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INFLUENCE OF IONIC HYDRATION'S INHIBITORS ON SWELLING OF CLAYS AND SHALES***

1. INTRODUCTION

About 75% of world's formations, where drilling processes are taken, are built of clay rock [1]. Those formations are especially sensitive to contact with water-based drilling muds. Clay rocks exposed to water and mud filtrate begin to react with them and as a consequence gradually lose compactness. Those phenomena are the major threat to borehole wall stability, may also result in borehole diameter decrease or even borehole caving. Hence, drilling mud formula plays significant role in the process of drilling. Incorrectly selected mud, filter into near-well zone layers of clay rock, causing its hydration, swelling and coherence loss. This can lead to break-downs and drilling complications.

Therefore, muds designed for drilling in clay rock and weakly compacted rock are developed based on inorganic or organic additions in order to improve inhibition of clay hydration.

In spite of numerous research being conducted all over the world, stability of the clay rock is challenging to control. Chemical additions blend perfectly matching one rock formation, may be inappropriate for another. For that reason, inhibitors should be adjusted individually [1–3].

Clay rock constitute volumetrically about 70% of sedimentary rock in earth's crust. More than 50% of those rocks contain clay fraction (politic grain-size) with grains smaller than 0.01 mm. This fraction originate from weathering magma rocks and subsequent

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sedimentation of the weathered grains. Ability to swell under influence of the water is one of main characteristics of clay rocks.

Most of clay minerals have layered structure (sheets), in other words its structure is composed of parallel layers linked into sheets. Among them there can be distinguished tetrahedral and octahedral layers. Tetrahedral layer is silicon oxygen layer built out of tetrahedrons, whereas octahedral layer is metal oxide-hydroxide layer created out of octahedrons. Specific minerals vary with sheet structure, way of layering in the crystalline structure and type of exchangeable cations.

In crystalline structure of clay, a phenomenon of diadochy can be observed, i.e. replacement of silicon ions (Si^{4+}) by other kinds of ions of lower valency, mainly aluminium ions (Al^{3+}). This substitution leads to a deficit of positive charge and majority of negative charge in mineral structure. In order to neutralize it, a cation is attaching in interlayer space. In presence of the water, the interlayer cations can substitute cations occurring in drilling mud. Those are termed exchangeable cations. The type and amount of exchangeable cations have essential meaning for the drilling muds technology considering its influence on clay rock properties (including swelling and dispersion). Ability of interlayer cations to substitute diminishes due to the range:

$$H^+ > Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ > NH_4{}^+ > Na^+ > Li^+$$

In the process of water adsorption in clay minerals, two steps of swelling can be distinguished: surface hydration and osmotic hydration [4].

Surface hydration is the adsorption of water by the interlayer cations and tetrahedral layers. The amount of adsorbed water depends on type of clay (its chemical structure). Minerals containing sodium cations have the highest water adsorption ability. In case of minerals containing potassium, magnesium or calcium cations, the adsorption ability is lower. Hence, surface hydration is caused by short range forces acting between the particles, interlayer cations hydration energy (enthalpy) is its driving power. Surface hydration represses the process of ions exchange. Among others, potassium ions K^+, ammonium ions $NH_4{}^+$ and calcium ions Ca^{2+} are examples of hydration inhibitors [4].

The osmotic hydration takes place because interlayer cations concentration exceeds its concentration in the mud. Therefore, its basis is absence of balance between activity of ions placed in the interlayer space and its activity in surrounding system (e.g. drilling mud). In consequence, osmosis of the solvent molecules takes place, from lower concentration of electrolytes to the higher, due to equalizing the osmotic pressure and settling the concentrations [4].

Above relations are used to design formulas of the drilling muds destined for clay rock drilling. One of the clay inhibition hydration is ionic inhibition – substitution of sodium ions (causing high swelling) by ions that cause lower clay rock swelling. Due to this, to the drilling mud are added so-called ionic inhibitors that deliver suitable ions. Those are usually low-molecular inorganic salts. Potassium chloride is the most common ionic inhibitor.

