

# OIL AND GAS PRODUCTION

## Interaction of silicate rocks with acid-cut clay muds under pt conditions in the reservoir. Part 2.

### The mechanism of formation component dissolution

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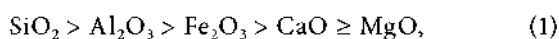
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*It was established that in case of excess rock to acid-cut clay mud at increase of interaction pressure the selectiveness of dissolution of oxides within Bentonite Clay disappears. In case of excess rock the mechanism of dissolution of these oxides at high pressures is unchanged. Increasing pressure from 0.1 to 15 MPa leads to decreasing Horodyshche gel powder dissolution at higher specific consumption of acid for its dissolution, which is associated with the occurrence of secondary reactions of newly produced neutralizing products.*

The proposed article is a continuation of a series of works [1, 2] that study the mechanism of interaction of clay-acid solutions (CAS) based on the mixture of 10% HCl and 1% HF with silicate rocks (clay-carbonate sandstone of Precarpathians and Gorodyshchenske clay Bentonite powders ) at different pressures (0.1 – 15 MPa) and temperatures (40 – 80°C). The previous studies have established that moderating or accelerating capacity of the pressure on the dissolution of terrigenous rocks is determined by the mineralogical composition of a particular rock, i.e. the content of carbonate and silicate rocks, and by the composition of the acid solution as silicon and aluminum oxides have different dissolution dependence compared with iron oxides and oxides of monovalent and divalent metals [2].

It also has been established that dissolution of the silicate rocks models at atmospheric pressure and a temperature greater than critical can vary depending on the rock excess or acidity [1]. If case of excess of acid, the dissolution of CAS clay powder oxide at temperature of interaction amounting to 40°C is as follows:



which corresponds to their initial content in the rock, and at a temperature of 80°C the given sequence is broken – removal of aluminum oxide predominates over the removal of silicon oxide. Relative removal of silicon oxide amounts to only 12.9 – 27% of the initial content in the sample; for aluminum oxide this value amounts to 20 – 60%, while the oxides of iron, calcium and magnesium are dissolved much more - from 65 to 100%. During the interaction of CAS with sandstone relative removal of silicon oxide is reduced to 10%; the removal rate for oxides of iron, aluminum, calcium and magnesium is 80 – 100%. Therefore, sandstone is most soluble in clay-carbonate cement while matrix solid material remains comparatively poorly soluble. In the event of rock excess, CAS acts selectively: interlayer cations and isomorphic impurities in powders and cement in sandstone are primarily dissolved. The oxides dissolution takes place in the following sequence:

The work is dedicated to studying of the dissolution mechanism of components of silicate minerals in the clay-acid solution based on a mixture of 10% HCl and 1% HF in thermobaric

conditions that are close to those of the bed (with the bed temperature of 40 to 80°C and pressures ranging from 0.1 to 15 MPa, contact time of the acid solution and the rock is 6 hours). The results of studies of the solubility of the clay powder in CAS over a short contact time (15 min) in the thermobaric conditions similar to those of the bed are given in [2].

