GOSPODARKA SUROWCAMI MINERALNYMI

Tom 25 2009 Zeszyt 4

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Biocatalized silicate gels in oil and geothermal industry

Introduction

In oil industry, especially in water flooding and water shut-off treatments there is a need of reservoir rocks permeability modification. It is also necessary in the case of elongation of geothermal water exploitation after specific exploitation time, when temperature of water significantly decreases. In above mentioned cases modification regards to considerable decrease of reservoir rocks permeability in strictly defined reservoir zone. That treatment lengthen the way and as a result time of water flow between injection and exploitation well.

By the injection of silicate colloidal solution to reservoir rock and then decreasing its pH the initial permeability of the rock might be lowered in meaningful grade and in reasonable volume. Decrease in pH of injected to the reservoir silicate solution cause its gellation and as a result permeability damage of the rock. Lower pH is a result of reaction with acids produced by the selected bacteria strains (Falkowicz et al. 2008).

Know-how of the gelling time regulation process according to treatment needs can be achieved only by laboratory research work. Results of the special tests on the reservoir rock porous samples, plugs, have shown the mechanism which decides about durability of modification of reservoir rocks filtration properties treatments.

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1. Background of the silicate-based methods used in a petroleum industry

Silicates are compounds of silica (silicon dioxide) and alkali metal oxides which are known to human race from the ancient Egypt. As non-toxic and environmentally friendly compounds with unique phisicochemical properties they are used for different application in wide range of industry branches. The most often silicates are used as liquid glasses (water glasses) that are why considerable attention has been paid in the literature to that form of silicates. Thanks to its low reactivity, unlimited solubility in water and high stability silicates can be used also as corrosion inhibitors. They not only inhibit corrosion but also prevent from precipitate accumulation (Koźlak 2005, 2006, 2007). But mechanism of silicate reactions is still unknown because there is no unambiguous view of the molecular composition of silicate solutions.

Soluble silicates contain three components: silica, alkali and water. Although silicates have been described as the metal salts of silicic acid, they actually exist as polymeric forms in solution. The fundamental building block of silicate solutions is SiO_4 monomer – the silicon atom at the centre of an oxygen-cornered, four-sided tetrahedral pyramid. In sodium silicate, typically, each oxygen atom is associated with a sodium or hydrogen atom, or it may be linked to another silica tetrahedron. The silica tetrahedra can link to form chains (Fig. 1), cyclic and larger polymeric structures.

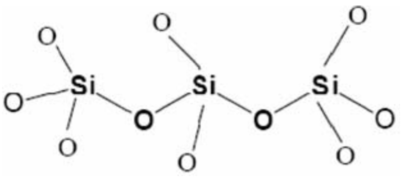

Fig. 1. Silicate Trimer

Rys. 1. Trimer SiO_4

During numerous experiments it was shown that on the silicates structures in solutions, except the method and production technology, great impact have following parameters: concentration, aging time, pH and silicate modulus (M_k) which is main factor affecting silicate properties and polymerization reaction. It was proved by several experiments (Vail 1952; Patterson 1994; Gronewald 2005), that SiO_2:Na_2O ratio, concentation and temperature plays a major role in producing and distribution of different polymeric structures in silicate solutions. In solutions with SiO_2:Na_2O ratio below 0.05, monomers dominate the distribution. Three-dimensional anions are most abundant at 2.5 and higher ratios. When SiO_2:Na_2O ratio is about 3.2 at increased temperature, the larger cyclic anions are relatively stable, while dimers and monomers increase. Moreover, it was shown that precipitation/ /gelling phenomenon occures during the reaction of silicates with polyvalent metal ions to produce metal silicate precipitates that are less soluble across a broader pH range than the metal hydroxides produced by non-silicate processes.

The ability of control phisicochemical properties of silicates by weight ratio of SiO_2 to Na_2O and advantages of silicates like environmentally friendly and low price should be a good alternative for polymers in the oil industry. Injection of silicate solutions into reservoir with the aim at enhancing the recovery factor through a diverting effect was proposed first by Hill (Hill 1922) claiming a patent in 1922. After many years results of laboratory reaserch and field tests of silicate gels for water shutt-off were presented (Robertson, Oefelein 1967). In the next papers (Cole, Mody, Pace 1981; Sparlin, Hagen 1984) phisicochemical properties of silicate were discussed, proving that the traditional grounting materials might be used successfully for IOR/EOR purposes.

Extensive review of patents and numerous papers concerning applying silicates in the EOR (Kurmine, Boyce 1985) was the base to express by the authors conviction that the permeability modification with silicate gel –based system is a viable alternative wherever the need arises. Krumrine and Boyce presented great variety of inorganic and organic compounds, and natural materials which cause gellation of water soluble silicates and thus the method might be adapted to diverse reservoir conditions. They noticed also that the silicates were inequitably neglated besides polymers in practice although in that technology using of toxic and carcinogenic chromium can be avoided, which is very often used, in the form of chromates and dichromates, as a crosslinking agent of polymers (Huang, Green, Willhite 1986; McCool, Green, Willhite 1991; Seright 1997).

By the laboratory studies researchers (Vinot, Schechter, Lake 1989) listed four possible reasons why the silicates have not been used more widely in practice, and among others they pointed out that the mechanism of silicate gelation, particularly under reservir conditions, is poorly understood, what in a significant extent impede designing and control of silicate injection process. Taking into account conclusions of Vinot and associates and also results of the previous investigations, in the Table 1 pros and cons of silicate well treatment techniques were summarized.

