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IMPROVING PRODUCTIVITY OF OIL WELLS BY USING POLYMER-MINERAL COMPOSITION

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ABSTRACT

Control some parameters bottomhole zone (CCD) can be used to change the productivity of wells. In the operation of wells productivity usually decreases for several reasons. Among the many methods of control wells productivity by exposing the CCD, not all have the same effectiveness, but each of them (or groups) can give the maximum positive effect only when the selection of a particular well informed. Therefore, when using a particular method of artificial impacts on the CCD problem of selection of the well is a principal. In this treatment, even efficient, carried out in individual wells may not produce a significant positive effect for the whole deposit or deposit from a position as an intensification of production of reserves, and in the improvement of the ultimate oil recovery factor.

Key words: Polymer-mineral, Bottomhole, Oil wells, Clay compounds.

INTRODUCTION

In this regard, developed technological fundamentals of fracturing fluids based on barn oil, sludge and mineral supplements for injection wells. However granary oil, as well as heavy tar oil are resistant to washing. Content of mechanical impurities, consisting of little grains of sand, silt, clay and other compounds. Granary in oils, according to Kul et al.,[1] ranging from 0.04 to 8.0 wt.%. Mechanical impurities may exist in the form of coarse aggregation of unstable suspensions or in the form of colloidal particles. Coarse sediment particles can settle in the gravitational field and can be removed simply by settling. Colloidal particles as representing an aggregate of a number of molecules of a substance forming aggregates of 10^{-4}-10^{-6} mm are present in the barn of oil in the form of middleware, and are not removed from the water and oil phases or by settling or filtration. Lower degree of

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dispersion of colloidal particles to a value at which the sedimentation of the solid phase, i.e. the process of coagulation can be achieved through the introduction of specific substances, the so-called coagulants or flocculants.

The study of deposition of clay compounds coagulants and flocculants

As coagulating agents most widely sulphates, chlorides of aluminum and iron, and mixtures thereof in various proportions. These salts are formed with multiply charged cations of weak bases and anions of strong acids, hydrolyzed stepwise according to the following equations (1-3):

$$[Al(H_2O)_6]^{3+} + HOH \longrightarrow [Al(H_2O)_5(OH)]^{2+} + H_3O^+ \quad ...(1)$$

$$[Al(H_2O)_5(OH)]^{2+} + HOH \longrightarrow [Al(H_2O)_4(OH)_2]^{+} + H_3O^+ \quad ...(2)$$

$$[Al(H_2O)_4(OH)_2]^{+} + HOH \longrightarrow [Al(H_2O)_3(OH)_3] + H_3O^+ \quad ...(3)$$

Formed in the hydrolysis process colloidal sols of aluminum and iron hydroxides are coagulated to form aggregates and, eventually, a more or less large flakes. Recently, sorbing colloidal particles of clay compounds are precipitated together with them. Coagulants most commonly used in the practice of purification of drinking and industrial water from suspended solids and clay impurities.

In addition coagulants for removal of mechanical impurities in the last decade of the XX century, widespread high-molecular flocculants inorganic and organic nature.

The best-known inorganic flocculant is active silicic acid produced by the condensation of low molecular weight silicic acids or insoluble salts and is an anionic polyelectrolyte[1,2]. Also a large number of flocculants of natural origin derived primarily from plant material. Most common starches, cellulose and its derivatives, humic substances, etc. The most common and effective nonionic flocculant is polyethylene oxide (PEO) or polyoxyethylene (POE). Composition of its elementary unit: $–CH_2–CH_2–O–$. CR is used in the flocculation of suspensions of clay minerals, coal, flotation concentrate and flotation tailings coal preparation, carbonate slurry and other dispersed systems.

One of the best known and most commonly used synthetic anionic flocculants is PAA, which is a polymer of acrylamide $–CH_2–CH–CONH_2–$ ca molecular weight in the range (1–6) x 10^6. Suitable anionic flocculants were used as copolymers of acrylamide, acrylonitrile and acrylates, the sodium salt of polyacrylic and polymethacrylic acid and polystyrenesulfonic acid. Flocculants based on PAA are mainly used for the deposition of suspended solids in the settling tanks treatment plants, domestic and industrial waste water, recycled water for cleaning coal preparation plants, the extraction of minerals from various ores, as well as in the food industry.