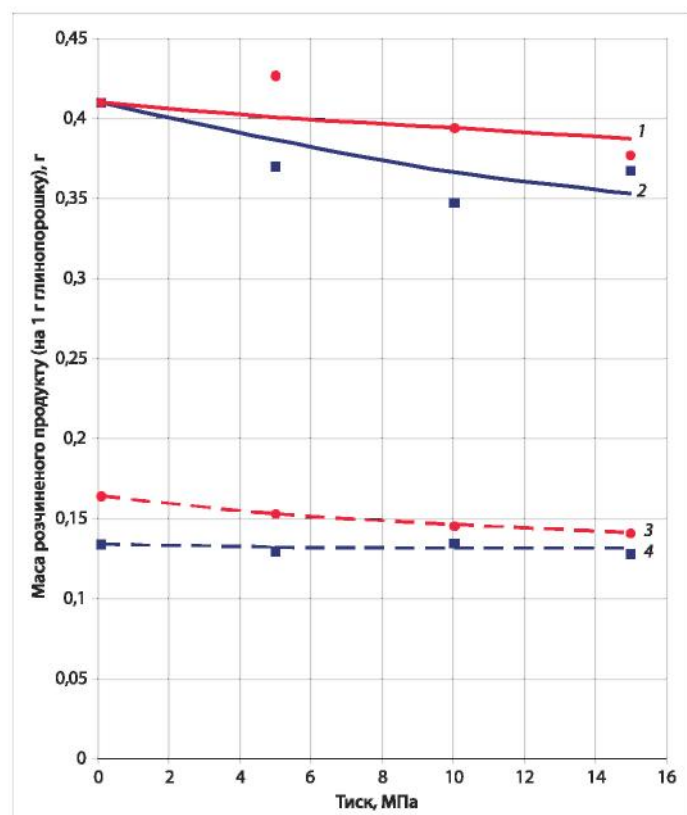


Fig. 1. The dependence of the solubility of the Gorodischensky clay powder on pressure and temperature: 40 °C - curves 2 and 4; at 80 °C - curves 1 and 3, with exposure time 6 h and excess: 1, 2 - acid, 3, 4 - rock

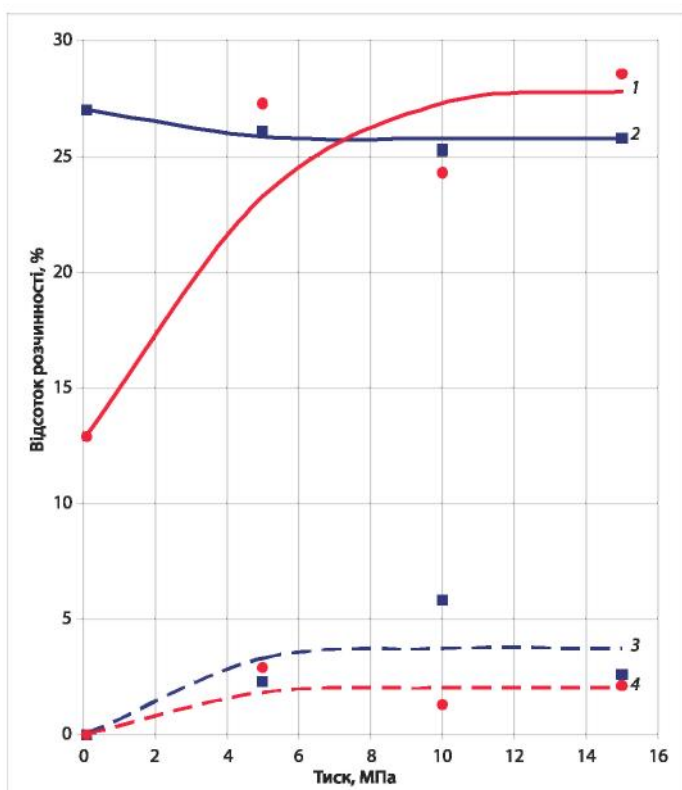
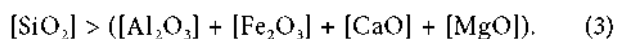


Fig. 2. The dependence of the solubility of the Gorodischensky silicon on pressure and temperature: 40 °C - curves 2 and 3; at 80 °C - curves 1 and 4, with exposure time 6 h and excess: 1, 2 - acid, 3, 4 – rock

Maximum time of the stay of the acid solution in the bed can be up to 6 hours (2 - 3 hours - injection into the layer 2-3 hours – exposure for interaction of the latter portions of the acid solution with rock components and beginning of well development). Therefore, further research of the solubility of Bentonite clay in CAS was conducted with the use of 6h exposure value that is optimal for maximum dissolution of rock. The results are shown in Fig. 1-6.