Recognizing the factors influencing unfavourably the properties of silicate gels as well as selection of the proper crosslinkers and structure and properties modifying additives were reported in the numerous papers and patents. Selection of the crosslinking agent is particularly important because it determines the radius of the silicate gel penetration. Interesting method of gelling silicates solutions was the proposition of enhanced oil recovery by the aplication of the reaction of silicates with injected into the well CO_2 by which the gel is form at some distance from the reservoir (Anderson 1946; Boston 1963; Elfrink 1966). In this kind of treatments dissolved in the water phase CO_2 as a carbonic acid (H_2CO_3) acts as the gelling agent by neutralizing the alkalinity. Using buffer slugs of natural gas or air were also proposed to isolate the silicate so that deeper penetration can be achived prior gelation. To the idea of CO_2 activated silica gels researchers came back as well later (Islam, Farouq 1993), cunducting a series of laboratory tests by which they proved that silicate activated by carbon dioxide can be applied in a wide range o permeability and thickness of the production zone and water zone. Moreover, authors showed that the optimum carbon dioxide requirement (in volume) was four time that of the sodium orthosilicate solution.

TABLE 1

Advantages and disadvantages of silicate well treatment techniques
(Vinot, Schechter, Lake 1989; Sandiford 1978)

TABELA 1

Zalety i wady stosowania w górnictwie naftowym żeli krzemianowych
(Vinot, Schechter, Lake 1989; Sandiford 1978)

Lp.	Advantages	Disadvantages
1.	Good placement selectivity caused by low viscosity of treating solutions	The gel is rigid and prone to fracture
2.	Short to moderate pumping time before onset of gelation	The gel show syneresis – it is prone to shrink
3.	Flexible chemical mechanism	Because of shrinking the blocking efficiency is changing in time, and it is never total
4.	Good chemical stability	Penetration of the treating solution is short if the buffer capacity of rock is high
5.	Excellent thermal and mechanical resistivity	It is hard to control the gelation mechanism because of the short setting time
6.	Easy gel breaking in case of technical failures	Silicates are prone to form precipitates instead of gel
7.	Simple and cost-effective surface technology	Alkaline silicates initiate intensive ion exchange, and hence, precipitation of multivalent cations
8.	The silicates are environmentally friendly materials (non-toxic chemicals)	Silicates change the interfacial properties, thus they enhance in-situ colloid chemical processes like emulsification, agglomeration etc.

As a result of measurments of the kinetics of polymerization of aqueous sodium silicate solutions upon acidification with sulfuric acid, it was found that for a given pH value, the polymerization rate increases with increasing SiO_2 concentration, ionic strength and accelerator concentration (Merril, Spencer 1950). Moreover, it was observed that an increase in temperature promotes more rapid gelation and pH value corresponding to the minimum gel time increased from 5.5 for salt-free solutions to 7 and above with increasing brine concentration.

Seventeen years later mixture of alkaline silicate and acid phosphate solution was proposed (Beecroft, Maier 1969). Addition of phosphates reduce influence of salinity of formation water on the gelling time. Two years later alkaline and acid silica gels were tested (Smith, Fast, Wagner 1969). Results of the laboratory and field tests excluded acid gel treatments because of the gelling time, which for alkaline silicates is up to several days what allows a much larger plug to be placed deeper into the formation. Typical acid gel treatments range up to a few hundred barrels whereas alkaline gel treatments have been applied in volumes ranging up to a few hundred barrels. In the case of using alkali silicates great impact on the treatment may have of alkali interaction with reservoir rock and ion exchange. As alkanity is depleted, the pH value falls therby accelerating gelation.

Chemical composition of the patented treatment fluid (Sandiford 1982) consisting of a water-soluble polmer (typically polyacrylamide or partialy hydrolyzed polyacrylamide) and an alkali metal silicate (typically a 3.2 ratio sodium silicate) for the purpose of making an effective plugging agent at times of two weeks to two months or more after injection of the reservoir, and then its modification (Sandiford 1973, 1977, 1978), is the example of avoiding chromium crosslinkers. The polymer and silicate were injected separately and mixed in the reservoir.

The silicate solution was thickened by a non-reactive cellulose polymer to improve and match the rate flow of both chemicals so that they were mixed and reacted uniformly. Such mixture were claimed to be free of gelling or crosslinking agent but form a high viscosity fluid with slight evidence of the gel structure.

Moreover, Sandiford proved that combination of the polymers and silicate gelling systems is more effective than either of the two systems individually. It was postulated that the silicates form stiff gels that can eventually breakdown if sufficient shear pressure is exerted by the reservoir fluids. On the other hand the polymer gels are much more flexible, but, they can be displaced and diluted by invading fluids. The combination makes a tougher resilient material, similar in its structure to copolymer ABS (acrylonitrile-butadiene-styrene) plastic blend, which can absorb a great deal of energy and retain its shape and properties.

This method is inexpensive, flexible and adaptable to any production technology what was proved during the treatments on Hungarian fields (Lakatos et al. 2000). Treatments which were conducted on Algyö field gave long lasting positive effects – water cut decreased significantly (>20%) immediately after the treatment and shown slow and gradual increase in time through many years and thereby substantial amount of oil production (over 8000 t).

In the patents claimed by Bernard and Sarem (Bernard 1970; Sarem 1974) was presented one of the most frequently used method of gelling time lengthening – sequentional injection of the fluid components. During the experiments alternate slugs of sodium silicate and calcium chloride solutions were injected to improve RF in heterogeneous reservoirs. Solutions of the silicate (from about 0.5 up to 5.0 weight percent) and calcium chloride (about 2% by weight) were mixed and reacted to provide precipitates at some distance into the reservoir. Such treatments were designed to affect permeability throughout the bulk reservoir, but not completely shut off any zone.

