A NOVEL METHOD FOR DETERMINING THE DEGREE OF CLAY SWELLING IN CLAY–POLYMER–WATER SYSTEMS

Gang Xie, Pingya Luo, and Mingyi Deng

The effectiveness of various clay-shale swelling inhibitors was evaluated, and the hydration mechanism was studied using information on the contents of adsorbed water in clay–polymer–water systems. Quantitative analysis was performed by UV-photodetection and thermogravimetric analysis. The evaluation of the degree of shale hydration could provide new ideas for well designs, and information regarding the most effective and ecologically friendly swelling inhibitors.

Keywords: *clay shale, clay shale swelling inhibitor, thermogravimetric analysis, UV photodetector.*

Generally, the drilling process is carried out using a drilling fluid, which often leads to loss of stability of the borehole walls. This, in turn, can lead to various problems such as borehole collapse, borehole narrowing, pipe sticking, bit balling, the occurrence of high torque and drag, all increasing drilling time and capital costs [1]. Problems of this nature generally occur in shale formations (mainly clays), especially in formations prone to hydration and swelling, which account for about 75% of all processed shale [2, 3]. Shale tends to swell, disperse, and crumble when it comes into contact with aqueous drilling fluid filtrate. As the main cause of borehole instability, this phenomenon has been studied for many years using various techniques [4-7].

Recently, horizontal wells have become widely used in shale gas development. Since the horizontal section of a shale-gas horizontal well is longer than the horizontal section of a conventional well, the contact

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time of the drilling fluid with the shale is also longer. Adsorption of the drilling fluid into the bedding clearance of the shale induces internal expansive stress with a powerful effect on the borehole walls leading to collapse.

In most cases (60-70%) oil-based drilling fluids are used due to the fact that they exhibit inhibitory ability and lubricity, providing sufficient wellbore stability and thermal stability. However, they do not meet environmental requirements, and are very costly [8]. In this regard, development of an environmentally friendly water-based drilling fluid exhibiting inhibitory action to hydration and swelling of clays is imperative [9, 10]. By various methods, some water-based inhibitory drilling fluids with a high content of inorganic salts, such as NaCl, KCl, $CaCl_2$, and organic and polymeric inhibitors were examined, however, these methods did not allow to quantify the degree of clay swelling, and the inhibitors themselves could not provide long-term stability of the borehole walls.

Through evaluation of changes in the degree of shale swelling, measured before and after contact with the drilling fluid, one can obtain reliable information about inhibitory action of the fluid components. Thus, the aim of this work was to study the method of assessing the inhibitory properties of drilling fluid by means of measuring the moisture content in clay – polymer – water systems.

Commercial organic inhibitors potassium polyacrylamide (KPAA), zwitterionic polymer (XY-27), and ammonium hydrolyzed polyacrylonitrile (NH_4-HPAN) were used without any further purification. Bentonite (Xinjiang Nonmetallic Minerals Xiazijie Bentonite Co., Ltd) – a natural clay mineral comprised of 69.04% smectite, 9.83% kaolinite, and 21.13% illite – was used for adsorption. Bentonite was pre-sieved to select granules under 4.76 mm in size, and then dried for 24 hours at 200 °C.