The laboratory studies have demonstrated that prolonged exposure (6 hours) of Gorodischensky Bentonite clay to the acid-clay solution of 10% HCl and 1% HF leads to changes in dependency of clay dissolution on the pressure: in all cases, a decrease in total solubility of Bentonite is observed with increasing interaction pressure. The decrease rate of the solubility of powders is usually less than 30% (see Fig. 1). This interaction mechanism significantly differs from dependence observed in the case of short-term exposure of clay to the acid mixture [2]. If there is a significant dissolution of Bentonite powder, which is achieved during its prolonged exposure to the acid solution, the effect of the solubility of the oxides of iron, magnesium and calcium dominates over the solubility of silicon and aluminum oxides. The result is a decrease in the Bentonite solubility with increase in pressure because this factor primarily affects the solubility of the above-mentioned oxides so that it decreases.

It has been also shown that overpressure leads to a change in the mechanism of dissolution of basic oxides of the Bentonite Clay. Thus, under conditions of acid excess with the increase in pressure from 0.1 to 15 MPa, the mechanism of removal of metal oxides from the clay powder is maintained in accordance with the following sequence (1). The amount of removed silicon oxide is always larger compared with other oxides:



The obtained order of removal of oxides expressed in absolute values in conditions of acid excess corresponds to their natural distribution in the clay powder.

In case of excess of the rock during the pressure increase from 0.1 to 15 MPa, the mechanism of the metal oxide removal from the clay powder changes. Consequently, a number

of metal oxides, which are removed from the clay powder, can be displayed as follows in decreasing order:

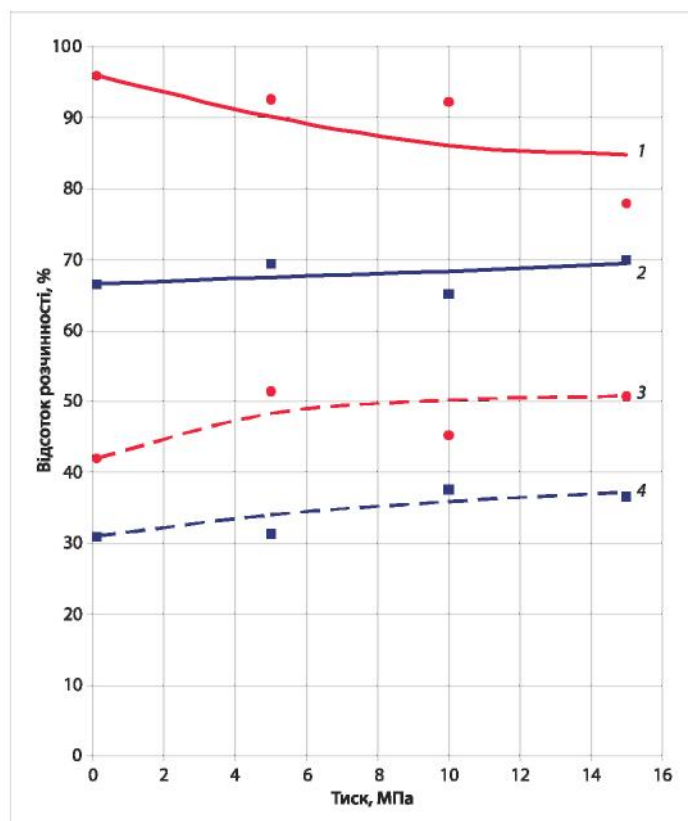
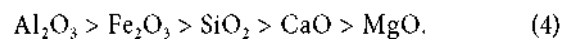


Fig. 3. The dependence of the solubility of the aluminum oxide from Gorodischensky powder on pressure and temperature: 40 °C - curves 2 and 4; at 80 °C - curves 1 and 3, with exposure time 6 h and excess: 1, 2 - acid, 3, 4 – rock.