This paper contains survey findings of a selected ionic hydration inhibitors and its various concentrations influence on swelling of clays. Studies were performed on five different salts:

- Potassium chloride (KCl) is colourless, crystalline powder, crystals or water-soluble granules with density of 1.99 Mg/m^3. Its water solution has a pH of 6 to 8.
- Potassium carbonate (K_2CO_3) called potash, is white crystalline powder with density of 2.43 Mg/m^3. It has hygroscopic properties, good solubility in water (dissolves with heat generation), forms strong alkaline solutions.
- Potassium formate (HCOOK) is white crystalline powder without odour. It is a highly hygroscopic substance and easily soluble in water. Its density in 20°C temperature is 1.48–1.58 Mg/m^3 and its water solution has a pH of approximately 8 to 11.
- Calcium chloride ($CaCl_2$) is a highly hygroscopic substance, easily soluble in water (temperature rise attends the solubility increase). Its density is about 1.70–2.15 Mg/m^3. Water solution of calcium chloride has a pH of approximately 7 to 10.
- Ammonium chloride (NH_4Cl) called salmiac, is a white crystalline powder or colourless crystalline solid. It is water-soluble and almost odour-free. Technical ammonium chloride contain anticaking agent (stearylamine). Its density is 1.53 Mg/m^3, its solution is acidic and has a pH of 5.

2. LABORATORY RESEARCH

Swelling test for influence of ionic inhibitors of hydration on clay formation has been achieved with GRACE Instrument M4600 HPHT Linear Swell Meter.

Three mass concentrations of salt water solutions were used for the research: 3%, 5% and 7%. Furthermore, bentonite mud (3% bentonite) with modified starch addition (1%) as a protective colloid, was examined for exposure to the salt. Salts used in drilling muds were in 5% mass concentration.

Tests were carried out for 20 hours with pellets obtained of Eocene shale samples.

3. CLAY SWELLING UNDER INFLUENCE OF STUDIED SALTS SOLUTIONS

The linear swelling tests (LST) of Eocene shale under influence of salts solutions with various concentrations were performed in order to investigate inhibitive properties of potassium chloride. Results are presented in Figures 1–5 and in Table 1–5.

Test findings show that the lowest value of linear swelling (LST) of Eocene shale was found for 7% solution of potassium chloride and after 20 h it is 39%. In case of 5% solution the swelling reaches 41.4%, for 3% solution it is 44.4%.

