

LABORATORY INVESTIGATIONS OF SILICATE MUD CONTAMINATION WITH CALCIUM

NEDILJKA GAURINA-MEĐIMUREC, KATARINA SIMON, DAVORIN MATANOVIĆ

Rudarsko-geološko-naftni fakultet Sveučilišta u Zagrebu, Pierottijeva 6, HR 10000 Zagreb, Hrvatska

Key words: drilling, wellbore instability, inhibition, contamination, silicate-based mud, lab tests

Abstract

The silicate-based drilling fluid is a low solids KCl/polymer system with the addition of soluble sodium or potassium silicate to enhance inhibition and wellbore stability. Silicate-based drilling fluids exhibit remarkable shale and chalk stabilizing properties, resulting in gauge hole and the formation of firm cuttings when drilling reactive shales and soft chalks. Silicates protect shales by in-situ gelation when exposed to the neutral pore fluid and precipitation, which occurs on contact with divalent ions present at the surface of the shale. Also, silicates prevent the dispersion and washouts when drilling soft chalk by reacting with the Ca^{2+} ions present on chalk surfaces of cutting and wellbore to form a protective film. The silicate-based drilling fluid can be used during drilling hole section through shale interbedded anhydrite formations because of its superior shale stabilizing characteristics. However, drilling through the anhydrite can decrease the silicate concentration and change rheological and filtration fluid properties. So, the critical concentration of si ions should be investigated by lab tests. This paper details the mechanism of shale inhibition using silicate-based drilling fluid, and presents results of lab tests conducted to ascertain the effect of Ca^{2+} ions on silicate level in the fluid and the fluid properties.

Introduction

Oil based muds (OBMs) and synthetic muds are considered as the most effective drilling fluids for drilling troublesome formations. Recently, increasing environmental and economic pressures strongly favour the substitution of those muds by new and technologically more efficient water based muds. An example of such water based mud is improved version of silicate mud that has been used in drilling technology for many years.

Water based muds base their inhibitive behaviour on soluble silicates were first introduced by Garrison, Barer and Vietti in the 1930s (van Oort et al., 1996). They were used for the drilling of shales that slough into the wellbore in sufficient quantities to interfere with the drilling operation. The main characteristic of such shales is sensitivity to water. Some shales swell on contact with water, others break up into fragments with little indication

Ključne riječi: bušenje, nestabilnost kanala, inhibicija, zagađenje, silikatna isplaka, laboratorijska ispitivanja

Sažetak

Silikatna isplaka je KCl/polimerna isplaka s malo čvrstih čestica i s dodatkom topivog natrijevog ili kalijevog silikata radi povećanja inhibicije i stabilnosti kanala bušotine. Silikatne isplake pokazuju izvanredna svojstva u stabiliziranju šejla i krede, čime se postiže nominalan promjer kanala bušotine i stvaranje čvrstih krhotina tijekom bušenja kroz reaktivne šejlove i meke krede. Silikati štite šejlove in-situ geliranjem u kontaktu s neutralnim slojnim fluidom i taloženjem do kojeg dolazi uslijed reakcije silikata s dvovalentnim ionima prisutnim na površini šejla. Tijekom bušenja kroz meku kedu silikati sprečavaju disperziju i proširenja jer reagiraju s Ca^{2+} ionima koji su prisutni na površini krhotina krede i stijenci kanala bušotine i formiraju zaštitni film. Zbog njenih superiornih svojstava u stabiliziranju šejla silikatna isplaka se može koristiti tijekom bušenja kroz naslage anhidrita sa proslojcima šejla. Međutim, bušenje kroz anhidrit može dovesti do prevelike potrošnje silikata odnosno smanjenja njegove koncentracije u isplaci, te promjene reoloških i filtracijskih svojstava isplake. Zbog toga je neophodno provođenje laboratorijskih ispitivanja radi utvrđivanja kritične koncentracije iona kalcija u isplaci. U, radu se opisuje mehanizam inhibicije šejla kad se koristi silikatna isplaka, i prikazuju rezultati laboratorijskih ispitivanja provedenih radi određivanja utjecaja Ca^{2+} iona na razinu silikata u isplaci i na njena svojstva.

of swelling. In the Gulf Coast Area, sodium silicate based mud contained high concentrations of silicates (20-50% by volume) was used successfully to drill more than one hundred wells. It showed improved shale stabilization but was extremely difficult to control because of excessive viscosities.

