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KINETICS OF A SILICATE COMPOSITION GELATION IN PRESENCE OF REACTION RATE REGULATING COMPOUNDS

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Abstract.*The influence of organic and inorganic additions on the formation rate of the silicate gels standard systems – sodium silicate solution in model fresh water was studied. As a result of the experiments were selected optimum concentrations of additives – gelation time regulators.*

Keywords: gelation time; inorganic additives; organic acids; sodium silicate; standard system.

1. Introduction

It is known that the rate of gelation of silicate compositions depends on the concentration of silicate, salinity and temperature. The most important factor determining the formation of silica gel is pH of a composition that characterizes the ratio of soluble silicates and insoluble silicate acid in solutions [Zhdanov 2001].

It is also known that the gel formation is accompanied by an increase in viscosity of the composition. The dependence of viscosity on time is very well described by the hyperbolic function. A similar pattern is observed at hydrogel formation in polymer systems.

The initial stage of gel formation is characterized by a slow increase in viscosity while dependence of viscosity on time is almost linear.

Probably the increase in viscosity is determined by the increase in the number and size of microgel particles and can be described by Einstein's famous equation

$$\mu = \mu_o (1+2{,}5\varphi),$$

where μ – viscosity of disperse systems;

μ_o – the viscosity of the solvent;

φ – volume concentration of microgel particles .

With increase of particle size and formation of spatial grid the Einstein's law is not applicable, the viscosity of the system increases dramatically, exceeding viscosity of the solvent in hundreds and thousands times.

2. Describing the problem

Mention above patterns were taken into account at choosing the different compounds used, and which had significantly affected the kinetics of gelation.

Primarily it was studied the effect of inorganic and organic compounds on the rate of gelation of silicate solutions.

During exposure the silicate to the layer as “crosslinking agent” is used mainly hydrochloric acid. Undoubtedly, the replacement of hydrochloric acid unto another, inorganic or organic acid will reflect in the kinetics of gelation. Selection of inorganic and organic compounds that could influence the kinetics of gelation of silicate solutions was carried out empirically, basing on general concepts of kinetic of regularities of gels formation in aqueous solutions [Burdunev, Saks 1978]. Thus the main objective was to find compounds that can significantly slow down the process of gelation. In the first stage of studies it was expected to find several effective additives.

The influence of various compounds on the rate of formation of silica gels study was performed on standard systems - solutions of sodium silicate in model fresh water. Gelation time was determined visually and evaluated by the loss of fluidity of the composition.

The range of investigated additives was quite broad and included more than 30 compounds. These compounds can be divided into several groups:

1) Organic substances:
- Monobasic acids;
- Two- and threebasic acids;
- Salts of organic acids;

2) Inorganic substances:
- Mineral acids;
- Hydrolysing salts;
- Additives that are used for the synthesis of polymers.

Regarding the latter it should be mentioned that some randomly selected compounds (thiourea, potassium iodide, sodium nitrate) normally used as stabilizers at polymers degradation, have shown some interesting properties.

It should be noted also that the most of the investigated substances either accelerate the gelation formation *t* compared with a standard “cross-linking” agent - hydrochloric acid at the same pH, or the gelation times in such systems and in the standard system remain the same.

Fig. 1 and Table 1 show the kinetic parameters of gel formation in 4% silicate composition, where the “crosslinking agent” are fatty acids C_1-C_3.

These acids are weaker than the hydrochloric acid.

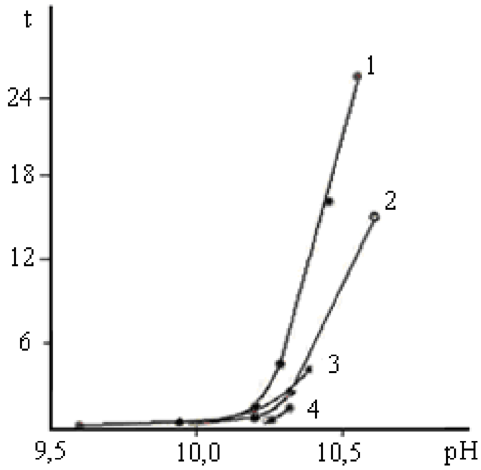

Fig. 1. Dependence of gelation time on pH at using acid as a “crosslinking agent”:
1 – hydrochloric acid;
2 – acetic acid;
3 – formic acid;
4 – propionic acid

In turn, the acid strength decreases with increasing number of alkyl substituents. In this case, formic acid is the most strong and propionic - the weakest.