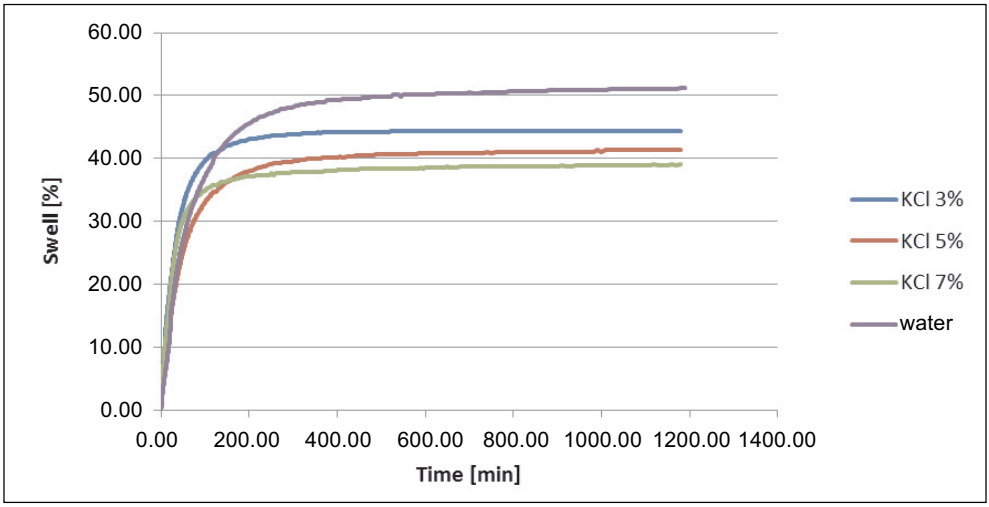

Fig. 1. Clay rock swelling under 20 h influence of potassium chloride solutions

Table 1

Clay swelling value of KCl solutions after 20 h test

Max swell			
KCl 3%	KCl 5%	KCl 7%	water
44.40%	41.40%	39.00%	51.20%

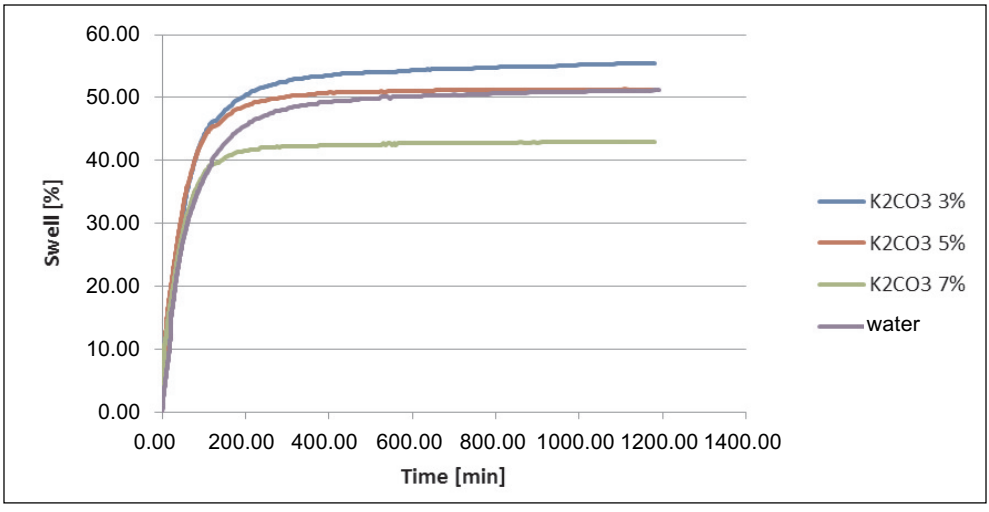

Fig. 2. Clay rock swelling under 20 h influence of potassium carbonate solutions

Table 2

Clay swelling value of K_2CO_3 solutions after 20 h test

Max swell			
K_2CO_3 3%	K_2CO_3 5%	K_2CO_3 7%	water
55.50%	51.30%	42.90%	51.20%

The lowest Eocene shale linear swelling was noticed for 7% potassium carbonate solution and after 20 h it is 42.9%. On the contrary, for 5% K_2CO_3 solution it is 51.3% and for 3% solution 55.5%. LST of the sample under influence of 5% and 3% solution of potassium carbonate is greater than under water influence.

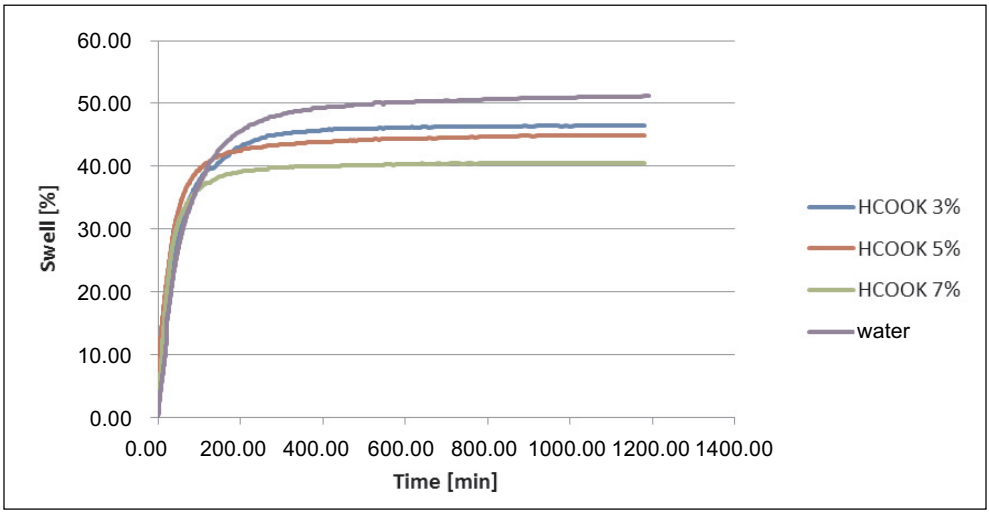

Fig. 3. Clay rock swelling under 20 h influence of potassium formate solutions

Table 3

Clay swelling value of HCOOK solutions after 20 h test

Max swell			
HCOOK 3%	HCOOK 5%	HCOOK 7%	water
46.40%	44.90%	40.40%	51.20%

Basing on the test findings, it was conducted that Eocene shale linear swelling is the lowest for 7% potassium formate solution and after 20 h its value is 40.4%. For 5% HCOOK solution it is 44.9%, whereas for 3% solution – 46.4%.