Representative cationic macromolecular flocculants is polyethyleneimine (PEI), consisting of two types of links: $–CH_2–CH_2–NH–$и$–CH_2–CH_2–N–CH_2–CH_2–NH_2$ and containing both primary and secondary, and tertiary amines. Despite the high effectiveness of PEI as a flocculating agent in the purification of highly dispersed clay impurities, its practical application is limited as PEI refers to moderately toxic substances, and its monomer-ethyleneimine carcinogenic compound. To clean the circulating water coal preparation plants, sewage refineries use flocculants BA series and the defense industry, which are quaternary ammonium salts based on polystyrene.

Some interest are synthetic high molecular weight flocculants, are of various classes of organic polymers or copolymers with different functional groups[1,3], but in Kazakhstan own production data flocculants missing and these reagents have to be imported from countries near and far abroad.

Despite the fact that in the last decade of the XX century, a number of studies on the synthesis of new flocculants and the study of various factors on the deposition conditions of dispersed particles, still for each case using an empirical approach to the selection of the optimal composition of flocculants and flocculation compositions effective dewatering water-oil emulsion and promoting desalination and deposition of mechanical impurities in the oil sludge. Research is conducted on model systems representing a suspension of kaolin in distilled water.

As a coagulant used aluminum sulfate, and flocculants were:

- Non-ionic high molecular flocculant POE;
- High molecular weight anionic flocculant PAA;
- Anionic inorganic flocculant AK.

About flocculating properties judged on the content of solids in sludges from measurements of optical density using photocolorimeter KFK-3.

The data obtained and the kinetic curves of coagulation of colloidal clay suspension (Fig. 4-7).

From the analysis of the data presented, it follows that the effective dose of coagulant $Al_2(SO_4)_3$, providing the maximum speed of the coagulation process and the degree of purification of water from the clay compounds 99.5% with the coagulation time of 240 minutes, a concentration of 80 mg/L (Fig. 1 curve 6).

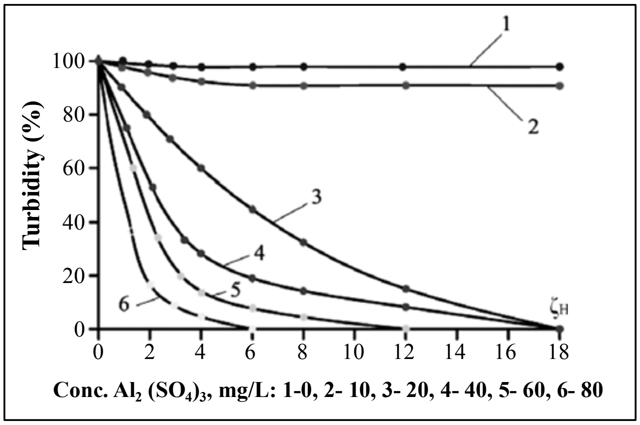


Fig. 1: The kinetics of coagulation of clay colloidal suspension aluminum sulphate

Introduction of aluminum sulphate at concentrations less than 10 mg/L does not affect coagulation, apparently due to the fact that the suspension introduced into the investigated aluminum cations Al^{3+} sorbed clay micelles and ion exchange ends before starting the hydrolysis. Increasing the concentration of coagulant causes that the exchange capacity of the clay micelles is exhausted and begins the hydrolysis of aluminum sulphate administered.

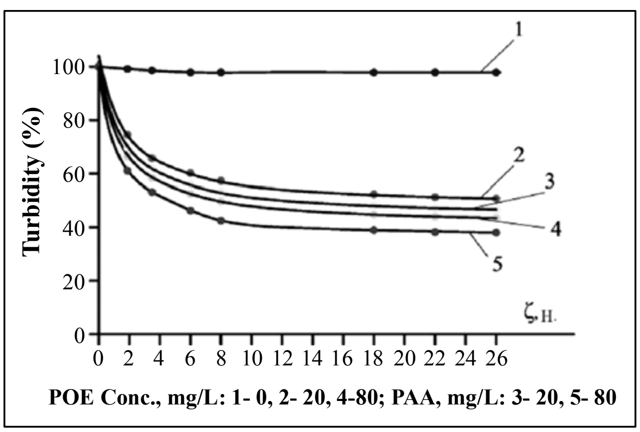


Fig. 2: Kinetics of flocculation of clay colloidal suspension of low-molecular organic flocculants

The resulting aluminum hydroxide gel particle kaolin connects large flakes, settling under gravity. Study of the kinetics of the flocculation kaolin suspension macromolecular flocculants POE PAA (Fig. 2) showed that the rate of flocculation in this case is much lower than in the presence of aluminum sulphate and is essentially independent of the dose of flocculant.