Fig. 1 and Table 1 show that the organic acids while neutralizing sodium silicate accelerate the formation of gel in comparison with hydrochloric acid. Moreover, with increasing length of the alkyl substituent (or decreasing acid strength) the rate of gelation increases. As a result formic acid reduces the gelation time in approximately 1.5 times in acetic in 2, and propionic in 5-6 times.

Perhaps this phenomenon is due to the fact that counter-ions (negatively charged alkyl groups) participating in the formation of the electrical double layer on the surface of colloidal particles affect the increase of its size.

With increasing the size of counter-ions increases the size of the particles and thus accelerates the gelation. Mineral acid - sulphuric, boric accelerate gelation only marginally. Kinetics of gelation in the presence of phosphoric acid is slightly different from the kinetics in the standard system.

At using salts that undergo hydrolysis was mostly observed a negative effect on the rate of gelation. In particular, the introduction of silicate solutions of one-, two-, and trisubstituted sodium phosphate in an amount of 0.5–1% the rate of gelation was increased by 2-4 times. Adding sodium tetraborate in the same amounts lowers gelation time approximately in order of one magnitude. This fact complicates the use of these compounds in reducing of the extraction of sand from the oil-bearing rock layer.

On the basis of the experiments it was found that quite promising additives - regulators gelation time are polybasic organic acids and inorganic additives - nitrates, iodides and thiourea.

Table 1. Gelation time in 4% sodium silicate solutions at 20 °C using different acids

Hydrochloric acid			Formic acid			Acetic acid			Propionic acid		
Concentration, %	pH	Gelation time, min	Concentration, %	pH	Gelation time, min	Concentration, %	pH	Gelation time, min	Concentration, %	pH	Gelation time, min
0,60	10,55	1500	0,97	10,38	240	1,15	10,61	900	1,60	10,32	65
0,65	10,46	1080	1,06	10,21	55	1,41	10,32	150	1,67	10,26	40
0,70	10,29	280	1,10	9,94	15	1,48	10,20	38	1,70	10,25	20
0,75	10,20	80	-	-	-	1,60	9,95	13	-	-	-
0,80	9,94	25	-	-	-	1,78	9,40	1	-	-	-
0,85	9,59	8	-	-	-	-	-	-	-	-	-
0,90	9,40	2	-	-	-	-	-	-	-	-	-
0,95	8,97	0,5	-	-	-	-	-	-	-	-	-
1,00	8,52	0,12	-	-	-	-	-	-	-	-	-

3. Discussion of Results

Based on the experiments were chosen most promising additives - regulators of gelation time.

Experiments show that neutralization of sodium silicate with simple dibasic acid - oxalic acid leads to an increase in gelation time compared to the standard system (Fig. 2, Table 2).

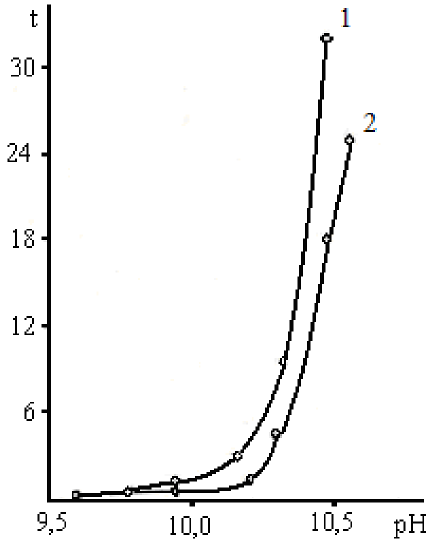

Fig. 2. Kinetics of gelation in 4% solution of sodium silicate in presence of acid as "crosslinking agent":
1 – oxalic acid;
2 – hydrochloric acid

The rate of formation of gel in the presence of oxalic acid was in 1.5-2 times smaller than in the standard system. Since oxalic acid is weaker than hydrochloric, then its spending was a bit greater.