In the early 1940s that silicate mud was replaced by lime-quebracho mud which was much easier to control rheologically. Silicate based fluids were re-introduced in the late 1960s by Darley who had found that most shales could be stabilized by use of more dilute silicate solutions of sodium or potassium silicate (<20 % by volume; typically 5-10% v/v).

Silicate drilling fluid with potassium silicate has appeared to be more effective than silicate fluid contained sodium silicate (van oort et al., 1996).

Addition of salts (e.g. KCl, K_2CO_3 , NaCl) or non-ionic soluble agents (e.g. glicerol, etilen glikol) into silicate

mud increased significantly the stability of the shales. This additional shale stabilizing effect Darley was attributed to shale dehydration through an osmotic pressure gradient that is result of presence of salts or non-ionic soluble agents in mud and its filtrate. Three wells were drilled using the formulations suggested by Darley and silicate mud showed the superior wellbore stabilizing properties but a general acceptance in the field did not result.

Wingrave et al. (1987) have investigated shale stability and found that silicates used together with potassium ion special polymers are effective chemically "package" for shale stabilization.

During last ten years industry have used successfully sodium silicate in conventional polymer muds to formulate water based mud for good shale stabilizing (Alford et al., 2001; Ward et al., 1999; van Oort et al., 1996; Bamfather et al., 1997; Stewart et al., 2000). Pore pressure transmission investigations have resulted in a strong renewed interest in silicate muds and a new improved silicate mud has been developed as a result of collaboration between Sell Research, BP Exploration, Mobil NSL and BW Mud. New silicate mud was first used in field in 1994 by BW/Mobil.

Silicate muds have been used on more than 200 wells worldwide with a significant degree of success. More than one-third have been drilled in the UK. In Australia and Pakistan a silicate inhibitive mud has been used not only to provide effective wellbore stability, but also for improved lithology identification and geological interpretation at the well site (Alford et al., 2001). The silicate mud has also been used in more than 20 wells in India where it effectively replaced the conventional diesel oil-based fluids used previously. Therefore, from environmental, wellbore stability and economic perspectives, the silicate mud has been field proven to be an excellent alternative to oil-base drilling fluids (Alford et al., 2001).

In Norway, the silicate mud has been used to provide wellbore stability where glycol muds had been ineffective. After the formation is exposed to a water-base mud, its integrity is time dependent. With glycol muds, wellbore stability typically is limited to three or four days, whereas with a silicate mud the wellbore was stable for 14 days. Further, an offset well was drilled successfully with a potassium silicate polymer mud where the troublesome interval was exposed to the inhibitive mud for 56 days (Alford et al., 2001).

In Qatar, a silicate-base mud was used to successfully drill the troublesome Laffan shale. An 8 1/2" high-angle sidetrack (49° - 76°), which included 70 m of Laffan shale, was drilled without any stability-related problems.

The development of equipment, additives and new realizations about wellbore instabilities have enabled re-introduction of silicate based muds. The improvements that were being done during last years have resulted from:

- ◆ a better understanding of the rheological control problems experienced with the previous silicate fluids,
- ◆ the availability of more compatible, high performance, polymeric viscosifiers and fluid loss agents,

- ◆ much improved solids control equipment,
- ◆ a better understanding of wellbore stability, in particular the adverse interactions of shales with water based drilling fluids.

Recently, it is generally accepted that successful drilling is not determined by mud chemistry alone, but is highly dependent on critical factors such as mud weight, hole cleaning capacity, surge and swab pressures etc.