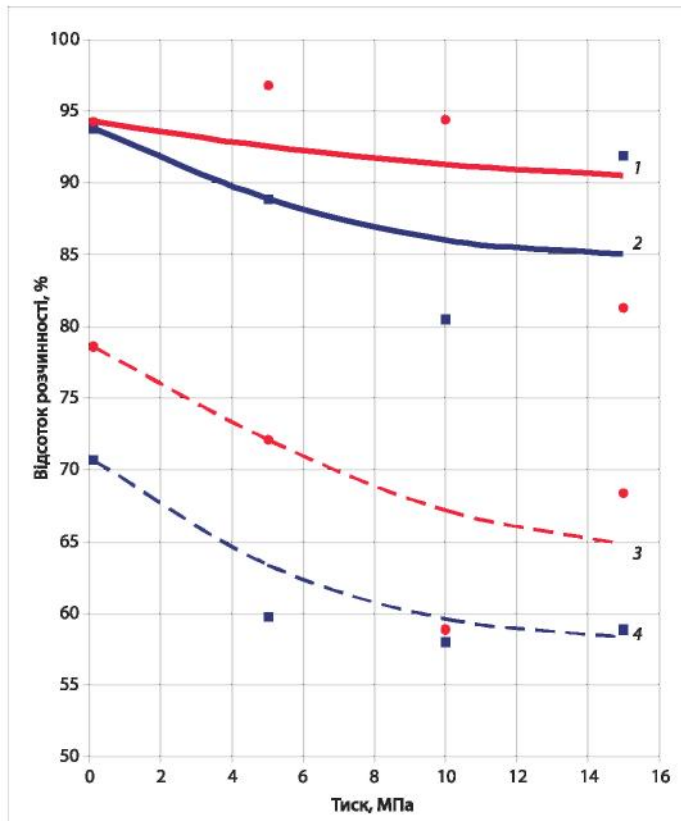


Fig. 4. The dependence of the solubility of the ferric oxide from Gorodischensky powder on pressure and temperature: 40 °C - curves 2 and 4; at 80 °C - curves 1 and 3, with exposure time 6 h and excess: 1, 2 - acid, 3, 4 - rock

A significant difference, at pressures high compared with atmospheric, is the increase of solubility of alumina and silica. The greatest effect of pressure is observed during the interaction of acid and silica, because it is practically insoluble with clay acid at atmospheric pressure. However, even low pressure (5 MPa) leads to partial dissolution of silica in the range of 2 to 3 % of its amount (see Fig. 2). Further increase in the pressure up to 15 MPa does not cause the increase in dissolution of silica. These results suggest that the increase in pressure enhances the movement of acid to the structure-forming silicon cations, ensuring their partial dissolution at the same time. After a slow dissolution speed of such oxides, their share in the total amount of dissolved oxides is negligible. These results support the earlier conclusion that with increase in pressure during interaction of the clay powder with CAS, with all other conditions being equal, an increase of loss of hydrofluoric acid for dissolution of the silicon oxide is observed, since it is the only acid capable of dissolution of the said oxide [2]. The greatest effect of pressure on the mechanism of dissolution of powders occurs when an insufficient amount of clay-acid solution in circumstances where the dissolution of oxides is determined primarily by the speed and area of contact with nitric acid (i.e. in case of the rock excess over the acid, which is characteristic for injection of the first portion of clay-acid solution into the pore space of the bed).

Another proof of increase in removal of the both acids from the clay-acid solution is the increase in the specific consumption of the acid for powder dissolution. It has been demonstrated that with increase in pressure from 0.1 to 15 MPa, the specific consumption of the acid for the dissolution of the metal oxides (amount of clay powders dissolved in 1 mg of the equivalent acid) dramatically increases 5-8 times (Fig. 7). These results indicate that with increase in pressure, maintenance of the gas products ( $\text{SiF}_4$ ,  $\text{CO}_2$ ) in the liquid state leads to better rock dissolution with the same amount number of acid. In combination with improved permeation ability of acid into the structure of clay minerals it provides intensification of clay powder dissolution with the acid mixture. The maximum growth rate of the specific acid consumption is observed at the pressure amounting to 10 MPa. This dependence is related to the proportion of the contribution of each individual oxide into the overall result of dissolution of the clay model.