When using citric acid as a "cross-linking" agent were obtained positive results, but an insufficient number of experiments can not categorically assert the efficiency of this reagent.

Very interesting results were obtained in the study of kinetics of gelation in the presence of salt additives - sodium nitrate $NaNO_3$, potassium iodide KI and thiourea $CS(NH_2)_2$.

In these experiments into solutions of sodium silicate the compounds mentioned above were introduced in different quantities, adjusted the concentration of additives in range 0,025–0,15%. Then in solution was added phosphoric acid to obtain the set value of pH.

It should be borne in mind that in the experiments with the indicated additives used another brand of liquid glass, which affected the position of the kinetic curves.

As it is known, the grade of sodium silicate, or rather its structure, greatly affects primarily the kinetics of the gelation. Mismatch of dependence of gelation time on pH in different experiments, in our opinion, is irrelevant, since in these studies the role of modifying additives were evaluated in parallel experiments under the same conditions when comparing solutions, in comparison with the standard system.

Naturally, in the case of industrial application of a modifying additive there will be counted gelation time of a sample of sodium silicate to be used in the processing of wells [Kleshchenko et al. 2003].

Table 3 presents data for the gelation time as a function of pH for the compositions in the presence of all three of these additives.

In Figs 3–5 is shown the influence of concentration of additives introduced during gelation.

Requires an additional study and explanation the fact that the optimum concentration of additives that most slows down gelation, lays within 0,025–0,05%. With further increase in the additives concentration the gelling process accelerates.

These trends are marked for all three additives in the study of the kinetics of gelation with viscosity metric method.

Table 2. Time of silica gel formation as a function of pH in the presence of hydrochloric and oxalic acids

Hydrochloric acid			Oxalic acid		
Concentration, %	pH	Gelation time, min	Concentration, %	pH	Gelation time, min
0,60	10,55	1500	0,95	10,46	1960
0,65	10,46	1080	1,00	10,31	560
0,70	10,29	280	1,05	10,15	180
0,75	10,20	80	1,10	9,94	70
0,80	9,94	25	1,15	9,78	20
0,85	9,59	8	-	-	-
0,90	9,40	2	-	-	-
0,95	8,97	0,5	-	-	-
1,00	8,52	0,12	-	-	-

Table 3. Gelation time for standard systems and compositions containing additives, %

pH	The standard system	Concentration of thiourea			Concentration of iodide potassium				Concentration of sodium nitrate		
		0,025	0,05	0,10	0,025	0,05	0,10	0,15	0,025	0,05	0,10
8,9	10	-	-	-	-	60	65	25	-	25	-
9,0	25	55	80	60	60	110	100	-	60	35	-
9,1	40	80	75	55	110	190	165	60	110	60	50
9,2	90	120	230	190	-	420	-	120	220	120	80
9,3	180	230	420	350	420	720	270	250	420	270	180
9,4	270	900	840	-	-	1400	-	500	-	540	-
9,5	400	1860	1800	720	1440	--	540	-	1260	1200	360
9,6	570	-	6400	-	-	--	-	1400	-	-	-

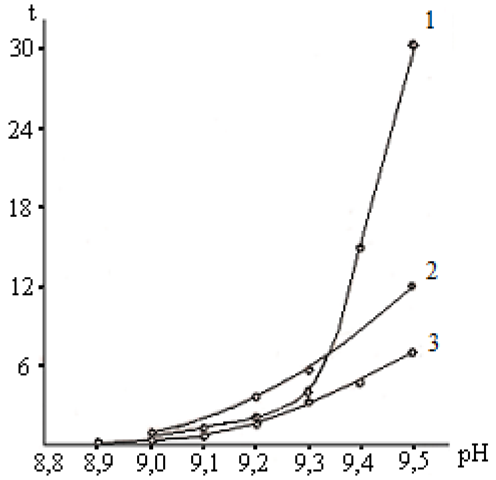

Fig. 3. Gelation time dependence on pH for compositions based on 4% sodium silicate solution:
1 – concentration of thiourea – 0,025%;
2 – concentration of thiourea – 0,105%;
3 – standard system

In Fig. 6 and Table 4 is shown the change in relative viscosity of silicate compositions over time, depending on the concentration of thiourea.