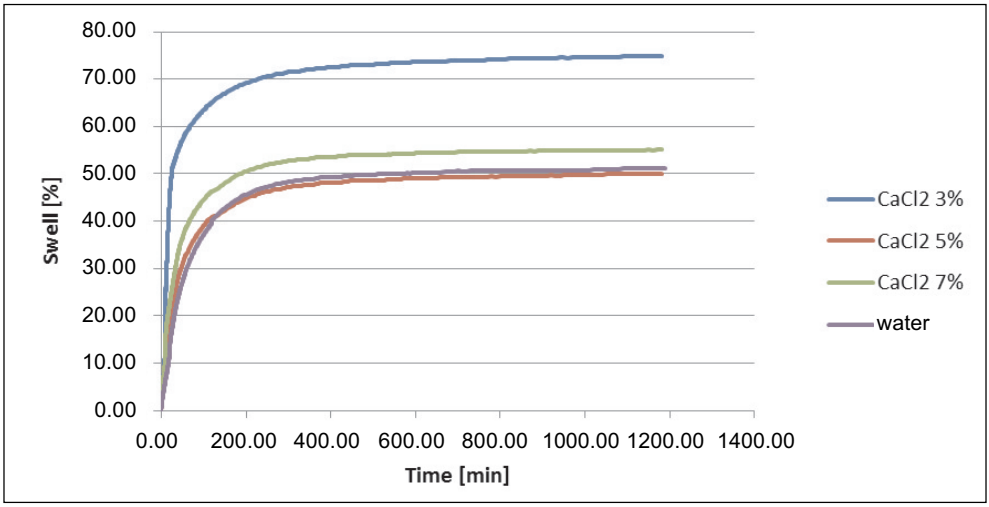

Fig. 4. Clay rock swelling under 20 h influence of calcium chloride solutions

Table 4

Clay swelling value of $CaCl_2$ solutions after 20 h test

Max swell			
$CaCl_2$ 3%	$CaCl_2$ 5%	$CaCl_2$ 7%	water
74.90%	50.00%	55.20%	51.20%

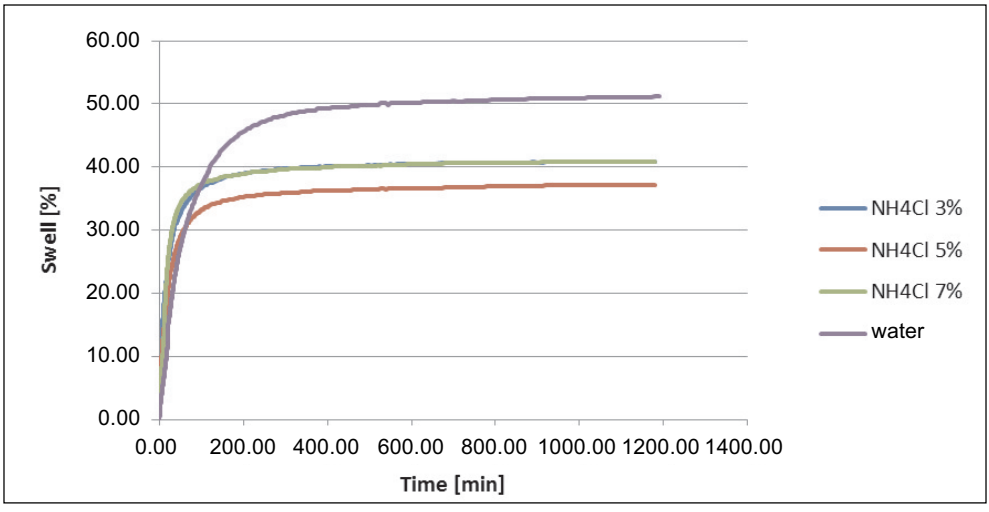

Fig. 5. Clay rock swelling under 20 h influence of ammonium chloride solutions

Table 5

Clay swelling value of NH_4Cl solutions after 20 h test

Max swell			
NH_4Cl 3%	NH_4Cl 5%	NH_4Cl 7%	water
40.90%	37.20%	40.90%	51.20%

On the basis of performed tests, it has been found that Eocene shale linear swelling is the lowest for 5% calcium chloride solution and it is 50% after 20 h. Linear swelling of Eocene shale for 7% solution of calcium chloride is 55.7%, while for 3%–74.9%.