Mechanisms of wellbore stabilisation by silicates

The soluble silicate starts out as monosilicate which polymerises rapidly to form negatively charged oligomers. They are small enough to penetrate the pores in the shale, transported by diffusion or hydraulic flow. When the oligomers enter the shale pore network, the following may happen (van Oort et al., 1996):

- ◆ Pore fluid pH is close to neutral (pH ~ 7) in almost all shales. When the oligomers (silicates solution) are diluted down to this neutral pH, they may overcome their mutual repulsion and coagulate, forming 3-D gel networks.
- ◆ In all shales pore fluids, there are free polyvalent ions present, (e.g. Ca^{2+} i Mg^{2+}) that will instantaneously react with the oligomers to form insoluble precipitates.

The gelled and/or precipitated silicates now become a means of stabilising shales, as they (van Oort et al., 1996):

- Provide a physical barrier that prevents further mud filtrate invasion and pressure penetration. Thus, the wellbore and shale formation are effectively pressure isolated. The gelation/precipitation process occurs very rapidly and is completed before significant fluid loss and pressure invasion has occurred.
- Enhance the efficiency of the shale-mud membrane. Silicates are well-known for their membrane building potential. To prevent destabilising osmotic water flow from the mud to the shale the water activity of the silicate-based mud should at least balance the shale activity (i.e. $a_w^{\text{df}} \leq a_w^{\text{sh}}$).

Silicate muds are more efficient when they are used in the presence of solutes, in particular monovalent salts like NaCl and KCl. The reasons for that are following (van Oort et al., 1996):

- Monovalent cations like Na^+ and K^+ may exchange at the shale clay surfaces for Ca^{2+} and Mg^{2+} , which then become available for precipitating silicate.
- High salt strength helps in the deposition of silicates as a gel by lowering characteristic gel times.
- Solutes can be used to balance the mud and shale activities (i.e. $a_w^{\text{df}} = a_w^{\text{sh}}$) to prevent osmotic water flow from the mud to the shale. It may be desirable to lower the water activity of the mud even further (i.e. $a_w^{\text{df}} \leq a_w^{\text{sh}}$), using an excess of solutes. The resulting dehydration and pore-pressure decrease may benefit shale stability.

Generally, water based muds are not good in drilling weak rocks like shales. Shales require an effective radial support stress for stability. This is provided by mud overbalance when the hydrostatic pressure is higher than pore pressure. Unfortunately, mud overbalance for radial support provides a hydraulic pressure gradient that drives the flow of mud filtrate and diffusion of mud pressure into shales. As a result, the near-wellbore zone invaded by the filtrate may hydrate and disintegrate.

The most profound of destabilising effects is near wellbore pore pressure elevation (pore pressure transmission) which effectively destroys the effective mud pressure support and it is lost in an extended zone where pore pressure has been elevated (Fig. 1). When near wellbore pore pressure is elevated by diffusion of mud pressure, this zone will yield in compression or tension. The radial stress may go tensile when pore pressure and mud pressure equilibrate due to the presence of the in-situ hydration or swelling stress in the clay. The in-situ stresses can overcome the shale strength causing plastic deformation and failure of the rock.

The application of silicate muds

According to previously mentioned mechanisms of inhibition, one can expect the silicate muds are the best choice for drilling troublesome formations like intact and (micro-) fractured shales and chalks. Until now silicate muds have been mostly used for that purpose, at the beginning in the Southern North Sea and in Netherlands.

Microfractured shales

Shales which contain small fracture are rapidly destabilised by muds that invade the cracks and elevate the fluid pressure in them (Fig. 2). It is necessary to note that oil-based muds and synthetic-base muds cannot stabilise such fractured shales as they are restricted from entering the shales due to capillary threshold pressures. These muds act primarily through capillary threshold pressures, which are significant for intact shales with small pores but negligible for shales with open fractures.

The silicate muds can provide even higher shale stabilisation than oil-based muds and synthetic-based muds. Generation of selective (osmotic) membrane is primary protection mechanism. For using the mechanism of induced dehydration of high reactive shales to increase their stability a basic fluid with high salinity (KCl or NaCl) is recommended.

