale specimens submerged in *Cat-MMw*, *Cat-co-AM* and *PAM* polymeric solutions showed that the amount of absorbed water was not dependent on the mechanisms and interactions between shale–polymer and remained the same as the shale specimens submerged in water (~5.0%). It suggests that this amount of water makes the shale to less stable. However, the specimens submerged in the polymeric solutions were more resistant to fracture and withstood the test for a longer time (9 min) compared to the shale specimens submerged in water (7 min), indicating a delay in the water diffusion into the shale (Fig. 7).

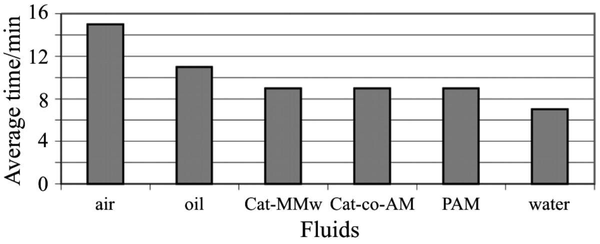

Fig. 7 Average time of the duration test for each shale–fluid system studied

According to Bailey and Keall [12], the driving force that causes the instability of the shale arises from the differences in chemical potentials of the water and ions in the shale and the drilling fluid. As the water diffuses into the shale to reduce the gradient of the chemical potential, the interactions between the layers are weakened, and despite of the presence of an efficient inhibitor were broken.

Conclusions

TG allowed the determination of the amount of absorbed water on the surface of the shale, making a better understanding of the mechanisms involved on the shale–fluid interactions possible.

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