In 1981 treatment fluid consisting of sodium silicate (SiO_2/Na_2O ratio 2.0–3.2 and concentration >0.4 wt.%) and lignosulfonates (2–5 wt.%) was claimed by Lawrence and Feiber (Lawrence, Feiber 1981). It was observed that gelation times and strengths may be varied by controlling the concentration and ratio of silicate to lignosulfonate. Moreover, was confirmed that divalent cations increase the gelation rates.

In the same year Sydansk (Syndansk 1981) claimed two ways of reservoir rocks permeability modification. One of them based on sequential injections of the caustic and magnesium chloride solutions. The chemicals were mixed in the reservoir to form a magnesium hydroxide precipitate that blocks pores and alters flow profiles in the reservoir. Second method employs caustic to form an in-situ sodium silicate solution which then reacts with subsequently injected slugs of amphoteric metal salts.

Vinot et al. (Vinot, Schechter, Lake 1989) have shown that applying hydrolizable esters, introduced into the alkaline silicate solution as a dispersed phase (microemulsion), the gelation of system ensued even though the pH remained constant (>11). They also stated that as a result of a unique gelation mechanism, the properties of gel and the chance to have permanent and efficient formation barrier under extreme reservoir conditions were significantly improved

The results of that works had great importance because it was shown that replacement of the inorganic additive on organic one may significantly improve gel properties.

At the begining of 1990s were presented the results of the field treatments in which colloidal silica was used. Colloidal silica refers to stable aqueous dispersions of discrete nonporous particles of amorphous SiO_2 (Jurinak, Summers 1991). In total, eleven wells were treated with colloidal silica to solve a wide range of reservoir fluid-flow problems. A few of the permeability modification treatments were technical and economic succes. This work shown all the pros and cons of using silica comparing to sodium silicate (Table 2). One of the main disadvantage of silica application require higher SiO_2 concentration and particle size of silica, which may block pores and prevent deeper penetration of the treatment fluid.

In Saudi Arabia (Nasr-El-Din, Taylor 2005) was prepared treatment fluid with two gelling activators – urea (internal activator) and calcium chloride (external activator). The results of the laboratory experiments and pilot treatments shown that sodium silicate – urea system form a gel only at temperatures greater than 70°C, where urea decomposed and

TABLE 2

Comparison of advantages and disadvantages of colloidal silica and sodium silicate gels
(Iler 1979; Jurinak et al. 1991; Nasr-El-Din, Taylor 2005)

TABELA 2

Porównanie żelu koloidalnego dwutlenku krzemu oraz krzemianu sodu (Nasr-El-Din, Taylor 2005)

	Advantages	Disadvantages
Colloidal silica	– High SiO_2:Na_2O ratio >50 to 1 – Longer gelling time at pH 9 –solutions without salt1000 days; addition of brine bring the gel times into the same range as those for silicate solution without salt. – Particles form 3D network	– Required higher SiO_2 concentration – 6–15 wt. % – Silica present as particles – Silica particle size in the range from 4 to 200 nm – Particles reduce injectivity into low permeability zones but requires higher silica concentration what makes this technique more expensive
Sodium silicate gels	– Required lower SiO_2 concentration – 5 – 10 wt. % – Silica is present in solution – Silica particles form in solution and then create a 3–D network	– Low SiO_2:Na_2O ratio >4 to 1 – Shorter gelling time at pH 9 solution without salt – 1000 min, addition of salt accelerate gellation – The gel is weaker

products induced gelation. It is unquestionably advanture in the field aplication, because that fluid may be stored by the long period of time at the ambient temperature. The gelation time depends on urea concentration – gelation time decreased with increasing urea concentration. It was also observed that when sodium silicate concentration was about 7–8 wt.% and urea concentration was 3.6 wt.% the relationship between the gelation time and sodium silicate concentration exhibited a minimum. Higher urea concentration cause shorter gelling time and invoke syneresis. Moreover, Nasr-El-Din et al. (Nasr-El-Din, Taylor 2005; Nasr-El-Din et al. 1998) shown that sodium silicate – urea solutions can tolerate sodium chloride concentrations up to 3 wt.% and calcium chloride up to nearly 0.08 wt.%. Because of the quite high sensitivity to water salinity gel solutions should be prepared with fresh water that contains low concetration of divalent cations, what in the field condition is a great inconvenience. However, coreflood experiments with sodium silicate – urea gelling systems gave promising results – the gel reduced core permeability by at least three orders of magnitude, and was stable in the core at pressure gradients up to 56.6 MPa/m.

Taylor and Nasr-El-Din (Taylor, Nasr-El-Din 2003) proposed new group of the thermally responsive gelation activators. It has been found that combined or joint use of chelating agent (e.g. Al^{3+}, Fe^{3+}, Cr^{3+} and Sn^{3+} chelating compounds), phosphonate and termall responsive activator (e.g. sodium trichloroacetate, ethylacetate, hydrochloric acid, urea) increase the divalent ion tolerance of the silicate solutions, without affecting the gellation time or gel characteristic. Moreover, modification of the silicates by organic compounds cause increase of gel elasticity (Al-Nuntasheri et al. 2007).