Soluble silicates have the ability to fill small cracks and pressure-seal them. The mechanism of action is rapid gellation and precipitation when the filtrate encounters the neutral pore fluid containing polyvalent ions in the microfractures (Fig. 2). Silicate muds are the most suitable for drilling high dispersive shales. Primary mechanism is decreasing of penetrating mud filtrate and pressure between shale solids by creating of the protective film.

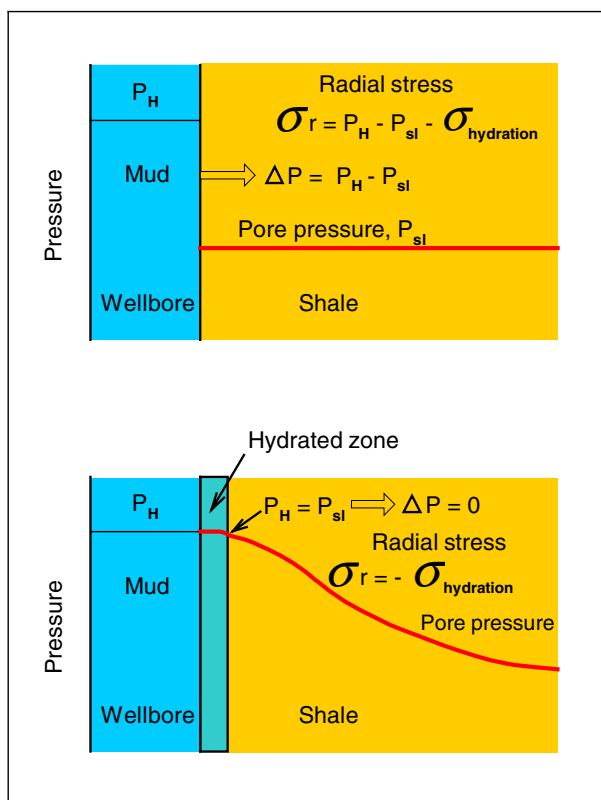


Figure 1. Principle of wellbore destabilisation by water-based muds

Slika 1. Princip destabilizacije kanala bušotine isplakama na bazi vode

Crack-sealing by silicates has been also observed visually in the lab tests performed on a shale sample with a relatively large fracture, cracks up to 0,5 mm in diameter have been sealed (van Oort et al., 1996).

In addition to, the minimum SiO₂ concentration for crack-sealing was found to be 10 000 mg/l (ppm), but concentration in excess of this amount are recommended (van Oort et al., 1996). Also, the addition of high-molecular weight polymers with an affinity for shale surfaces was beneficial for filling larger cracks. Possibly, the polymers are generating a bridging network in the cracks, acting as a supporting template for the silicates.

Chalk

Some chalks (CaCO₃) are soft and extremely dispersible, so chalk drilling can be problematic (e.g. in some North Sea areas). They tend to wash out and rapidly disperse in the water-based muds requiring high mud dilution rates. Other resulting problems include difficult directional control in build-up sections and poor primary cementation (3).

Silicates can prevent dispersion and wash out of chalks through the reaction with Ca²⁺ ions that are present on surfaces of chalk cuttings and formations. As the result, products of that reaction are precipitated and a protective film is formed (Fig. 3).