The pH, which was achieved by neutralization of phosphoric acid silicate, in all experiments was constant and equal to 9.1. Dynamic method for studying the kinetics of gelation clearly shows the effect of thiourea concentration on the rate of formation of gel.

In all the studied systems based on sodium silicate, no matter which acid is used, the viscosity of the composition increases according hyperbolic law. The correlation coefficient in most experiments exceeded the value of 0.99. This dependence remains the same at addition in the silicate system some polymeric additives. In order to accelerate the process of analysing the influence of the studied additives on gelation, in some cases there were used a visual method of evaluation.

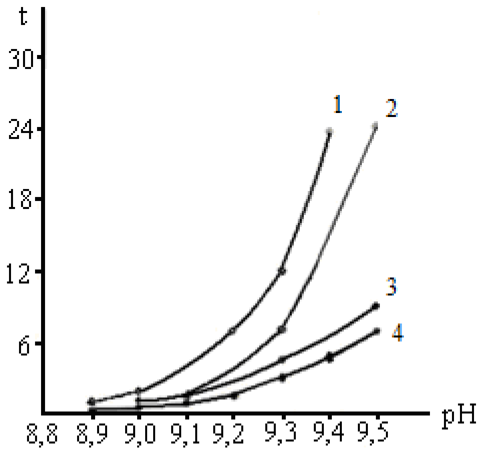

Fig. 4. Effect of potassium iodide addition on the kinetics of gelation in silicate solutions:
1 – system with 0,05% potassium iodide;
2 – system with 0,025% potassium iodide;
3 – system with 0,10% potassium iodide;
4 – standard system

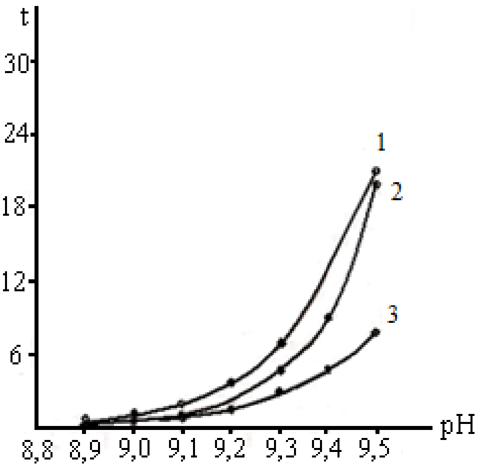

Fig. 5. Effect of sodium nitrate addition during gelation in 4% solution of sodium silicate:
1 – 0,025% sodium nitrate solution;
2 – 0,05% sodium nitrate solution;
3 – standard system

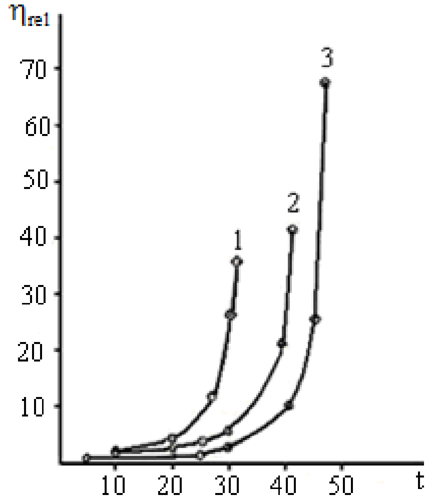

Fig. 6. Changing the relative viscosity in the 4% solution of sodium silicate with the addition of thiourea at process of gel formation:
1 – 0,10% thiourea solution;
2 – 0,05% thiourea solution;
3 – 0,025% thiourea solution

Table 4 shows the values of gelation time, which were determined visually, for the investigated systems.

The gelation time in static conditions is approximately 1.5 times greater than in the dynamic, i.e. in this case we can assume that there is a dynamic structure forming of the systems.

In the case of use of viscosity metric test method the gelation time corresponds to the relative viscosity η_{rel} of the solution, which is equal to 40-60 units. In case of the visual method, where gelation time is measured by loss of liquid composition strength, the value of the viscosity is much higher.

4. Conclusions

1. Organic acids accelerate the formation of gel in comparison with hydrochloric acid, and with increasing length of the alkyl substituent increases the rate of gelation.