2. Laboratory researches

One of the methods of reservoir energy subsistence during its exploitation is e.g. waterflooding. Water, prepared according to special procedure is injected into the reservoir by the system of the injection wells, which are situated on the reservoir contour in the most favorable way. If oil-water contour is plane the waterflooding process is carried out in a proper way. But very often reservoir is inhomogeneous because of differences in the reservoir rock permeabilities and water from waterflooding, in accordance with the Darcy law, flows first and foremost by the zones with higher permeability – by so called “preferential pathways”. In extreme cases water hold-up may occur and water from waterflooding appears in the producing well. In such a condition further exploitation has no sense because in practice there will be no increase of reservoir energy and production well will produce substantial amount of water.

The easiest way to avoid those problems is canceling of that “preferential pathways”. Injection of the chemical compounds to the high permeability zones is the easiest method for reducing water flow between injection and production well. Polymers are the most frequently used chemical compounds because during the gellation process they cause loss of filtration properties of the high permeability zones.

High molecular weight polymers, which are mixed with gelling reagents before the injection, are the current most frequently used method for permeability modification. The most popular and widely used types of systems are petroleum-based polyacrylamide polymers crosslinked with chromium ions Cr^{3+}. It was estimated that chromium-based polymer gel has been used in more than 1,400 treatments worldwide. It shows, not only broad applicability of that systems but also the extent of environmental risk associated with use of toxic chromium. Because of the restrictions connected with environmental protection and high price of used polyacrylamide oil industry has searched new ways of canceling high permeability zones.

There is one main reason of searching for new systems for permeability modification of reservoir rocks. Average distance between exploitation and injection wells has a few hundred meters. To obtain permeability modification the high-permeability layer has to be filled with gelling system to the maximum. And here appear very serious technical problem because the longer zone to make injection the treatment will take longer period of time what force longer gelling time of the used treatment fluid.

The most often gelling time of the treatment fluid is extended by using lower concentration of gelling fluid or by addition of reaction inhibitors. However, that has natural limitation resulting from the fact that with lower initial concentration of treatment fluid deterioration of the gel properties can be found what may cause very short durability of the results of that kind of treatment. In Oil and Gas Institute in Krakow (POGI), within the works carried out associated with preparing of the technology for water shut-off treatments several commercial chemical agents were tested. All of the evaluated systems performed in accordance with above-mentioned scheme.

Application of pH-dependent gels during the permeability modification treatments is interesting alternative to chemical crosslinked gels. Chemical compounds which gellation is pH-depentent usually are stable at high pH and low viscosity and form gel as a result of decreasing pH. Gellation mechanism of that kind of systems consists of injection of alkaline solution of pH-dependent gelling agent and subsequently sequential injection (introduction) of the pH modifying agent. Apparently mechanism of that treatment seems to be easy but injection of the pH modifying agent with appropriate delay pose very comlex problem because of the unknown reactions mechanism which take place in reservoir condition.

Results of the research work which were performed at the begining of the 21-st century in which as a pH modifying agent were used hydrolysable esters, urea or ion exchange with reservoir rock have shown that all of the above mentioned systems are extremely complex and because of it very difficult to apply in practice.

Taking into account all the above mentioned results, factors which have influence on effectiveness of the reservoir rock permeability modification treatments can be summarized as follows:

- reservoir conditions (lithology, reservoir temperature, salinity, homogenous of the reservoir structure),
- well acompletion,

- mechanism of water inflow to the well,
- appropriate selection of the gelling system (polymers, resins or silicates),
- the way of gelling system injection to the proper reservoir zone (using of Coiled Tubing, simultaneous injection to two zones).

To recapitulate can be said that all the works connected with gelling system injection to high-permeability zone should be completed before the end of few hours. Taking into account that during that few hours gelling system has to be prepared next injected to the formation and extruded from the CT treatment time seems to be very short. One of the most promising agents to modification of the high-permeability zones are biocatalyzed silicate gels.

Despite very intensive research work gelling mechanism of the silicate system in the reservoir conditions is still unknown. Lack of that information cause that selection of appropriate additives extending gelling time and improving gel properties is very difficult. Moreover, complexity of the systems which contains organic and inorganic additives cause difficulties in industrial applications. Gelling time can be extended by the using microbiology to the pH modification what limit the number of chemical additives, facilitate process control and improve treatment economy.

At the end of the nineties Bailey at all (Bailey, Bryant, Duncan 2000) showed that fairly sufficient way of Curdlan biopolymer gelling process initiation and control is using of special bacterias strains. Curdlan biopolyer at pH about 10 is a low viscous solution. At solution pH equal to 9.5 gelling process is initiated and solution is converted into gel. Lowering the pH was performed by a special bacteria strains which produce acid (acetic acid, formic acid etc.), that is by using biocatalyst. Several laboratory experiments were performed which tentatively confirmed usefullness of isolated strains to the permeability modification of the porous rocks. It was shown by the several experimental works that gelling process with addition of biocatalyst may last from a few to a few hundred hours, what has great importance in practical applications. Using that kind of systems permit significant extension of the injection time of low viscosity gelants.

Such a process could be adapted to alkaline silicate solutions, although there are still a great number of technical problems (Table 1) which prevent immediate commercialization of that technology.

To make this technology useful to commercial use is advisable to perform appropriate laboratory tests e. g. by factor method of succesive approximation. These experiments should simulate in the maximum way reservoir conditions as regards thermobaric and technological conditions. With the high probability that process can be simulated by the lab stand of the Temco Inc Company (USA), which there is in POGI Krakow.

3. Experimental studies

During the years 2007–2008 introductory tests of the effectiveness of biocatalyzed silicate gel system in permeability modification of porous rock were performed in POGI.