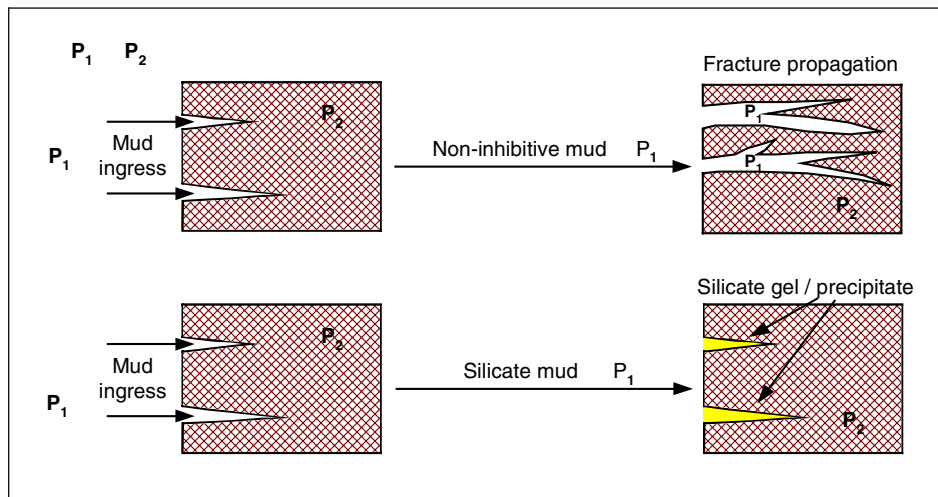


Figure 2. Sealing of microfractured shales by silicates

Slika 2. Zatvaranje mikrofrakturiranih šejlova silikatima

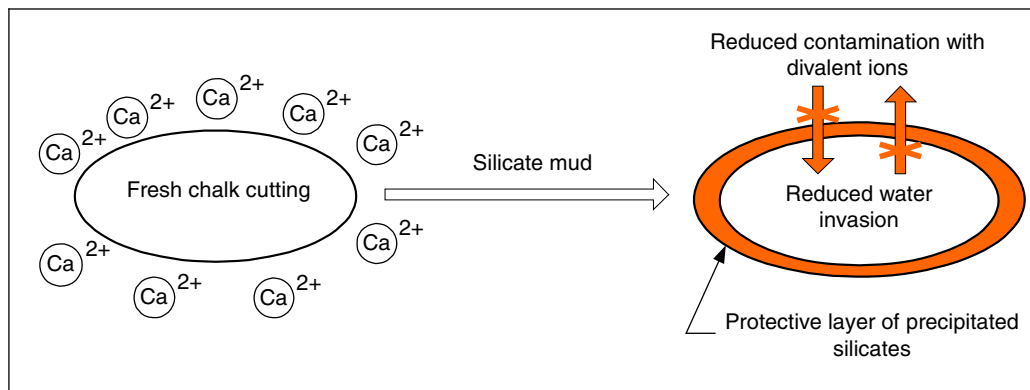


Figure 3. Stabilisation of chalk by silicates

Slika 3. Stabilizacija krede silikatima

This protective film has two functions:

- ◆ it prevents water penetrating the chalk thus minimising dispersion, and
- ◆ it retards Ca^{2+} ions contaminating the mud.

It has been reported that when drilling in a particularly soft chalk with a silicate mud in the field, large firm cuttings with visible bit teeth marks were observed. Excellent cuttings definition had never been observed before when drilling that formation with any water-based mud (van Oort et al., 1996). The silicate mud can seal fractured chinks in the same manner as fractured shales, i.e. precipitation and gellation.

Experimental work

Laboratory investigation of the influence Ca-ions on silicate mud properties has been carried out. Basic formulation of silicate mud is presented in table 1. Additives are presented according to order of addition. Salt saturated solution of NaCl with density 1200 kg/m^3 , were prepared by solution of 312 g NaCl in 888 ml of water (Gaurina-Medimurec et al., 2003).

Liquid sodium silicate ($n=2,6$) was used to assure clay inhibition. The calcium chloride (CaCl_2) and gyp, in concentration of 5, 10, 25, 50 and 100 g, were used as the source of calcium ion.

The influence of CaCl_2 and gyp on the rheological properties of silicate mud was determined by using of rotational viscometer – Fann VG meter – model 35. Testing procedure was carried out according to API RP 13B. The testing of the rheological parameters was carried out at the temperature of 50°C .

The influence of CaCl_2 and gyp on the filtration properties of tested silicate mud was determined by using the standard API filter press, so the static filtration at pressure of 6,9 bar (100 psi.) was determined, and the cake thickness was measured, also. Measurements were carried out at room temperature.

