

OIL AND GAS PRODUCTION

Interaction of silicate rocks with clay-cut acid muds in thermobaric conditions of bed.P.I. Influence of pressure on the solubility of rock.

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The paper examines dissolution properties of each component of oxides (silicon, aluminum, iron, calcium and magnesium) of Alta-Mud by acid-cut clay mud with increasing pressure. Dissolution of clay mineral sample by acids depending on pressure is an amount of dissolution of each metal oxide. In this case, dissolution of silicon and aluminum oxides with raising pressure increases and concerning other oxides it decreases.

To receive the maximum technologic effect (CAM) on the base of hydrochloric and hydrofluoric acids during the acting to the terrigene rocks it is necessary to consider the mechanism of interaction of acid mixture with the rock components. During the projecting of technology of clay and acid acting it is necessary to consider the degree of rock solubility of CAM which depends on temperature and pressure and possibility of creation of water-insoluble products of geterogeneous response, which presence influences upon the increasing of penetrating of producing formation.

The influence of pressure during interaction of acid solution with silicate rock is not studied enough nowadays. If the response of acid neutralization passes without the emission of gaseous carbon dioxide (CO₂) and silicon fluoride (SiF₄), the pressure is almost not affect the speed of the response. If the response takes place with the emission of gaseous products, the increase of pressure causes the slowdown of the response. For example, the half-time (half decrease of the concentration of acid) of hydrochloric acid in the interaction with calcium carbonate (marble) increases 8-9 times when pressure is 5-9 MPa and temperatures lower than 37 degrees, compared with atmospheric conditions [1].

The proposed research is the continuation of works as for the studying of CAM (10 % HCl+1 % HF) with silicate rocks of Prykarpattia (dispersed clay and carbon sandstones and gorodyschensky clay powder) under the atmosphere pressure) and depending the temperature in the range 40–80 °C. The indicated researches were conducted at the atmosphere pressure and temperature more than the critical one at which the gasous products of response are releasedThe indicated conditions do not correspond the conditions of interaction of CAM with the formation during the clay and acid action (CAA)when the formation pressure is significantly higher than the atmosphere one [2]. Therefore to understand the process of interaction of silicate rocks with CAM and study the peculiarities of geterogeneous response it is necessary to conduct thye experiments with mixture of phases at the simultaneous action of tension and temperature id est in thermobaric conditions close to the formation ones.

The researches were made by means of simultaneous influence of temperature and tension on the dissolution of samples of silicate rocks and the order of release of metal oxides from ther was defined. The interaction of different acid solutions (10 % HCl solution 1, 3 % HF solution, CAM at the base of mixture 10 % HCl and 1 % HF) with gorodyschenskyi bentonite clay powder was studied in autoclave at the temperatures 40 i 80°C and pressure 5, 10 and 15 MPa [3]. Bentonite clay powder from gorodyschenskyi mine was used for dissolution which contains

0,667g SiO₂, 0,124 g Al₂O₃, 0,056 g Fe₂O₃, 0,014 g CaO 0,012 g MgO in one gram of batch.

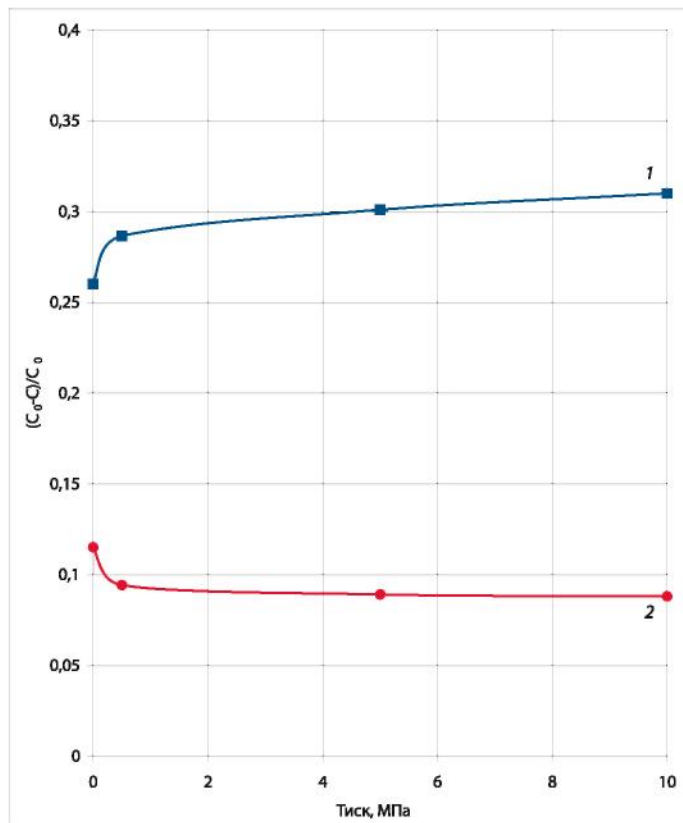


Fig. 1. Influence of pressure to the consumption of acid during the dissolving of gorodyschensky clay powder by the hydrochloride or hydrofluoride acid : 1 – 10 % HCl; 2 – 3 % HF