Nine cylindrical plugs were cut from sandstone. Plugs dimensions were following: diameter: 25.2 mm, length: 400 mm. According to a standard procedures (Falkowicz 2000) absolute permeability k_{abs} and effective initial permeabilities $k_{p\mathrm{s}}$ for brine at non-reducible gas saturation (S_{gi}) of plugs were estimated. Then buffer fluid to the plugs was injected. This operation has very big practical significance. As it was mentioned before the idea of biocatalyzed silicate treatment fluid base on changes of silicates rheological properties under the influence of pH changes. Initial pH of treatment fluid is equal to 11. During the treatment fluid is injected to the reservoir where pH of formation water usually assume values from the range from 6 to 8. The result of the direct contact of treatment fluid with formation water would be rapid gelling of silicate. In vast majority of cases process would occur in near wellbore area so permeability modification of larger reservoir zones would be from technical poin of view impossible. This problem in practice is solved by applying buffer so called "spearhead". During the experimental works solution of sodium carbonate with addition of phenolphtalein was used as a buffer fluid. The solution pH was equal to 11, what makes its colour turn to violet. The solution was injected to the plug till the fluid which was flowing out from the core had initial colour of the buffer fluid. It meant that whole sample is full of the alkaline fuid with pH = 11.

For coreflood experiments, sodium silicate gel systems were prepared using solution of sodium silicate with following properties: SiO_2:Na_2O ratio – 3.11, content of Na_2O – 9.5%; content of SiO_2 – 29.5%; density ca. 1420 kg/m^3; pH = 11.5. In prepared systems sodium silicate concentration lower than 2% were used because at higher concentrations gellation process has started in the course of few hours.

Four treatment fluid systems with different sodium silicate concentration (1 – 0.5%; 2 – 0.75%; 3 – 0.1%; 4 – 0.75%) were prepared. In the case of fluid number 4, basis of previous tests, modified bacterial nutrition was applied. To all fluids alkaliphilic bacteria were added in the proper amounts to obtain final concentration ca. 1×10^2 in 1 ml. After injection of the fluid to the plugs in anaerobic conditions two-week incubation period at the temperature equal to 40°C was applied. After that period final plugs permeabilities k_{ks} for brine were obtained and thereby changes (loss) of permeability were evaluated.

4. Results and discussion

The aim of laboratory work was preliminary confirmation about usefulness of silicate solutions to permeability modification of porous reservoir rocks with addition of biocatalyst. Results of the tests are shown in a Table 3.

4.1. Loss of permeability

To the plugs marked as 1 and 2 the treatment fluid number 1 were injected. During two-weeks incubation period neither noticeable pH changes nor viscosity changes of the

TABLE 3

Results of lab tests

TABELA 3

Uszkodzenie przepuszczalności piaskowca biokatalizowanym żelem krzemianowym

Plug	Treatment fluids	pH changes of treatment fluid	Initial viscosity of treatment fluids [mPas]	Viscosity of treatment fluids after 14 days [mPas]	Absolute permeability of plug for gas k_{abs} [mD]	Initial permeability k_{ps} for 2% KCl [mD]	Final permeability k_{ks} for 2% KCl [mD]	Loss of permeability [%]
1	1	No changes	1.02	1.4	921	61.0	18.0	**70.5**
2	1	No changes	1.02	1.4	177	2.3	2.2	**4.3**
3	2	No changes	1.07	1.4	1 208	160.0	44.0	**72.5**
4	2	No changes	1.07	1.4	392	11.0	4.3	**60.9**
5	3	from 11 to 8	2.6	4.77	456	9.5	2.2	**76.8**
6	3	from 11 to 8	2.6	4.77	381	19.0	3.8	**80.0**
7	4	11 na 8.5	2.7	6.05	491	61.0	20.0	**67.2**
8	4	11 na 8.5	2.7	6.05	392	8.8	0.9	**89.9**
9	4	11 na 8.5	2.7	6.05	264	28.2	2.12	**92.5**

prepared fluid were noticed. Only insignificant precipitation of silicates from the treatment fluid occurred and its sedimentation on the bottom of the vessels on which incubation of cores were performed. Loss of permeability of the plugs marked as 1 and 2 were estimated on the level of 70% and 4%, respectively (Table 3). During the tests of final permeability whole out flowing brine was collected in a transparent vessel. It was noticed that bottoms of the vessels were covered by the removed from cores gelled silicates precipitates.

Similar results were observed in case of cores marked as 3 and 4 but it was noticed that precipitates on the bottoms of the vessels were bigger than in the case of cores 1 and 2. It was caused by the higher concentration of silicates in initial fluid. In this case also changes of pH were not observed. Losses of permeability (formation damage) were noted as equal to 73% and 61%, respectively.

Fluid number 3 was modified and injected to the core 5 and 6. In that case process exhibit similar effects as it was expected. First of all, after ca. 14 days change in pH from 11 to 8 and gelling within the whole volume was noticed. Moreover, there was no precipitate on the bottom of the vessel in which fluid flowed out from the core 3 was collected. Permeability damage was noted on the level of 77 and 80% respectively.

Experiment was repeated, but as treatment fluid was used fluid number 4, which was injected to cores marked as 7, 8 and 9. After ca. 72 hours precipitation of silicate gel was observed. The drop in the pH values was noticed after 12 days from fluid treatment preparation. In the these plugs permeability losses were observed on the level of 67%, 90%, 93%, respectively. Like in the previous tests filtrate, which flowed out from cores during final permeability measurement, was accumulated in the vessels. There was no evidence of silicate in the filtrate.