At pressures less than 10 MPa, an increase in the specific consumption of the acid is related to the solubility of silica and alumina. Further increase in pressure stabilizes the process of dissolution at a certain level. The removal of the remaining oxides tends to decrease with increasing pressure. Therefore, at pressures higher than 10 MPa a partial decrease of this value is observed.

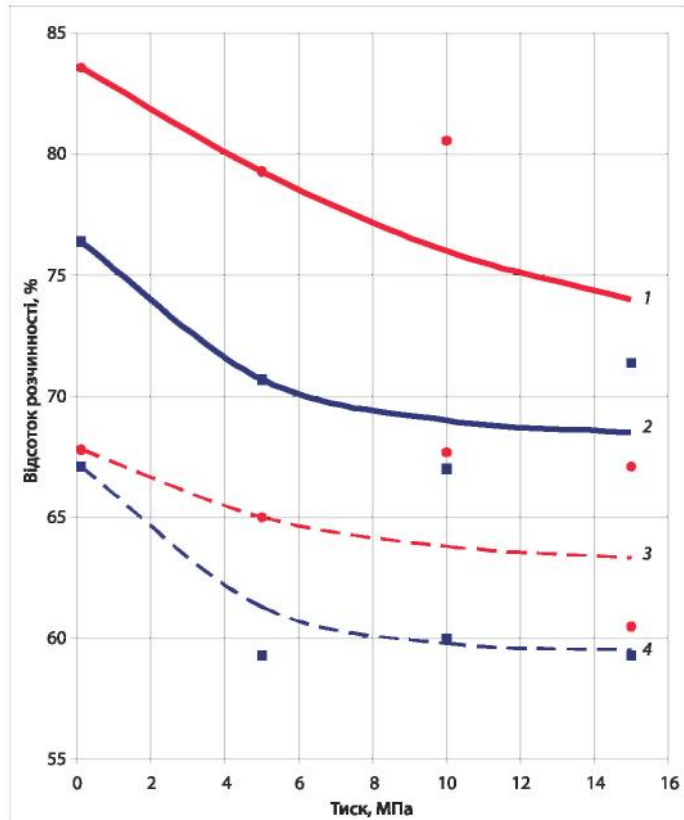


Fig. 5. The dependence of the solubility of the calcium oxide from Gorodischensky powder on pressure and temperature: 40 °C - curves 2 and 4; at 80 °C - curves 1 and 3, with exposure time 6 h and excess: 1, 2 - acid, 3, 4 – rock

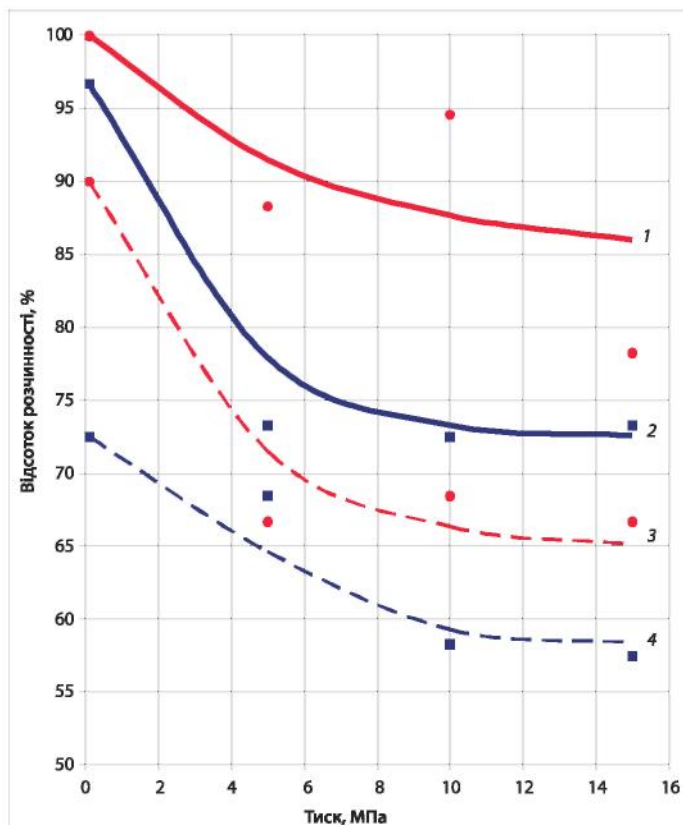
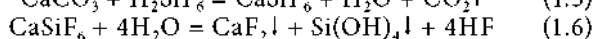
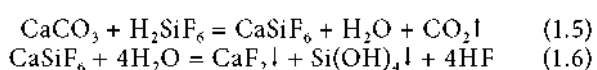