The concentration of silicate inside silicate mud, after contamination with different concentration of CaCl_2 and gyp ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), was determined by using the titration method for analyzing silicate that is described by van Oort (1996). In his paper, the measurement procedure and calculation of alkalinity, as well as concentration of Na_2O and SiO_2 in mud filtrate were described in detail.

Table 1. The formulation of basic silicate mud

Tablica 1. Sastav osnovne silikatne isplake

Component	Quantity	
Saturated solution of NaCl, $\rho=1200 \text{ kg/m}^3$	880 ml	
Potassium carbonate	40 g	
Sodium silicate	80 ml	
Clarified Xanthan gum	3 g	
Polyanionic cellulose	8 g	
Starch	5 g	
Biocide	1 g	
CaCO ₃ fine	25 g	
CaCO ₃ medium	25 g	
CaCl ₂	0, 5, 10, 25, 50, 100 g	
Gypsum		0, 5, 10, 25, 50, 100 g

Results and discussion

Concentration of calcium ions for used quantities of calcium chloride and gyp was calculated and shown in Fig. 4. It can be seen that the same weight of calcium chloride and gyp contains different concentration of calcium ion. In the case of the addition of certain weight of calcium chloride in silicate mud will be present about 1,8 times more calcium ion than in case of addition of the same weight of gyp, so calcium chloride will cause more pronounced depletion of present silicates than gyp.

Results of laboratory investigations of influence of Ca-ion on rheological and filtration properties of silicate mud are shown in figure from 4 to 10.

The increasing of Ca-ions concentration in silicate mud causes slightly increasing in rheological properties (except for 100 g of gyp), but decreasing of pH value was essentially for more than 50 g CaCl₂ or gyp (Figures 5 and 6).

The value of API filtration is increasing with increasing the concentration of Ca-ions in silicate mud, but there is the tendency of decreasing filtration at concentrations higher than 5000 ppm partly because of thicker cake (Figures 7 and 8).

The concentration of Na₂O and SiO₂ in filtrate is decreasing to the completely depletion with increasing of concentration of Ca-ions in silicate mud. The same influence the calcium ions have on filtrate. At approximately 2500 ppm of calcium ion in the silicate mud, only 10 000 ppm SiO₂ is present what is the minimum SiO₂ concentration for crack-sealing (Fig. 9 and Fig. 10).

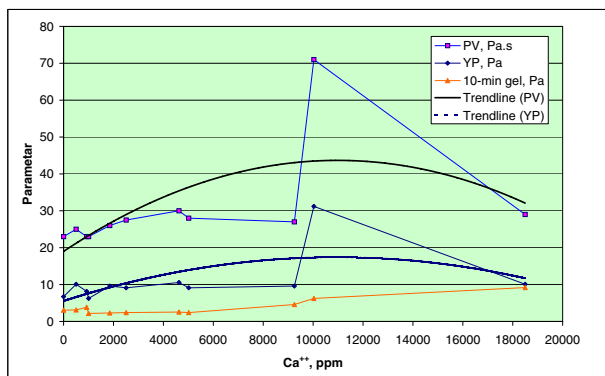


Figure 5. The influence of Ca⁺⁺ ions on PV, YP and 10-min gel

Slika 5. Utjecaj Ca⁺⁺ iona na plastičnu viskoznost, naprezanje pri pokretanju i 10-min čvrstoću gela