The data obtained indicate that linear swelling of Eocene shale is the lowest for 5% ammonium chloride solution and after 20 h it is 37.2%. For 7% and 3% solution of NH_4Cl it is 40.9%.

4. COMPARISON OF CLAY SWELLING VALUES UNDER INFLUENCE OF 3% CONCENTRATION SALT SOLUTIONS

Findings of Eocene shale LST measurements are summarized on Figure 6 and in Table 6 to compare inhibitive properties of different salts with 3% concentration.

Basing on summarized results of the 3% salt solutions test, it has been found that ammonium chloride and potassium chloride has the best inhibitive properties. While the worst inhibitive properties were observed for calcium chloride and potassium carbonate (increase of the sample hydration in relation to swelling measurement under water influence).

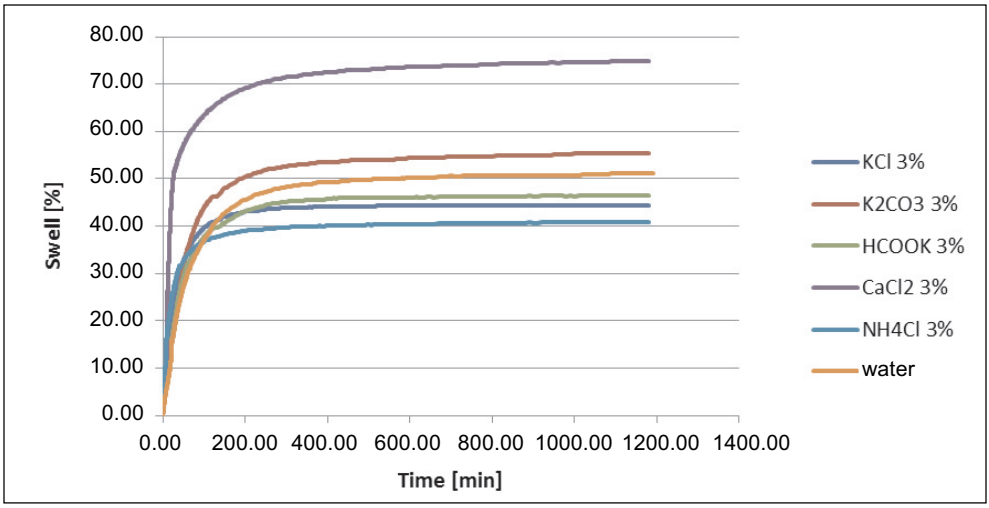

Fig. 6. Clay rock swelling under 20 h influence of 3% salts solutions

Table 6

Clay swelling value of the studied 3% salts solutions after 20 h test

Max swell					
KCl 3%	K_2CO_3 3%	HCOOK 3%	$CaCl_2$ 3%	NH_4Cl 3%	water
44.40%	55.50%	46.40%	74.90%	40.90%	51.20%

5. COMPARISON OF CLAY SWELLING VALUES UNDER INFLUENCE OF 5% CONCENTRATION SALT SOLUTIONS

In order to compare inhibitive properties of 5% concentration different salts solutions, test findings are summarized in Figure 7 and in Table 7.