Figure 1 shows changes in differential pressure gradient in the cores number 4 and 8 during the final permeability k_{ks} measurement. That curves have typical course for that kind of experiments. The shape of the both curves gives us significant information regarding phenomenon which occurs in the porous space of the tested sandstone samples during brine flow. At the beginning pressure gradient increase rapidly and reach maximum value. After maximum point less or more sharply drop was observed and then after some time stabilization was reached. The scale and dynamics of the changes in pressure gradient result from the range and rate of silicate removal which were injected to the tested cores.

The more particles of silicate is removed by brine the more decline in pressure gradient will be observed. The trend of the curves depicted on Fig. 2 show that from core number 4 (treatment fluid number 2), flowing brine removed more silicates then from the core number 8 to which treatment fluid number 4 was injected. In the case of core number 8 displacing forces were too small to defeat adsorption forces of silicate molecules on the walls of sandstone pores and silicate was not removed what caused 90% drop of permeability of that core. The factor, which control the process are electrokinetic phenomena which occures on the silicate surface in brine environment with different pH.

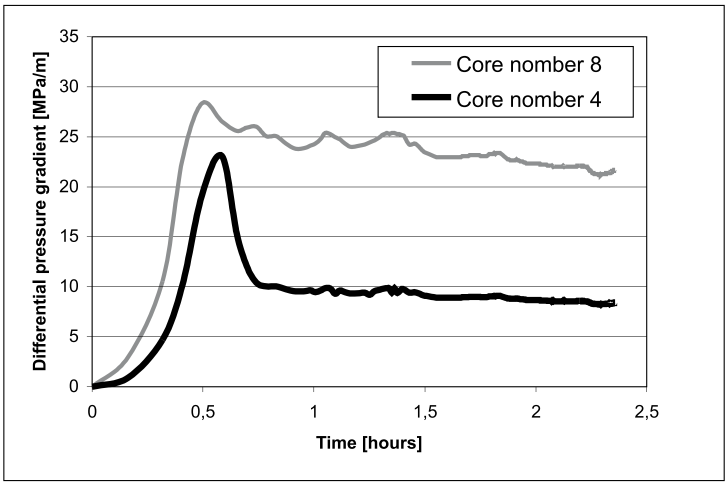

Fig. 2. Differential pressure gradient changes during final permeability measurement

Rys. 2. Zmiany gradientu różnicy ciśnienia w rdzeniu podczas pomiaru przepuszczalności końcowej piaskowca

4.2. Electrokinetic phenomena in biocatalysis process

Silicates like every colloidal solution have very high surface and as a result high excess in free energy. It always in spontaneous process pursues to decrease in free energy excess and as a result to decrease of its surface. Colloidal particles will aggregate in bigger units what cause formation more or less steady gel and precipitation from solution. Above mentioned process is controlled by the balance of the electric forces which are results of electric charge adsorbed at the colloidal particles surface.

Surface potential is estimated by means of electrokinetic potential or zeta potential ξ (zeta or dzeta), which potential difference between the adsorbed layer and bulk solution. In laboratory practice ξ potential is calculated from Smoluchowski equation (1) that combine velocity v of mobility of colloidal particle charged in the electric field with known intensity E at the centre with dielectric constant ε and dynamic viscosity coefficient η:

$$v = \frac{E \cdot \varepsilon \cdot \xi}{4 \cdot \pi \cdot \eta} \tag{1}$$

Plugging of the sandstone porous space was the main aim of injectin colloidal solution of sodium silicate in experiments described above. Average diameter of sandstone pores which were used in experiments is ca. 10^{-5} m, and size of the silicate colloidal particle is about $5 \cdot 10^{-8}$ m. At low silicate concentrations in treatment fluids mechanical and short time of experiments (only a few PVs have been pumped through the plug) permanent sandstone plugging seems to be hardly propably. That process is permanent only when silicates colloidal particles are permanently adsorbed at the sandstone pore walls. In that specific case in all probability may be said that double-layer potential of silicate particles in standstone pores is in sign and value similar to double-layer potential of quartz grains which forms sandstone. Double-layer potential depends on pH value and brine mineralization level which contact with silicate particles or sandstone grains.

Zeta potential, decrease with salinity increase and decrease of pH solution. It explains why used sodium silicate solutions were steady at pH ca. 11 and salinity not higher than 0.5% NaCl. That regularity may be explanation of phenomenon which was described above i.e. the presence of the silicates in filtrate. Brine pumped through plugged core removed significantly less silicate particles in the case when decrease of treatment fluid pH ensued. In that case second from described conditions occurred. At lower pH, forces binding solution particles to sandstone grains (Van der Waals bonds) are sufficient to bind them with sandstone grains and oppose to displacements forces. However, confirmation of that conclusion requires undoubtedly arduous laboratory research work from practical point of view is very profitable. After treatment fluid pH decrese, silicate particles are harder removed from sandstone by the flowing fluid. That kind of permeability modification will be permanent and treatment effectiveness will be good.

How it was mentioned before during the discussion of the results shown in Table 3 the highest permeability changes were observed in the case of treatment fluids number 3 and 4. That fact was explained by significant stabilization of the accumulation condition of silicate particles in the sandstone plug.