Fig. 6. The dependence of the solubility of the magnesium oxide from Gorodischensky powder on pressure and temperature: 40 °C - curves 2 and 4; at 80 °C - curves 1 and 3, with exposure time 6 h and excess: 1, 2 - acid, 3, 4 – rock

However, during the dissolution of some Bentonite Clay oxides deviations from the general trends are observed. This is especially true for silica (see Fig. 2). In case of rock excess and at 40° C the process of dissolution of silica is intensified with the increase in exposure time, and at pressures higher than 5 MPa it stabilizes at a certain level. The increase in the interaction temperature to 80° C leads to a decrease in the solubility of silica. The increase in the exposure time from 0.25 to 6 hours only worsens the process of dissolution of the said oxide. Deviations from the general trends of acid dissolution of oxides for silicon oxide are also observed in the case of an excess of the acid over the rock. The general downward trend in solubility with increasing pressure for silicon oxide is observed only with prolonged exposure to CAS at 40°C. In all other cases (higher temperature, short-term exposure at 40°C) there is an increase of solubility of silica with increasing pressure. Other deviations from the general trends of the process is reduce in the solubility of silica with the temperature increase from 40 to 80°C at atmospheric pressure; and increase in exposure time and of the temperature to 80°C. If Bentonite Clay is dissolved with the solution of 10% HCl and 1% HF, the maximum solubility of silica is achieved under the following conditions: excess of the acid over the rock at 80°C and short-term (15 min) exposure.

In our opinion, the deviation of the solubility of silica in the event of the rock or acid excess or from the general trend, especially with the increase in temperature and exposure time, associated with the occurrence of secondary reactions during contact of the acids with neutralization products. This results is a partial return of the dissolved silica in an insoluble form (according to the formulas 1.5-1.9), which understates the actual values of dissolution of silicon oxide. The formation of the silicon hydrofluoric acid provides even further dissolution of carbonate and silicate components, but this may lead to the formation of water-insoluble products and blocking of the pore channels:



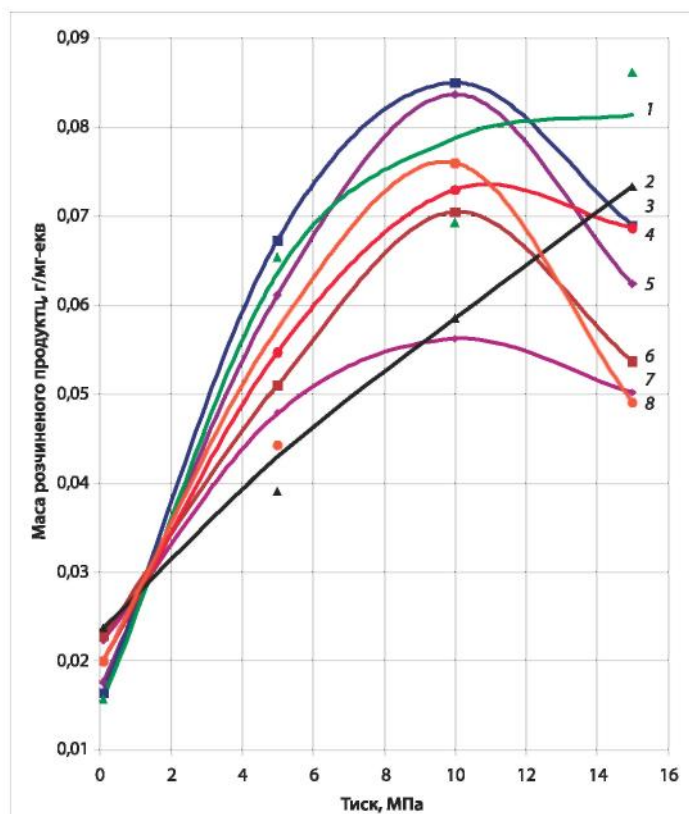
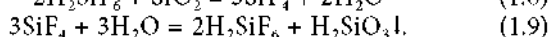
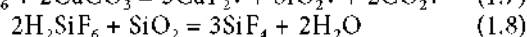
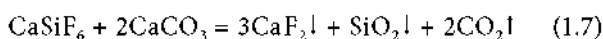
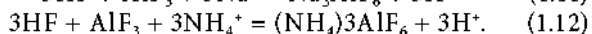
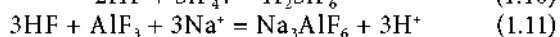


Fig. 7. Dependence of the specific consumption of the acid for solution of 1 mg equivalent of Gorodischensky clay powder from pressure and temperature (at 40 °C - curves 3, 5, 6, and 7; at 80 °C - curves 1, 2, 4, and 8), acid excess (curves 1, 3, 4, and 5) or rock excess (curves 2, 6, 7, and 8) and exposure time: 1, 2, 5, and 7 - 15 min; 3, 4, 6, and 8 - 6 hours



Besides that, hydrofluoric acid is capable of interaction with silica and aluminum fluorides that are formed during the reaction:



The formation of complex aluminum salts in the present of excess of hydrofluoric acid is possible because the solubility of such salts is much higher than that of the initial salt (from 0.41 to 7.6% for the ammonium salt). The presence of hydrochloric acid in the clay acid solution mostly provides dissolution of oxides of calcium, magnesium and iron and converting of soluble fluoride salts of aluminum and iron into more soluble chloride salts.

Since the duration of secondary reactions increases with increasing temperature and exposure time, the amount of silica that is returned from the solution to the surface also increases thus leading to decrease in the observed rate of silicon oxide dissolution. Therefore, the increase in pressure, temperature and exposure time to such extent when the interaction between clay acid solution and silica takes place, does not slow down the dissolution, but rather accelerates it, resulting in the occurrence of secondary reactions and return of silicon dioxide into the surface of rocks in a modified form (water and anhydrous compounds of SiO<sub>2</sub>).

If there is an excess of the acid compared with rocks increase of the interaction pressure does not change the basic mechanism of dissolution of the clay powder oxides: it reaches its maximum and is associated mainly with the quantitative content of oxides in the rock. If there is an excess of the rock over the acid increase of the interaction pressure leads to the disappearance



of the selectivity of dissolution of the oxides, which occurs due to the acceleration of the penetration of the active acid into clay minerals and with increasing solubility of silica and alumina, which are a structure-forming cations of siliceous tetrahedral of the clay powder. However, the obtained figures for the solubility of the silicon, aluminum and iron oxides in these conditions are less than the values obtained in the conditions of the acid excess. The established mechanism of interaction suggests that during filtering of clay acid solution based on hydrochloric and hydrofluoric acids through a given volume of porous reservoir during the passage of the first portion of the solution (subject to an excess of acid rocks) only partial dissolution of basic rock oxides is observed, which is determined by the speed their dissolution. Indicative in this process is silica. At atmospheric pressure, it is not dissolved by clay acid solution. Increase in pressure causes the start of its dissolution (2-3% of the total). Only the excess of acid over rock while filtering of the bulk CAS volume provides intensive dissolution of silicon oxide, which is part of the silicate minerals.