Aqueous drilling fluids with concentrations ranging from 0.001 to 0.005 g/mL were prepared for adsorption tests. The ability of an inhibitor of a known concentration to adsorb on rock surface was determined using a UV photodetector (Shanghai Onlab Instruments Co. Ltd). For further experiments, samples were prepared by adding 5 g of bentonite to 50-mL aliquots of 0.005 g/mL inhibitor solutions, and the system was stirred for 24 hours at 25 °C, allowing the organic inhibitors adsorbed on the clay to reach an adsorption equilibrium. The residual concentration of the organic inhibitor solutions was obtained from the calibration curve of adsorbance as a function of organic inhibitor solution concentration. The volume of organic inhibitors adsorbed
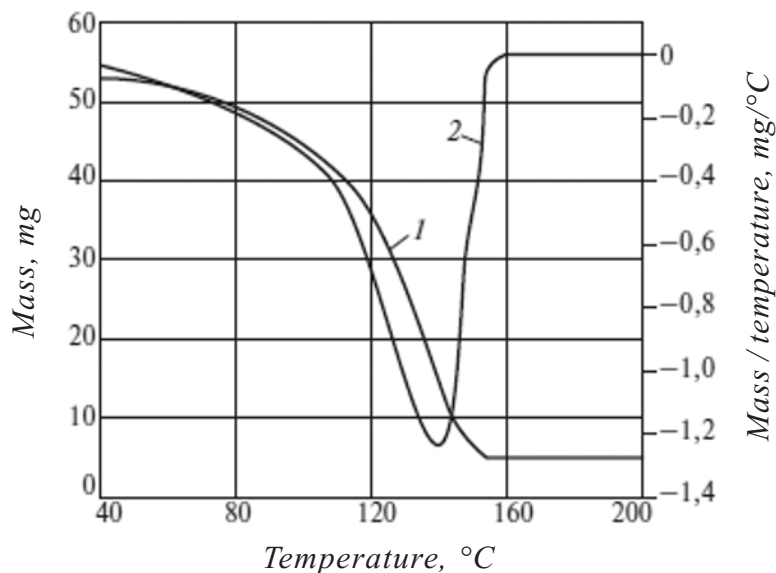

Fig. 1. Results of TG (*1*) and DTA (*2*) analyses for the clay – water system.

on the clay was calculated from the initial dosage of organic inhibitors, the volume of organic inhibitor solution, and the mass of the clay. The calculation results are presented below.

Amount of adsorbed inhibitor, g/g:

KPAA 0.013
XY-27 .... 0.028
NH_4-HPAN 0.022

The amount of water adsorbed in clay – water, polymer – water, and clay – polymer – water systems was determined by the TG/DTA thermogravimetric method using a TG/DSC1 analyzer (Mettler Toledo, USA). Samples of known mass were heated from 30 °C to 200 °C at 10 °C/min and then held at 200 °C for 4 hr. In the course of the experiment, the TGA chamber was continuously purged with dry nitrogen gas at 60 mL/min.

On the DTA curve for the clay – water system (Fig. 1), stepwise loss of water is clearly visible in the range of temperatures from 30 to 200 °C, which occurs due to evaporation of water adsorbed on the outer surface and the inner layers of the clay. According to the analysis results, the change in the mass of clay was within the limits of permissible error and was below 2%, indicating that water adsorbed on clay was completely removed from the system by heating, while the clay itself did not undergo any changes. The amount of water adsorbed on the clay w_a in the clay – water system was 2.31 g/g as calculated using equation (1):

$$w_a = \frac{m_1 - m_s}{m_s} \qquad (1)$$

where m_1 is the mass on the TG curve that corresponds to the lowest temperature on the DTA curve, and m_s is the mass on the TG curve corresponding to the zero value on the DTA curve.

TG/DTA results were also obtained for the polymer – water systems (Fig. 2). According to the data, the change in the mass of the polymer was outside the margin of error and was more than 10%, indicating that the polymer was not stable above 200 °C. When the temperature is at the minimum on the DTA curve, the value on the TG curve corresponds to the sum of the masses of water adsorbed on the polymer and dry organic inhibitor, m_1. When the value of the ordinate on the DTA curve is 0, the value on the TG curve corresponds to the mass of the dry inhibitor, m_2. The amount of adsorbed water for each polymer was calculated using equation (2). Calculation results are presented below.

$$w_s = \frac{m_1 - m_2}{m_2} \qquad (2)$$

Amount of adsorbed water w_s (g/g) for:

KPAA... 12.64
XY-27 .... 4.20
NH_4-HPAN 5.90

The results of TG/DTA analysis for the clay – polymer – water systems are shown in Fig. 3. The lowest temperature on the DTA curve in this case corresponds to the sum of the masses (m_T) of solids (m_s) and liquids (m_L) on the TG curve. When the value of the ordinate on the DTA curve is 0, the value of the abscissa of the TG curve corresponds to the value of the ordinate equal to the mass of clay, m_1, which remains constant throughout the entire process. Equations for calculating the amount of water adsorbed on clay are as follows:

$$m_T = m_s + m_L \tag{3}$$
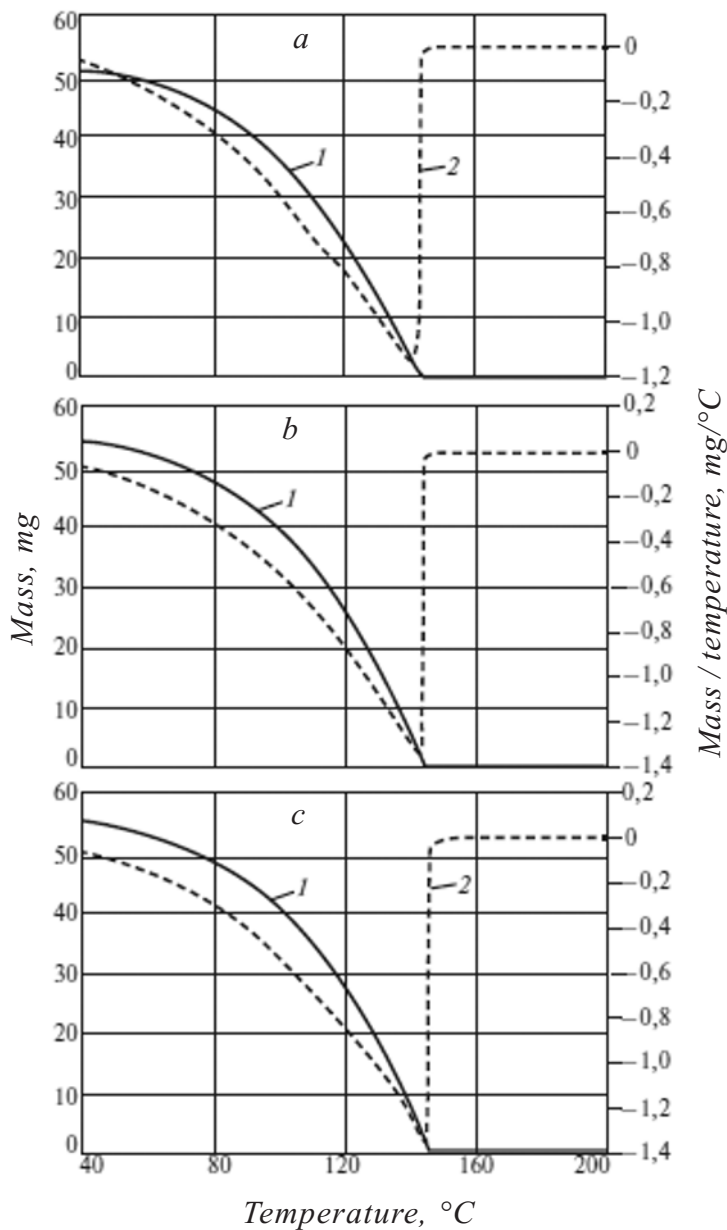
$$m_s + m_L = m_1 + m_2 + m_3 + m_4 + m_5 + m_6 \tag{4}$$

Fig. 2. Results of TG (*1*) and DTA (*2*) analyses for the systems KPAA – water (*a*), XY-27 – water (*b*), NH$_4$-HPAN – water (*c*).