The degree of purification of water during the test period of 240 min (under optimum time of coagulation with aluminum sulphate) does not exceed 50% (Fig. 2 curves 2 and 3).

The inorganic flocculating agent-active silicic acid has a higher flocculation ability as compared with the high molecular weight organic polymers. AK can be effective flocculant, especially in combination with other inorganic compounds. AK is not a commercial product, and preparing in situ activation by using solid sodium silicate solution - the so-called waterglass. It is known that the process of activating the waterglass solution consists in decomposing sodium silicate, hydrated alkali neutralization and the preparation of silicic acid or a sparingly soluble salt. Occurring during this neutralization reaction can be summarized by the following scheme:

$$2\ HA + Na_2O.MSiO_2.xH_2O \longrightarrow 2\ NaA + M[SiO_2].yH_2O \quad ...(4)$$

$$2\ Si(OH)_4 \longrightarrow HO{-}Si(OH)_2{-}O{-}Si(OH)_2{-}OH + H_2O \quad ...(5)$$

Where M - siliceous modulus of sodium silicate; A - anion of an acid.

The deposition rate of the clay particles in the above case (Fig. 3), and the degree of water purification in a concentration range of 10-30 mg SiO_2/L with silica modulus $M_{\text{к}}$ = 2,6 is 60-62%. The optimum dose of flocculant should be considered at this concentration 20 mg SiO_2/L.

It should be noted that further increases in the concentration of the active silicic somewhat reduces the rate of the deposition of clay particles and water degrades the quality of the purification (Fig. 3, curve 3).

Besides AK obtained based on the solution of sodium trisilicate, we investigated flocculating properties AK based waterglass solution obtained by dissolving autoclaved amorphous silica in alkali NaOH with silica modulus $M_{\text{к}}$ = 4,0. Kinetics of flocculation of clay suspension flocculant data shown in Fig. 7, which shows that, unlike with AK $M_к$ = 2.6, introduced flocculant concentration has a significant impact on its flocculating properties and increasing the dose increases the degree of purification of water from clay compounds (Fig. 4, curve 3).

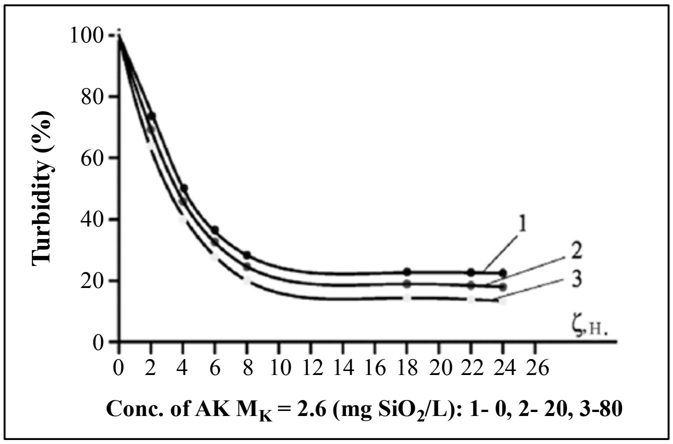


Fig. 3: Kinetics of flocculation of clay colloidal suspension of inorganic flocculant-AK