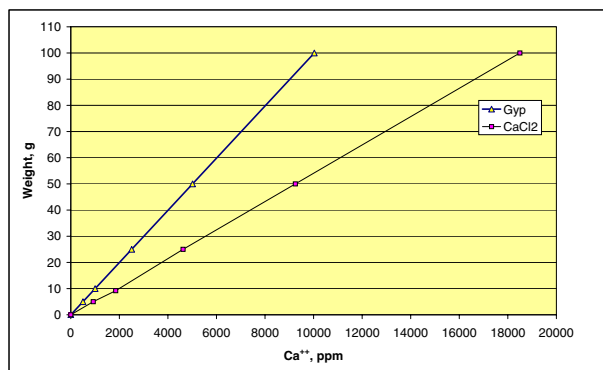


Figure 4. Concentration of calcium ion in calcium chloride and gyp

Slika 4. Koncentracija iona kalcija u kalcijevu kloridu i gipsu

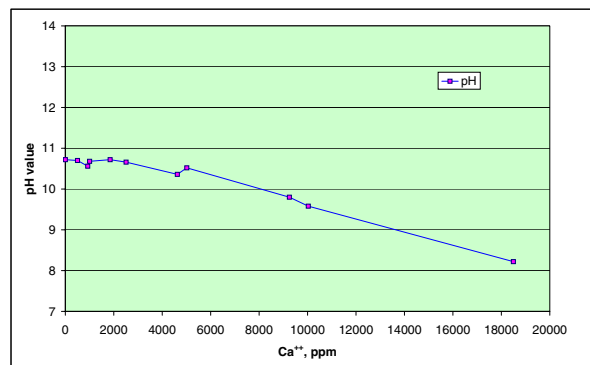
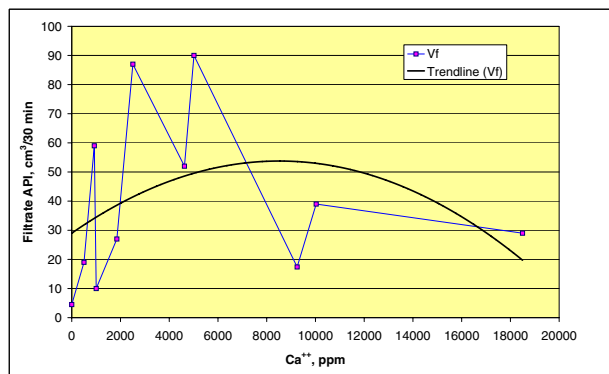
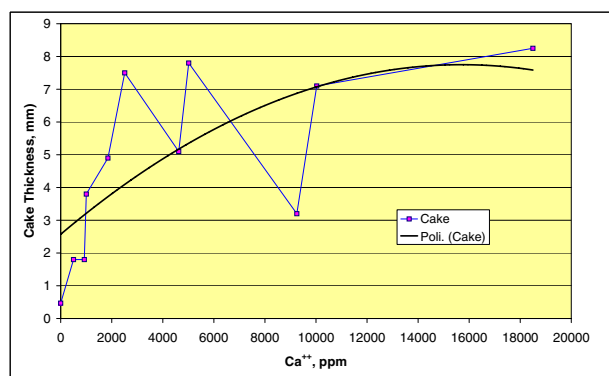
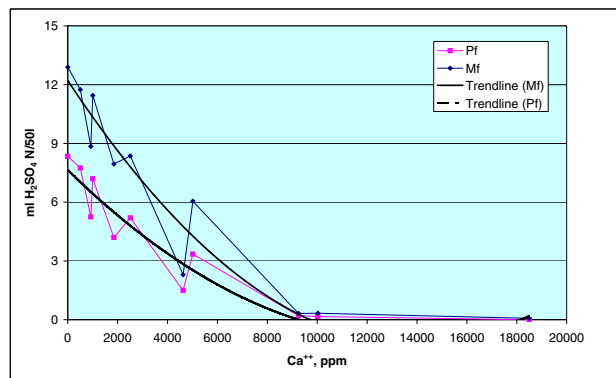


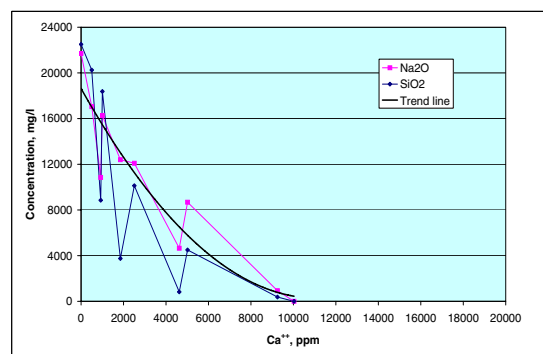
Figure 6. The influence of Ca⁺⁺ ions on pH value of silicate mud