Table 4. Change of relative viscosity of 4%- silicate solutions at the values of pH = 9,1 at presence of thiourea

Concentration of thiourea, %	Gelatin time, min	Relative viscosity	Gelation time by a viscosity metric method, min	Coefficient of correlation	Gelation time in static conditions, min
0,0250	5	1,52	48,3±1,9	0,9985	80
	17	2,12			
	25	2,91			
	30	3,93			
	36	6,55			
	40	10,03			
	43	16,19			
	44	20,14			
	45	25,75			
	46	34,04			
	47	74,88			
0,05	7	1,62	43,2±1,1	0,9996	75
	20	2,64			
	25	3,45			
	30	5,21			
	35	6,52			
	38	16,31			
	39	21,31			
	39,5	24,31			
	41	40,89			
0,10	10	2,34	33,26±2,2	0,9966	55
	16	3,09			
	20	4,15			
	23	5,74			
	24	6,79			
	27	11,45			
	28	14,53			
	29	17,09			
	30	26,70			
	31	35,95			

2. A mixture of salts with phosphoric acid slows down the gelation processes compared with the standard “crosslinking agent” - hydrochloric acid.
3. The optimum concentration of additives that most slow down gelation, lies within the 0,025–0,05%. With further increase in the concentration of additives gelling process accelerates.
4. At addition of acid, viscosity of the compositions based on sodium silicate, no matter which acid is used, grows, according hyperbolic law.
5. When passing through a layer of rock in compositions based on sodium silicate proceeds a dynamic structuring of the system.

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О.С. Тітова[1], В.В. Трачевський[2], З.В. Грушак[3], Н.В. Столярова[4]. Кінетичні закономірності гелеутворення силікатних композицій у присутності сполук, регулюючих швидкість гелеутворення

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Досліджено вплив різноманітних органічних та неорганічних добавок на швидкість утворення силікатних гелів на основі стандартних систем – розчин силікату натрію в моделі прісної води. Установлено, що перспективними добавками (регулювальниками часу гелеутворення) є багатоосновні органічні кислоти і неорганічні добавки – нітрати, йодиди та тіосечовина. Зазначено, що органічні кислоти прискорюють утворення гелю порівняно з соляною кислотою, причому зі збільшенням довжини алкільного замісника швидкість гелеутворення збільшується. Наведено межі оптимальної концентрації добавок, що найбільшою мірою уповільнюють гелеутворення: 0,025–0,05%. Показано, що зі збільшенням концентрації добавок гелеутворення прискорюється. Описано, як при введенні кислоти в’язкість композиції на основі силікату натрію незалежно від того, яка кислота використовується, зростає за гіперболічним законом. Експериментально підтверджено, що при проходженні композиції на основі силікату натрію крізь шар породи відбувається динамічна структуризація систем.

Ключові слова: неорганічні добавки; органічні кислоти; силікат натрію; стандартна система; час гелеутворення.

О.С. Титова[1], В.В. Трачевский[2], З.В. Грушак[3], Н.В. Столярова[4]. Кинетические закономерности гелеобразования силикатных композиций в присутствии соединений, регулирующих скорость гелеобразования

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Исследовано влияние разнообразных органических и неорганических добавок на скорость образования силикатных гелей на основе стандартных систем – раствор силиката натрия в модели пресной воды. Установлено, что перспективными добавками (регуляторами времени гелеобразования) являются многоосновные органические кислоты и неорганические добавки – нитраты, йодиды и тиомочевина. Отмечено, что органические кислоты ускоряют образование геля по сравнению с соляной кислотой, причем с увеличением длины алкильного заместителя скорость гелеобразования увеличивается. Приведены пределы оптимальной концентрации добавок, которые в наибольшей степени замедляют гелеобразование: 0,025–0,05%. Показано, что с увеличением концентрации добавок гелеобразование ускоряется. Описано, как при введении кислоты вязкость композиции на основе силиката натрия независимо от того, какая кислота используется, растет по гиперболическому закону. Экспериментально подтверждено, что при прохождении композиции на основе силиката натрия сквозь слой породы наблюдается динамическая структуризация систем.

Ключевые слова: время гелеобразования; неорганические добавки; органические кислоты; силикат натрия; стандартная система.

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