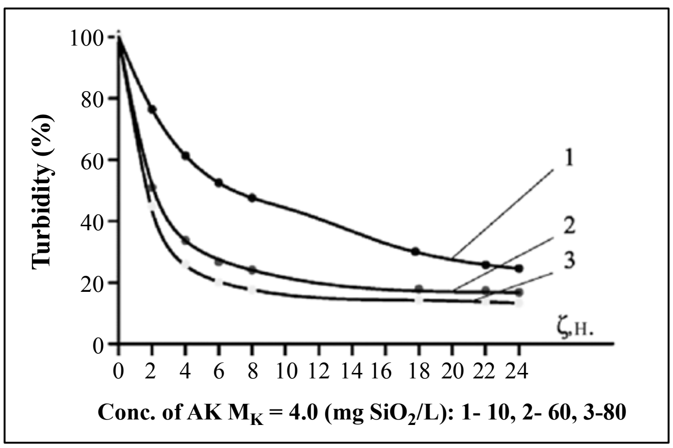
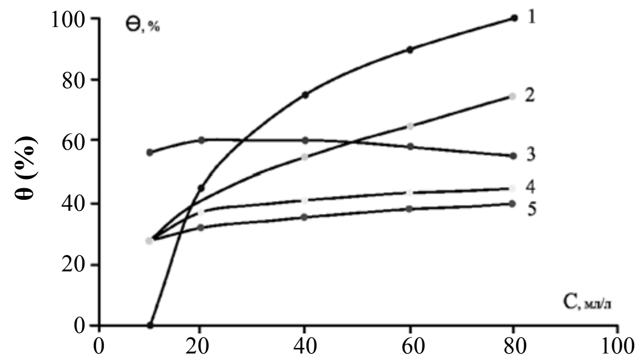


Fig. 4: Kinetics of flocculation of clay colloidal suspension of inorganic flocculant-AK

From the analysis of the data shows that the degree of purification of water is determined by the nature of the flocculant. Comparative assessment of the flocculating properties shows that the greatest reduction in turbidity of the suspension after the aluminum sulphate is achieved by using AК with $M_к$ = 2,6 (Fig. 5). The optimal concentration of the flocculant should be considered administered at 80 mg SiO_2/L, whereby the degree of water purification is 71% in 240 min.



1- $Al_2(SO_4)_3$; AK with M_K = 2.6; 3- AK with M_K = 4.0; 4- PAA; 5- POE

Fig. 5: The degree of purification of water from the clay compounds depending on the nature and concentration of the coagulant (1) and flocculant (2 - 5)

It should be noted that domestic production of high molecular weight organic flocculants in Kazakhstan there is no data and reagents are imported from the CIS countries, while getting the AK can be arranged directly on the basis of local raw materials of the country. Development of research in this area will create a technology for the production and use of import-substituting products that will reduce the economic costs and improve the technological characteristics of the process of purification of water from the clay compounds.

Activation flocculant AK inorganic compounds

In this paper, we study the properties of flocculation AK module $M_{к}$ = 2.6, received activation waterglass solution phosphoric acid (1:1) hydrochloric acid, 3% aqueous solution of lead nitrate (salt formed with a weak base and a strong acid is acidic) and a mixture of phosphoric acid, and lead nitrate. Activation of sodium silicate solutions indicated activators conducted by the method of Kul L. A.[4] mixing up to pH 7.0-7.2 solution of 2% (by SiO_2) waterglass with silica modulus $M_{к}$ = 2.6 (prepared by dissolving autoclave sodium trisilicate) and diluted (1:1) phosphoric acid (EFA) with the percentage of P_2O_5 14.5%. The resulting solution was allowed to stand for 20 minutes for aging the sol, and then diluted with water to a 0.1% solution (by SiO_2). Activation of other activators is similar.

The results of studies of the processes of flocculation of clay colloidal suspension of this reagent are given in Tables 1 and 2 from the analysis of the data shows that minimal residual turbidity test solutions, corresponding to the maximum degree of purification of water from the clay compounds -79.2% achieved in the case of use as an activator lead nitrate. Activating waterglass solution with hydrochloric acid leads to a certain degree decrease the effectiveness of cleaning. Despite the high purification process water from the clay compounds AK obtained by mixing solutions of sodium silicate and lead nitrate, it should be noted high consumption of the latter during the preparation of the sol of silicic acid - liquid ratio of glass: $Pb(NO_3)_2$ = 1:1. Moreover, in the neutralization process are formed hydrated alkali metasilicate sparingly soluble salt of lead.