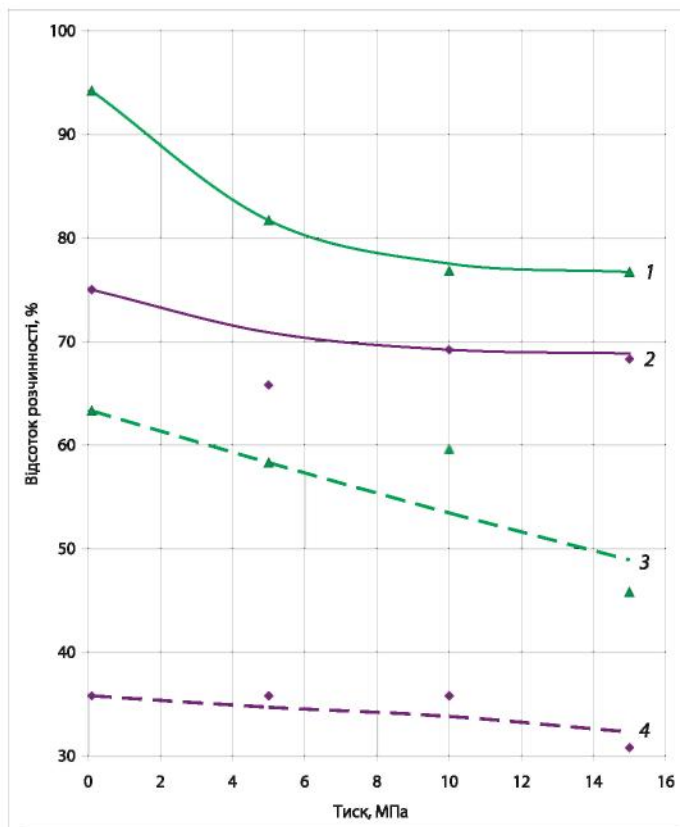


Fig. 2. Dependence of solubility of gorodyschensky clay powder of the pressure at the temperature 40 °C – curves 2, 4, at 80 °C – curves 1, 3;

at curing time 15 min and excess: 1,2 – acids; 3,4 - rocks

The using of gorodyschensky clay powder gives an opportunity the results of researches received preliminary for comparison. [2]. The surface area of clay powder defined by the method of sedimentation analysis is 0,08 m²/g. So, the ratio of acid volume to the external rock surface is in the range from 310·10⁻⁴ cm³/cm², which corresponds to the ratio of acid solution volume to the cylindrical channel surface with a radius 40–620 μm. The described methods of researches conduction ensured the creation of conditions of passing of dissolution response similar to the formation ones. The analysis of chemical content of clay powder and undissolved rest was made according the standard methods of analysis of silicate rocks. [4, 5]. Determination of general acidity of initial filtrate of acid solution are made by the methods [6], which provide the defining of free acid if the salts of aluminium and iron are present.

The mining zone of formation from the well bore to the front of movement of active acid in the pore environment can be divided into two large zones. The first one is the zone of excess of acid over the rock which is characterized by the high residual acidity of the solution (from 99% at the input to the perforation holes to 10% at certain distance from the well bore). The second is the zone of excess of rock over the acid which is characterized either with the slight acidity of Solution (up to 10%) or the full neutralization of acid solution and possibility of sedimentation of slightly soluble and non-soluble products of the response. The indicated zone is located closer to the front of movement of active acid. Therefore the experimental researches of solubility of rock must be carried out as for the conditions of excess of acid over the rock and the excess of rock over the acid. The ratio of volume of acid to the mass of clay powder was chosen so to model the indicated opposite conditions: the excess of acid was created at the correlation 2 g of rock for 50 cm³ of acid solution and the excess of rock - 10 cm³ CAM for 5,5 g of rock. Curing time of acid solutions for the solubility of rock was 15 min. It is connected with that. Earlier it was found out that the neutralization of clay and acid solution in the pore environment occurred during first minutes of its pumping which ensures the dissolution of 85% of soluble components of silicate mineral during 15 min [7]. Consequently the indicator of curing (15 min) is rather informative and defining for understanding of mechanism of interaction of acid solution with rock components in the initial period of pumping of the acid to the formation.

Solubility of bentonite powder from gorodyschenskyi mine under different pressure was studied both in separate solutions of hydrochloride and hydrofluoride acids and in the clay and acid mixture.