Conclusions

1. One of the most promising agents to shutting off reservoir zones with high permeability rocks are silicate gels with addition of biocatalyst used for pH control of treatment fluid.
2. The results of the experiments which were performed at POGI shown that in the case when decrease in pH of treatment fluid occured less particles of silicates was removed by brine pumped through plugged core. Results presented in Table 3 shown that the highest permeability changes were observed of treatment fluid number 3 and 4. That fact was explained by significant stabilization of the accumulation condition of silicate particles in the sandstone core.
3. The more molecules of silicate is removed by brine the more decline in pressure grabient is observed (Fig. 2). The trend of the curves depicted on Fig. 2 shows that from core number 4 (treatment fluid number 2), flowing brine removed more silicates then from the core number 8 to which treatment fluid number 4 was injected. In the case of core number 8 hydraulic flow forces were too small to defeat adsorption forces of silicate molecules on the walls of sandstone pores and silicate was not removed what caused 90% drop of permeability of that core. The factor, which control the process are electrokinetic phenomena which occures on the silicate surface in brine environment with different pH.

Acknowledgments. The authors wish to thank Piotr Kapusta Ph.D. from POGI Krakow for manufacturing solutions of microbes used in lab tests.

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BIOCATALIZED SILICATE GELS IN OIL AND GEOTHERMAL INDUSTRY

Key words

Water shut-off, oil and geothermal water exploitation, improved oil recovery, reservoir rocks permeability modification, laboratory testing of silicate gels, biocatalysis

Abstract

Technologies using silicates have become accepted worldwide as cost-effective solutions for enhancing oil production. Despite very intensive research work gelling mechanism of the silicate system in the reservoir conditions is still unknown. Selection of appropriate additives extending gelling time and improving gel properties is very difficult because of the lack of that information. Moreover, complexity of the systems which contains organic and inorganic additives cause difficulties in industrial applications.

This paper presents complex literature review which gives complete picture on the use and application of silicate based systems for water shut-off and enhancing oil recovery. Moreover, it shows new way of pH-dependent silicate gels application during the permeability modification treatments as an interesting alternative to chemical crosslinked gels. Gelling time of that system can be extended by the using microbiology to the pH modification what limit the number of chemical additives, facilitate process control and improve treatment competitiveness.

The effect of biocatalyzed silicate gels on porous rocks was tested in the reservoir conditions on the lab stand of the Temco Inc Company (USA). Experimental results of coreflooding experiments indicated that silicate gel system may cause decrease of core permeability in the range from 60 to 90%.

BIOKATALIZOWANY ŻEL KRZEMIANOWY W PROCESACH EKSPLOATACJI ZŁÓŻ ROPY NAFTOWEJ I WÓD GEOTERMALNYCH

Słowa kluczowe

Eksploatacja złóż ropy naftowej oraz wód termalnych, modyfikacja przepuszczalności skał zbiornikowych, badania laboratoryjne żeli krzemianowych, biokataliza

Streszczenie

W publikacji przedstawiono kompleksowy przegląd literatury fachowej dotyczącej zastosowań żeli krzemianowych w górnictwie naftowym. Jak wynika z przytoczonych wyników wieloletnich badań, do czynników wpływających na skuteczność zabiegu modyfikacji przepuszczalności skał złożowych można zaliczyć:

— rodzaj warunków złożowych (litologia, temperatura złożowa, zasolenie, jednorodność budowy złoża),

- sposób udostępnienia warstwy produktywnej,
- mechanizm dopływu wody do odwiertu,
- odpowiedni dobór układu żelującego (polimery, żywice lub krzemiany),
- sposób zatłaczania żelu do właściwej strefy złożowej (użycie Coiled Tubingu, jednoczesne zatłaczanie do dwóch stref).

Reasumując można stwierdzić, że wszystkie prace związane z zatłoczeniem żelu do strefy o podwyższonej przepuszczalności należy zakończyć przed upływem kilku godzin. Wliczając w to czas potrzebny na przygotowanie żelu oraz wytłoczenia żelu z Colied Tubingu, jest to czas bardzo krótki. Jednymi z najbardziej obiecujących środków do likwidacji stref złożowych o wysokich przepuszczalnościach skał są żele oparte na bazie krzemianów.

Mimo intensywnych badań w dalszym ciągu nie został do końca poznany mechanizm żelowania krzemianów w złożu, co utrudnia dobór odpowiednich dodatków wydłużających czas żelowania oraz poprawiających właściwości żelu, a złożoność systemów zawierających dodatki organiczne i nieorganiczne powoduje utrudnienia w zastosowaniach przemysłowych. Zastosowanie mikrobiologii w celu modyfikacji pH znacznie wydłuża czas żelowania, a ponadto ogranicza liczbę dodatków chemicznych, przez co ułatwia kontrolę i poprawia również ekonomikę zabiegu.

Jednak, aby technologia ta była przydatna do komercyjnego wykorzystania wskazane jest wykonanie odpowiednich testów laboratoryjnych, np. metodą czynnikową kolejnych przybliżeń. Testy te powinny w maksymalnym stopniu symulować warunki złożowe pod względem termobarycznym i technologicznym.

Ze znacznym podobieństwem proces ten można symulować dzięki aparaturze firmy Temco Inc (USA) będącej na wyposażeniu Instytutu Nafty i Gazu w Krakowie. Celem przeprowadzonych badań laboratoryjnych była wstępna ocena przydatności roztworów krzemianów do likwidacji przepuszczalności porowatych skał zbiornikowych z wykorzystaniem biokatalizatorów. Do przygotowania cieczy zabiegowej użyto roztworu krzemianu sodu o następujących właściwościach: stosunek SiO_2/Na_2O – 3,11; zawartość Na_2O – 9,5%; zawartość SiO_2 – 29,5%; gęstość około 1420 kg/m^3; pH = 11,5. W przygotowanych cieczach stosowano stężenia krzemianu sodu niższe niż 2%, bowiem po przekroczeniu tego stężenia proces żelowania krzemianu rozpoczynał się w przeciągu kilku godzin, co jest czasem zbyt krótkim z punktu widzenia wykorzystania tej technologii w praktyce.