$$m_s = m_1 + m_2 + m_3 \tag{5}$$

$$m_L = m_4 + m_5 + m_6 \tag{6}$$

$$m_2 = m_1 r \tag{7}$$

$$m_3 = (m_s - m_1 - m_2)r \tag{8}$$

$$m_5 = m_2 s \tag{9}$$

$$m_6 = m_3 s \tag{10}$$

$$w_1 = m_4 / m_1 \tag{11}$$

$$w_2 = (m_4 + m_5)/(m_1 + m_2) \tag{12}$$

$$w_3 = (w_2 / w_a)100\% \tag{13}$$

where m_T is the sum of the mass of solids m_s and the mass of liquid m_L, mg; m_1 is the mass of clay, mg (where m_1 = 5.00 mg in the clay – KPAA – water system, m_1 = 5.03 mg in the clay – XY-27 – water system, and m_1 = 5.00 mg in the clay – NH$_4$-HPAN – water system); m_2 is the mass of organic inhibitors adsorbed on clay, mg; m_3 is the mass of organic inhibitors not adsorbed on clay, mg; m_4 is the mass of water adsorbed on clay; m_5 is the mass of polymer-adsorbed water on clay, mg; m_6 is the mass of polymer-adsorbed water not adsorbed on clay; r is the fraction of organic inhibitor adsorbed on clay, g/g; s is the fraction of water adsorbed both on the clay and the polymer, g/g; w_1 is the fraction of water adsorbed only on clay, mg/mg; w_2 is the fraction of water adsorbed on the solid (polymer + clay), %; mg/mg; w_3 is the ratio w_2/w_a (w_a is the fraction of water adsorbed on the clay in the clay-water system).

As stated earlier, the fraction of water adsorbed on clay in the clay-water system was 2.31 g/g. According to Table 1, after the addition of polymers the fraction of water adsorbed on clay (w_1) decreased significantly. This means that these three components have strong inhibitory properties, which increase in order: XY-27 < KPAA < NH$_4$-HPAN. Also, Table 1 presents data on the content of water in the entire volume of the solid phase (clay + polymer) w_2 calculated using equation (12), and the extent of inhibition w_3 expressed by the ratio of the mass of water adsorbed on the surface and in the bulk of the solid phase in the system with the addition of an inhibitor to the weight of water adsorbed in the clay-water system. It is seen that the drilling fluid that uses NH$_4$-HPAN exhibits the best inhibitory effect.

Various organic inhibitors of clay swelling exert their effects by different mechanisms [12]. For example, the polymer XY-27 surrounds the outer surface of the clay particles, preventing them from contact with water molecules. Both anionic and cationic groups can be found in the structure of this inhibitor; cationic groups are responsible for the strength and the rate of polymer adsorption on the clay surface. In the case of NH$_4$-HPAN, ion exchange may occur between the ammonium ions and the cations present in the interlayer space of the clay. Neutralization of the negative charge in the intermicellar space suspends the clay hydration process. KPAA molecules can adsorb both in the interlayer space and on the outer surface of the clay. Upon introduction of aqueous drilling fluid into the system, the water first comes in contact with the rock, so the polymer cannot completely desorb it as a whole, and only partial inhibition takes place.

The water adsorbed on the shale may be present there in two forms: strongly- and weakly-bound [13, 14]. In the clay – water system the water interacting with the solid surface forms so-called bimolecular "pseudo-layers" on it. The adsorption process is accompanied by the formation of hydrogen bonds, and such water is