Table 1: Kinetics of flocculation of colloidal clay mixture of the active silicic acid (20 mg SiO_2/L) obtained by activating the waterglass solution with various reagents

Time (hr)	Residual turbidity (%) when using the activator			
	HCl	H_3PO_4	$Pb(NO_3)_2$	$H_3PO_4 : Pb(NO_3)_2$ = 1: 0,1
1	78.4	76.3	69.7	79.2
2	66.4	59.8	35.6	56.0
4	49.8	42.5	20.8	34.3
6	43.2	34.7	17.2	29.6
8	39.4	27.2	16.5	22.8
20	23.5	16.4	15.4	17.5
22	22.0	16.3	15.4	17.3
24	21.8	16.3	15.3	17.3

It is known that lead compounds are very toxic, so to reduce the flow of the activator $Pb(NO_3)_2$ has been proposed as an activating agent to use a mixture of phosphoric acid with lead nitrate. As shown by studies of the kinetics of flocculation. In this case, the deposition rate of the clay slurry at concentrations AK 20 mg SiO_2/liter higher than that in the case of activation of water glass with mineral acids (Table 5). Increasing the concentration of flocculant to 80 mg SiO_2/liter leads to a decrease in the rate of flocculation, possibly due to stabilization of the colloidal suspension of clay particles flocculant (Table 2). Study flocculating properties AK derived activation waterglass solution H_3PO_4, $Pb(NO_3)_2$ and a mixture thereof at various ratios of components at the dose of 20 mg of flocculant SiO_2/Liter, showed that the introduction of small amounts of lead nitrate to phosphoric acid ratio H_3PO_4: $Pb(NO_3)_2$ = (1:0,025) – (1:0,05) and using the mixture as an activator waterglass solution reduces the effectiveness of the water treatment process of the clay compounds by almost 10%, whereas a further increase of the content of lead nitrate in the activation mixture to a ratio of 1: 0.1 improves the purification rate up to 66% (during flocculation 4 H).

Table 2: Kinetics of flocculation of colloidal clay mixture of the active silicic acid (80 mg SiO_2/Liter) obtained by activating the waterglass solution with various reagents

Time (hr)	Residual turbidity (%) when using an activator			
	HCl	H_3PO_4	$Pb(NO_3)_2$	$H_3PO_4 : Pb(NO_3)_2$ 1: 0,1
1	86.4	79.7	57.8	84.5
2	75.7	64.1	34.6	72.5
4	60.3	45.3	21.4	60.1
6	51.8	35.6	16.8	55.6
8	43.7	29.8	16.5	51.4
20	26.4	16.9	16.4	33.7
22	25.9	16.3	16.3	32.4
24	25.8	16.3	16.3	29.3

It should be noted that the flocculating effect AK obtained by activating a silicate solution of phosphoric acid is slightly higher than the activation with hydrochloric acid, due to the difference of structures formed sol AK. Thus, from the analysis of the infrared spectra (Fig. 6, curve 1) that the initial solution of water glass contains 2 main absorption band of alkali-silicate glass in the area of 700-800 and 1000-1100 cm^{-1}, corresponding to stretching vibrations of SiO_4-tetrahedron. The band in the region 950 cm^{-1} corresponds to vibrations of the Si-O-. Upon activation waterglass solution of hydrochloric acid (Fig. 6, curve 2), along with increasing intensity and hypochromic shift main absorption bands, there is an increase in the number of bands 500-800 cm^{-1}, which is an indication of increasing the degree of polymerization of the siloxane chain.

IR spectrum AK obtained by activating waterglass solution EPA (Fig. 6, curve 3) differs from the previous range, not only the presence of the absorption bands at 980 and 1170 cm^{-1}, corresponding symmetric and asymmetric stretching vibrations PO_4^{3-} tetrahedron, but the absorption bands in the 2400 and 2800 cm^{-1}, attesting to the vibrations of hydroxyl ions, hydrogen bonds. Moreover, compared with the IR spectrum of AA, activated with hydrochloric acid, is substantially increased intensity of absorption bands in the 870, 720, 650, 540 cm^{-1} and appear on the shoulders 820 and 620 cm^{-1}, that corresponds to the structure of wollastonite. The analysis of the IR spectra suggests that the activation of solutions of sodium silicate EPA, unlike hydrochloric acid, the basis of the sol AK are single wollastonite chains linked by hydrogen bonds with anion. Increasing the size of the macromolecule flocculant leads to increased efficiency of its flocculating action.