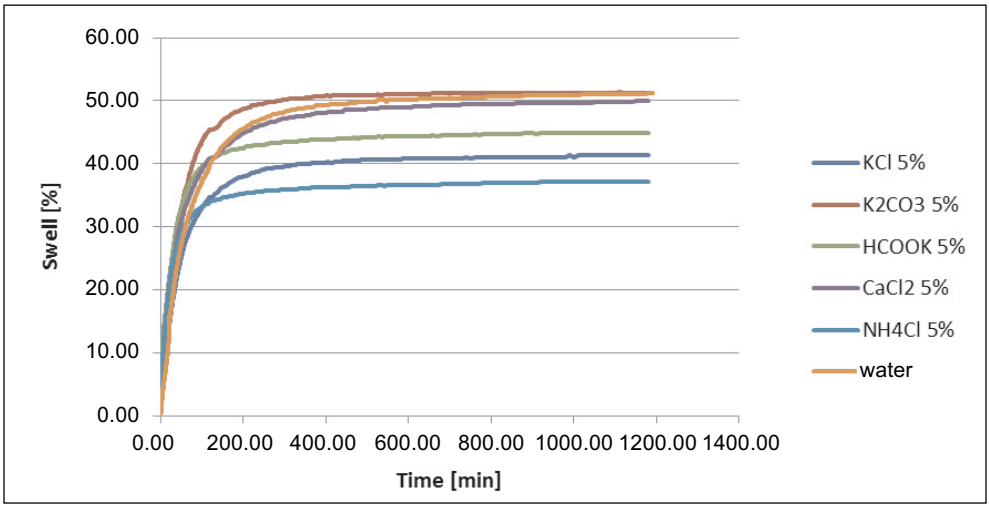

Fig. 7. Clay rock swelling under 20 h influence of 5% salts solutions

Table 7

Clay swelling value of the studied 5% salts solutions after 20 h test

Max swell					
KCl 5%	K_2CO_3 5%	HCOOK 5%	$CaCl_2$ 5%	NH_4Cl 5%	water
41.40%	51.30%	44.90%	50.00%	37.20%	51.20%

Summing up the outcome of 5% salts solutions, it can be concluded that ammonium chloride and potassium chloride has the best inhibitive properties, whereas worst – potassium carbonate.

6. COMPARISON OF CLAY SWELLING VALUES UNDER INFLUENCE OF 7% CONCENTRATION SALT SOLUTIONS

For the purpose of inhibitive properties comparison, the overall findings of 7% concentration different salts solutions are summarized in Figure 8 and in Table 8.

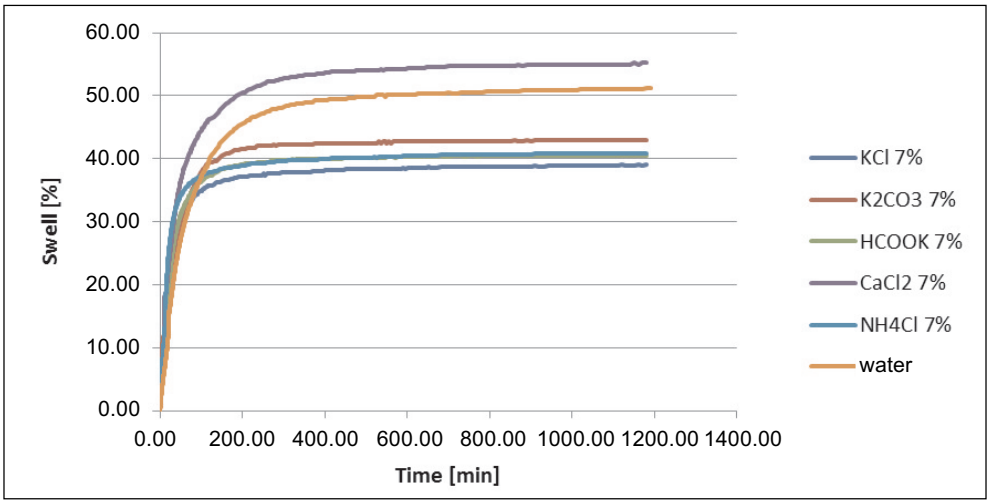

Fig. 8. Clay rock swelling under 20 h influence of 7% salts solutions

Table 8

Clay swelling value of the studied 7% salts solutions after 20 h test

Max swell					
KCl 7%	K_2CO_3 7%	HCOOK 7%	$CaCl_2$ 7%	NH_4Cl 7%	water
39.00%	42.90%	40.40%	55.20%	40.90%	51.20%

The results of performed tests indicate that the best inhibitive properties has ammonium chloride, potassium chloride and potassium formate, whereas worst – calcium chloride.

7. CLAY SWELLING VALUES UNDER INFLUENCE OF 3% BENTONITE MUDS WITH 5% SALT ADDITION

To validate the effectiveness of hydration inhibition of different salts with bentonite suspension, it has been conducted a swelling test of Eocene shale under influence of bentonite suspensions (with 3% bentonite concentration) with addition of 1% of starch

and 5% of salt. For comparison, mud with 1% of starch addition without inhibitors has been applied. The formulas of studied suspensions are summarized in Table 9. Test outcome is presented in Figure 9.