called strongly-bound water. Water, the molecules of which interact on the clay surface only with each other is called weakly-bound [15-17]. The swelling mechanism and hydraulic characteristics of the formation are largely dependent on the content and the type of adsorbed water [18, 19]. Strongly-bound water is the main reason for the expansion of crystalline layers of clay, whereas weakly-bound water causes swelling of clay particles, leading to the loss of stability of the borehole walls. Most of the organic inhibitors can only desorb weakly-bound water from the system, probably due to the fact that strongly-bound water adsorption on clay has a higher energy than adsorption of polymer. For this reason, water always remains in the system. Further studies are focused on the development and study of new intercalators for shale. Low molecular weight intercalators can penetrate into the interlayer space of clay, and by the action of electrostatic
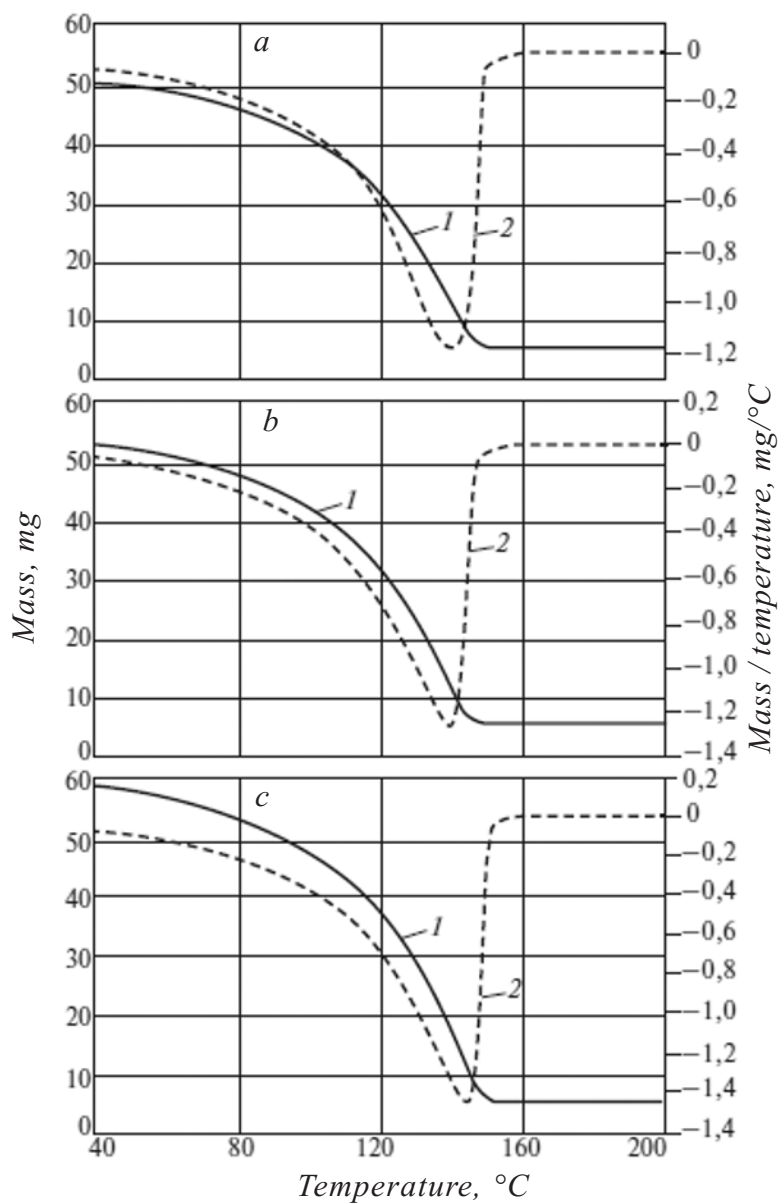

Fig. 3. Results of TG (*1*) and DTA (*2*) for the systems clay – KPAA – water (*a*), clay – XY-27 – water (*b*), clay – NH_4-HPAN – water (*c*).

Table 1

Indices	KPAA	XY-27	NH$_4$-HPAN
w_1, g/g	0.957	1.19	0.657
w_2, g/g	0.958	1.27	0.770
w_3, %	41.5	55.1	33.3

interaction, van der Waals forces, and hydrogen bonding, adjacent clay layers are attracted towards each other, thereby significantly reducing the degree of swelling and hydration.

Thus, all the examined organic inhibitors are useful as components of aqueous drilling fluids, but NH$_4$-HPAN polymer exhibits the best inhibiting properties. This was found by applying a new rapid and simple inhibitor evaluation method using thermogravimetry.

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