The conducted studies show that strong hydrofluoric acid at high temperatures (80° C and above) and long exposure time is impractical for the use in the clay acid solution due to the high dissolution rate of silicate and clay minerals and the occurrence of secondary reactions that result in both inefficient use of hydrofluoric acid for reaction with fluorides of silicon, aluminum and iron, as well as in secondary formation of hydrous and anhydrous silicon oxides (which can result in blocking of the pores of the pore collector). It is reasonable to use slow acting forms of acid-clay solutions (a mixture of hydrochloric and hydrofluoric acids with a reduced concentration or the relevant additives, or a mixture of a weak acid, HF or its salts or acids of silicon hydrofluoric acid or boron hydrofluoric acid [3]). In the case of low concentration of clay acid solutions for HF it leads to reduction of the depth of acidic action, especially for silicate and clay components. Since the use of silicon hydrofluoric acid is optimal only in layers of clay cement alone, the boron hydrofluoric acid is a promising acid base, because it can be used in the layers of carbonate, clay carbonate or clay-cement [4].

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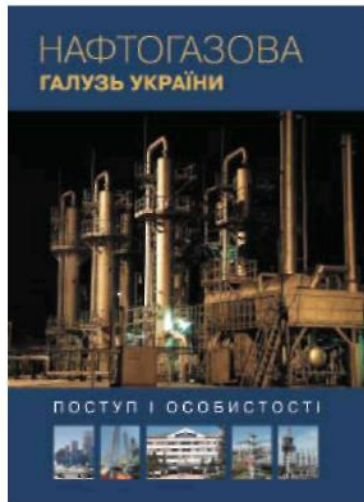
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## NEW BOOKS



*On the occasion of the 20th anniversary of Ukrainian Oil and Gas Academy (UOGA) a publishing center "Logos", with Candidate of Engineering Sciences Z.P. Osinchuk being the chief editor, issued a large format book called "Oil and gas industry of Ukraine: progress and personality". The book has 322 pages, its preparation and printing was possible because of the participation of 22 members of the UOGA and five Ukrainian companies that sponsored the publishing. It is unique in its content and scope of information. It consists of two sections. The first deals with historical aspects of seven areas of oil and gas complex of Ukraine: geology of oil and gas, well drilling, oil and gas extraction, transportation, refining, gas supply and gasification and providing field personnel. The descriptions of all directions represent the concentrated chronological summary of production activities with numbers, personalities, and results of scientific research, current issues and directions for further work. The direction of well drilling and refining of oil and gas are distinguished by completeness and highly outlining exposition.*

*The second section includes brief biographies and employment up to 515 persons, among them twelve women. The section covers stories about experts within age range from 1854 to 1984. The vast majority of them were born, studied and worked in Ukraine, 15% came to Ukraine mainly from Russia and Azerbaijan. 8% of professionals were born and educated in Ukraine, worked outside the country (mainly in Russia) and achieved considerable manufacturing success.*

*The insistence and desire to self-development are the distinguished character traits and manners of many oil and gas industry workers. This was the key to the industry flourishing in the second half of the twentieth century. During the period of the oil and gas sector establishing family dynasties of professionals rose, like Kysel, Mikhalevich, Mrozek, Rudko, etc.*

*Unfortunately, the book does not include the biographies of S.P. Vitryk, V.Yu. Zaichenko, V.P. Kozak, V.I. Miasnikov, V.M. Stefanyshyn, S.Ye. Cherpak, M.V. Chervinska who have made outstanding contributions to develop the base of oil and gas and their output in eastern Ukraine.*

*The book will be useful not only for professionals and students of the oil and gas industry, but also for the local historians, economists and ethnographers.*

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