Slika 6. Utjecaj Ca⁺⁺ iona na pH vrijednost silikatne isplake

Figure 7. The influence of Ca^{++} ions on filtration of silicate mudSlika 7. Utjecaj Ca^{++} iona na filtraciju silikatne isplakeFigure 8. The influence Ca^{++} ions on the cake thicknessSlika 8. Utjecaj Ca^{++} iona na debljinu isplačnog obloga silikatne isplakeFigure 9. The influence of Ca^{++} ions on alkalinity (Pf and Mf) of silicate mud filtrateSlika 9. Utjecaj Ca^{++} iona na alkalnost (Pf i Mf) filtrate silikatne isplake

CONCLUSIONS

Silicate mud has shown stable rheological properties in presence of calcium chloride and gyp, but higher values of filtration and lower pH values as well as lower alkalinity have been observed. Also, the higher

Figure 10. The influence of Ca^{++} ions on concentration of Na_2O and SiO_2 in filtrateSlika 10. Utjecaj Ca^{++} iona na koncentraciju Na_2O i SiO_2 u filtrate silikatne isplake

concentration of Ca -ions the lower concentration of silicates is in mud.

The presence of divalent calcium ions in concentration higher than 100 g/l causes the precipitation of soluble silicate. As a result stabilising effect of silicate mud is lost because pressure transmission is not stopped.

The monitoring of silicate mud contamination with divalent ions is the best achieved by monitoring of SiO_2 concentration in mud that should never be allowed to deplete below 30 g/l SiO_2 . It can be achieved by frequent testing and addition of sodium silicate as required.

Received: 15.6.2004.

Accepted: 17.9.2004.

REFERENCES

- Alford, S., Dzialowski, A, Jiang, P. Ullmann, H. (2001): Research Into Lubricity, Formation Damage Promises to Expand Application for Silicate Drilling Fluids; SPE/IADC 67737, SPE/IADC Drilling Conference, Amsterdam, The Netherlands, 27 Feb.-1 March 2001.
- Ward, I., Chapman, J.W., Williamson, R. (1999): Silicate Based Muds: Chemical Optimization Based on Field Experience, SPE 55054, SPE Drill. & Completion 14 (1), March 1999.
- van Oort, E., Ripley, D., Ward, I., Chapman, J. W., Williamson, R., Aston, M. (1996): Silicate-Based Drilling Fluids: Competent, Cost-effective and Benign Solution to Wellbore Stability Problems, IADC/SPE 35059, IADC/SPE Drilling Conference, New Orleans, 12-15 March 1996.
- Bamfater, J.L., Bax, D.J., van Oort, E., Nielsen, O. J. (1997): Application of Silicate-Based Drilling Fluid in Tertiary Clays Offshore Norway, SPE 38569, SPE Annual Technical Conference and Exhibition, San Antonio, Texas, 5-8 October 1997.
- Stewart, M. R., Kosich, B., Warren, B. K., Urquhart, J. C., McDonald, M. J. (2000): Use of Silicate Mud to Control Borehole Stability and Overpressured Gas Formations in Northeastern British Columbia, SPE59751, 2000 SPE/CERI Gas Technology Symposium, Calgary, Alberta Canada, 3-5 April 2000.
- Gaurina-Međimurec, N., Simon, K., Krištafor, Z., Matanović, D.: The Effect of Calcium Ion on Silicate Mud Rheological Properties, Project, Faculty of Mining, Geology and Petroleum Engineering, Zagreb, 2003.
- Gaurina-Međimurec, N., Simon, K., Sorić, T.: The Influence of Calcium Ion on Silicate Mud properties, Proceedings, 2. International Oil and Gas Conference, Zadar, September 30-October 03, 2003