Table 9

Clay swelling value of salted muds after 20 h test

Mud	Composition [%]	Max swell [%]
Mud A	Bentonite 3 Starch 1 KCl 5	34.7
Mud B	Bentonite 3 Starch 1 K_2CO_3 5	31.6
Mud C	Bentonite 3 Starch 1 HCOOK 5	40.0
Mud D	Bentonite 3 Starch 1 $CaCl_2$ 5	35.4
Mud E	Bentonite 3 Starch 1 NH_4Cl 5	33.6
Mud 0	Bentonite 3 Starch 1	43.9

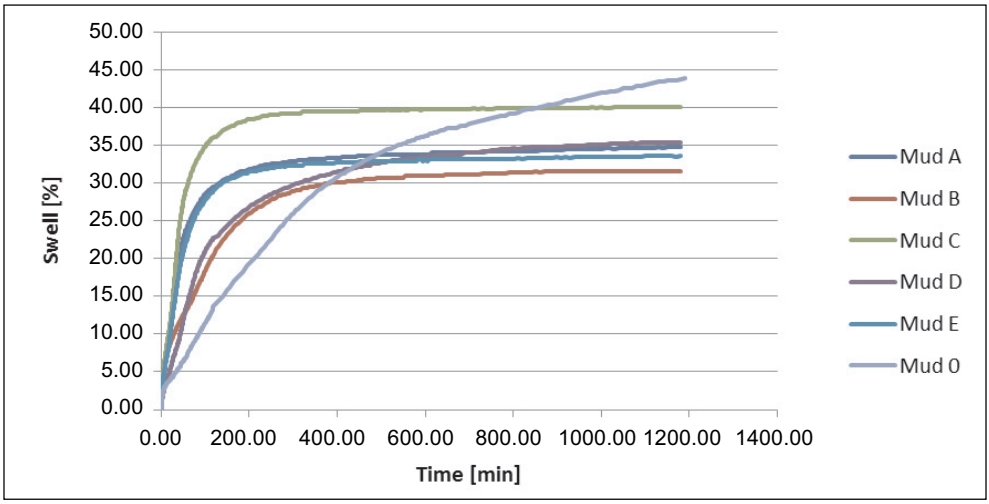

Fig. 9. Clay rock swelling under 20 h influence of salted muds

From the test of bentonite suspension with 1% starch and 5% salt addition outcome, it can be observed that clay swelling values are in range of 31.6–40%. Compared with measurement of clay swelling under influence of mud without inhibitor, each applied salt exhibits stabilizing and hydration inhibiting properties.

Mud with potassium carbonate and ammonium chloride addition has the best inhibitive properties – linear swelling of Eocene shale is 31.6% and 33.6%. The greatest value of shale linear swelling has been noticed for suspension with addition of potassium formate and it is 40%.

8. CONCLUSIONS

Basing on the Eocene shale linear swelling (LST) survey under influence of salts water-solutions, it can be concluded that inhibitive properties have: each solution of potassium chloride, 7% solution of potassium carbonate and all studied concentrations of potassium formate solutions and of ammonium chloride solutions. Best results (lowest value of swelling) were achieved for 5% solution of ammonium chloride NH_4Cl and 7% solution of potassium chloride KCl. In either case, the swelling of clay sample was lower than 40%, it is decrease of 10% comparing to shale swelling under water influence. The worst inhibitive properties were observed during application of calcium chloride solution.

From the linear swelling test under influence of bentonite suspension with addition of 1% modified starch and 5% salt, it has been conducted that each studied salt (potassium chloride, potassium carbonate, ammonium chloride, potassium formate, calcium chloride) inhibits hydration of clay rocks. The best inhibition outcome was observed under influence of potassium carbonate and ammonium chloride – shale swelling after 20h measurement was lower than 34%, that is over 10% decrease regarding to swelling under influence of mud without inhibitor addition.

Analysis of the obtained data showed that effectiveness of the salts used in water solutions preparation is different than effectiveness of the same salts used as an addition to the bentonite mud. Moreover, addition of 5% potassium carbonate to the bentonite suspension causes best hydration inhibition of the shale in comparison to other studied salts, whereas 5% K_2CO_3 solution caused adverse impact on the hydration. Potassium formate as a 5% addition to the mud stands out as least profitable swelling inhibition, while as a 5% HCOOK water solution exhibited relatively good inhibition properties.

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