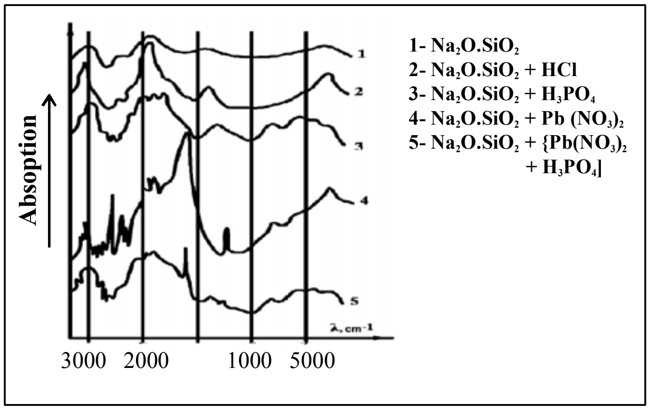


Fig. 6: IR spectra of flocculants based on liquid glass

Since lead is a toxic element and its concentration in industrial waters is limited MPC (less than 0.1 mg/L), then to reduce the flow of the activator $Pb(NO_3)_2$ has been suggested as the activating agent waterglass solutions use a mixture of phosphoric acid and lead nitrate with different ratios of the reactants.

Flocculation effect of the compositions obtained were evaluated in this case, the relative value of the dimensionless parameter D (16), equal

$$Д = \frac{\overline{U}}{\overline{U}_0} - 1 \quad \ldots(6)$$

Where $\overline{U}$ and $\overline{U}_0$ – maximum rate of sedimentation of dispersed phase, respectively, with and without flocculant (Fig. 7).

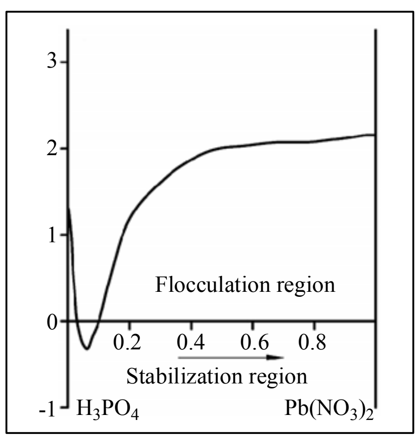


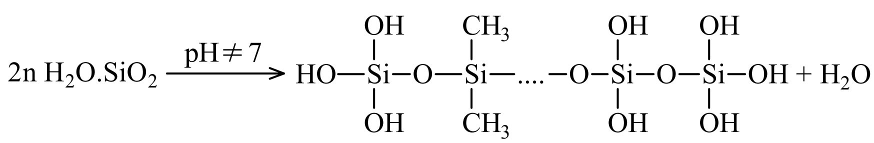
Fig. 7: Dependence of flocculation effect of the composition

Strengthening the flocculation ability of AA in the presence of multiply charged cation d-element, apparently due to the formation of complex bridges due to the binding of multiply charged ions with the functional groups of the adsorbed polyelectrolyte. However, given the new approach to the description of the classical mechanism of flocculation mostikoobrazovaniya developed by Nurabaev et al.[4] Flocculation of the dispersed phase can be regarded as a process of formation of insoluble polymer complexes and stabilization, a reaction that promotes the formation of water-soluble non-stoichiometric polycomplexes.

The hypothesis of the mechanism mostikoobrazovaniya when activated with a mixture of liquid glass and EPA lead nitrate is confirmed by analysis of the IR spectra (Fig. 6, curve 5) obtained flocculants. Thus, the bathochromic shift of the absorption band in the region 1080 cm^{-1} and the intensity and number of bands in the 500-800 cm^{-1} evidence of distorting cation Pb^{+2} anionic skeleton and crosslinking. Below is a classic mechanism of activation of sodium silicate:

(1) Activator – HCl

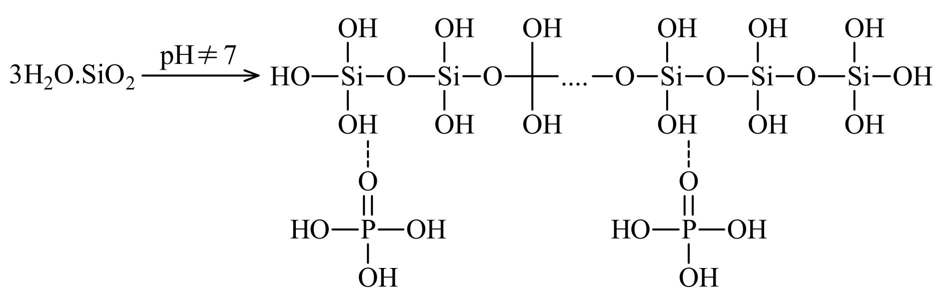
$$2Na_2O.SiO_2 + 4HCl \xrightarrow{pH\neq 7} 4NaCl + 2H_2O.SiO_2 \qquad \ldots(7)$$



...(8)

(2) Activator – H_3PO_4

$$3Na_2O.SiO_2 + 6H_3PO_4 \xrightarrow{pH\neq 7} 6NaH_2PO_4 + 3H_2O.SiO_2 \qquad \ldots(9)$$



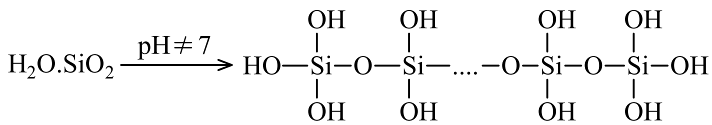
...(10)

(3) Activator - $Pb(NO_3)_2$

$$Pb(NO_3)_2 + HOH \rightarrow PbOH(NO_3) + HNO_3 \quad ...(11)$$

$$PbOH(NO_3) + HOH \rightarrow Pb(OH)_2 + HNO_3 \quad ...(12)$$

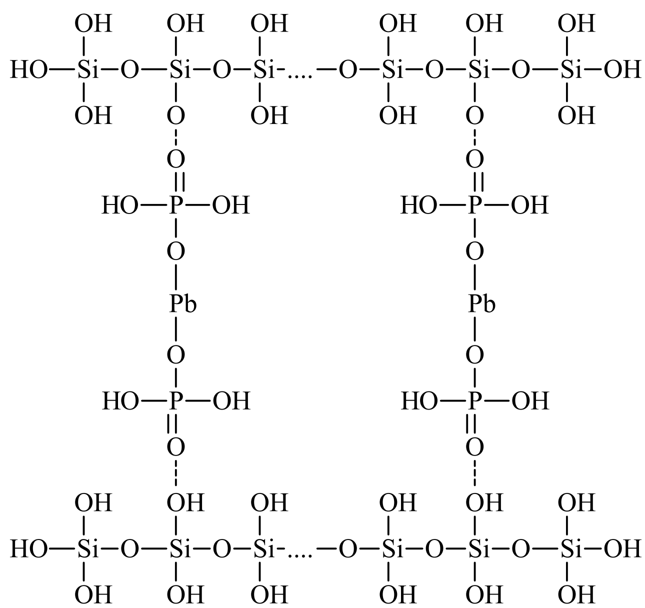
$$Na_2O \cdot SiO_2 + 2HNO_3 \rightarrow 2NaNO_3 + H_2O \cdot SiO_2 \quad ...(13)$$



...(14)

$$\{[SiO_2] \cdot nSiO_3^{-2\cdot}\} + 2\{[Pb(OH)_2 \cdot n(PbOH)^+]\} \rightarrow \{[SiO_2] \cdot nSiO_3^{-2\cdot} 2[Pb(OH)_2 \cdot 2n(PbOH)^+]\} \quad ...(15)$$

(4) Activator - $H_3PO_4 + Pb(NO_3)_2$



...(16)

CONCLUSION

From the literature[3,4], as well as on the results of their own research known prospects of using AK as a flocculant in water purification processes of clay compounds. Wherein AA is not a commercial product, and carried out directly on the application site by neutralizing acidic reagent hydrate alkalinity of sodium trisilicate (liquid glass), and obtaining a sol of silicic acid. As activators may be used a wide range of different materials, namely, mineral acids, acidic salts, etc.

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