Przygotowano cztery ciecze zabiegowe różniące się stężeniem krzemianu sodu:1 – 0,5%; 2 – 0,75%; 3 – 0,1%; 4 – 0,75%.W przypadku cieczy nr 4, na podstawie wyników wcześniejszych testów, zastosowano zmodyfikowaną pożywkę dla mikroorganizmów. Do wszystkich cieczy dodawano mikroorganizmy alkalifilne w ilościach takich, aby ich końcowe stężenie wynosiło około $1 \cdot 10^2$ w 1 ml. Po zatłoczeniu do rdzeni cieczy zabiegowej w warunkach beztlenowych, poddawano procesowi dwutygodniowej inkubacji w temperaturze 40°C. Po tym okresie określano przepuszczalność końcową rdzeni k_{ks} dla solanki, a tym samym określano zmiany (utratę) ich przepuszczalności.

Do rdzeni oznaczonych numerami 1 i 2 zatłoczono ciecz oznaczoną nr 1. W czasie dwutygodniowej inkubacji nie stwierdzono zauważalnych zmian pH, ani lepkości przygotowanej cieczy. Nastąpiło tylko nieznaczne wytrącenie się krzemianów z cieczy i ich sedymentacja na dnie naczynia, w którym inkubowano rdzenie. Stwierdzono uszkodzenia przepuszczalności rdzeni o numerach 1 i 2 odpowiednio 70% i 4% (tab. 3). Podczas pomiaru przepuszczalności końcowej solanka przepływająca przez testowany rdzeń w całości gromadzona była w przezroczystym naczyniu. Stwierdzono, iż dno naczynia pokrywa zżelowany osad usuniętych z rdzenia krzemianów.

Podobną sytuację stwierdzono w przypadku rdzeni oznaczonych numerami 3 i 4. Daje się jednak zauważyć na dnie naczynia większą ilość usuniętych krzemianów, niż w przypadku rdzeni 1 i 2. Jest to spowodowane większą ilością krzemianów w roztworze wyjściowym. W tym przypadku również nie stwierdzono zmian pH cieczy żelującej. Zanotowano odpowiednio 73% i 61% uszkodzenie przepuszczalności rdzeni.

Wprowadzono modyfikację w składzie cieczy nr 3, którą zatłoczono do rdzeni 5 i 6. W tym przypadku proces przebiegał w sposób zbliżony do oczekiwanego. Po pierwsze, stwierdzono po ok. 14 dniach zmianę pH cieczy z 11 na 8 i żelowanie cieczy w całej objętości. Nie stwierdzono osadu w pojemniku, w którym zgromadzono ciecz wypływającą z rdzenia 3. Tak więc, przepływająca solanka nie usuwała w tym przypadku z rdzenia krzemianów. Stwierdzono uszkodzenia przepuszczalności na poziomie 77% i 80%.

Następnie przygotowano ciecz oznaczoną numerem 4, którą zatłoczono do rdzeni o numerach 7, 8 i 9. Po około trzech dobach zaobserwowano wytrącanie się żelu krzemianowego. Zmiany pH roztworu odnotowano po

12 dniach od przygotowania cieczy roboczej. W testowanych rdzeniach stwierdzono zmiany przepuszczalności odpowiednio 67%, 90% i 93%. Były to największe, a zarazem najtrwalsze zmiany przepuszczalności ze wszystkich testowanych rdzeni. Jak w poprzednich eksperymentach, również w tym przypadku gromadzony był filtrat wypływający z rdzenia podczas pomiaru przepuszczalności końcowej. Wizualnie nie stwierdzono obecności krzemianów w zgromadzonym filtracie.

Na rysunku 1 pokazano zmiany gradientu różnicy ciśnienia w rdzeniach nr 4 i 8 w trakcie pomiaru przepuszczalności końcowej $k_{ks.}$ Zmiany te mają typowy przebieg dla tego typu eksperymentów. Kształt obu krzywych dostarcza istotnych informacji, co do zjawisk zachodzących w przestrzeni porowej testowanych piaskowców podczas przepływu przez nie solanki. Na początku gradient ciśnienia gwałtownie rośnie i osiąga wartość maksymalną, aby potem mniej lub bardziej gwałtownie spadać i po pewnym czasie osiągnąć stabilizację. Wielkość i dynamika zmian (spadku) wartości gradientu różnicy ciśnienia wynika z zakresu i tempa usuwania krzemianów jakie zostały zatłoczone do testowanych rdzeni. Im więcej przepływająca solanka usunie z rdzenia cząsteczek krzemianów tym spadki gradientu różnicy ciśnienia będą większe. Kształt krzywych pokazanych na rysunku 1 pozwala na stwierdzanie że z rdzenia 4 (ciecz robocza 2) przepływająca solanka usunęła więcej krzemianów niż z rdzenia 8, do którego zatłoczono ciecz roboczą 4. W przypadku rdzenia 8 siły hydraulicznego unoszenia nie były w stanie pokonać sił adsorbujących cząsteczki krzemianu na ścianach por piaskowca i krzemian nie został usunięty powodując 90% spadek przepuszczalności tego rdzenia. Czynnikiem, który steruje tym procesem są zjawiska elektrokinetyczne zachodzące na powierzchni krzemianów w środowisku solanek o różnym pH.