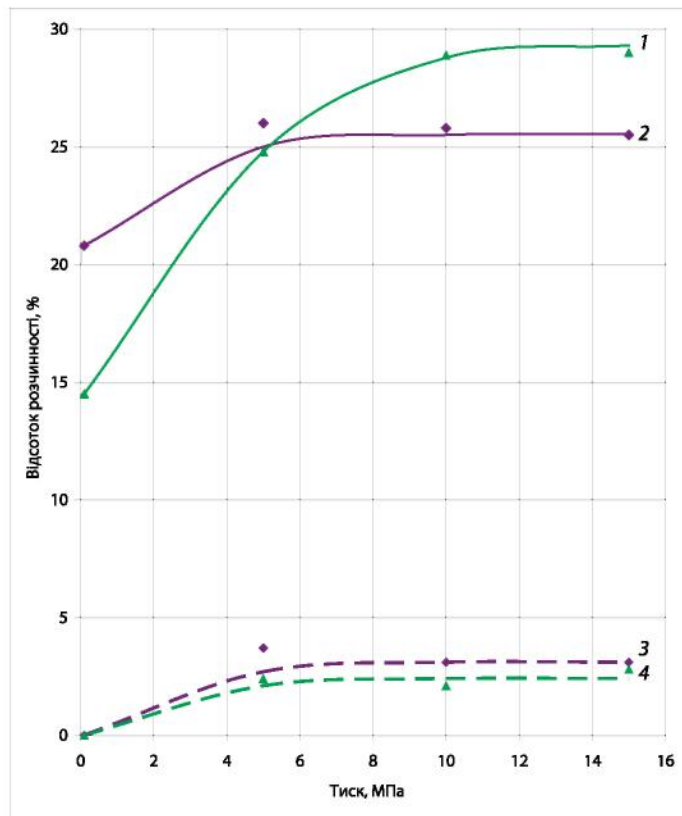


Fig. 3. Dependence of solubility of silicon oxide from gorodyshchensky clay powder of the pressure and temperature: at 40 °C – curves 2, 3, at 80 °C – curves 1, 4; at curing time 15 minutes and excess of : 1, 2 – acid; 3, 4 – rock

The solubility of clay powder in 10% solution HCl or 3% solution HF was defined at the temperature 80 °C and during the curing during 30 min with the correlation of the batch to the volume of the acid as 1g to 50 cm³ (condition of excess of acid over the rock). Received results are given on Fig.1. They testify that the pressure increasing up to 10MPa causes the increasing of consumption of hydrofluoride acid approximately 20% and slowing down of degree of neutralization of hydrochloride acid on 30%. As a result the solubility of bentonite is decreased from 10,7 to 7,7% during the using of the hydrochloride acid. As for hydrofluoride acid the solubility of bentonite with increased pressure up to 10 MPa is increased from 56 to 75%. At this the biggest influence of pressure is observed in the interval from 0,1 to 1 MPa and its further increasing practically does not influence on the change of consumption of one or another acid.

The studying of process of dissolution of gorodyshchenskyi bentonite clay powder in the mixture of hydrochloride and hydrofluoride acids in different conditions (temperature 40 and 80 °C, excess of acid or rock) shows that increasing of pressure from 0,1 to 15 MPa in the case of short-time curing (0,25 h) practically does not influence the sample solubility – it is stabilized at the certain level. (Fig.2). The received results testify that researches of soluble ability of bentonite clays in the different acid solutions can be conducted at atmosphere pressure to simplify the methods of researches, because the maximum deviation of true meaning at the given pressure on this material does not exceed 10 % (which is within the admissible errors of the experience). The indicated exception does not concern the other samples of silicate rocks for which the significant influence of pressure upon the solubility capacity is possible (it is necessary to conduct the corresponding researches for each specific mineral).

The quantity of received results is not sufficient to define the influence of pressure to the dissolving capacity of acid solutions for silicate materials. Such factors as temperature increasing, curing time and correlation of acid volume to the rock surface ensure the increasing to some extent of the solubility of clay powder in the mixture of hydrochloric and hydrofluoric

acids. The most important factors as for the increasing of speed of solutability is the correlation of the volume of acid to the rock surface and increasing of temperature. It is set that the mass of dissolved rock for one gram of its initial mass of sample for 15 minutes of interaction at the excess of acid (curves 1, 2, fig. 2), in comparison with the excess of rock (curves 3, fig. 2), are increased three (from 0,1-0,12 g/g to 0,34-0,36 g/g). Correspondingly the temperature increasing from 40 to 80°C to less extent but also ensures the increasing of solutability of clay powder in the acid mixture.

The dissolution of base oxides which are the base of bentonite clay powder is the critical for understanding of the mechanism of influence of pressure on the speed of dissolution of silicate rocks. (fig. 3-7). The previous researches found out that that at the excess of rock for 15 minutes of curing at the temperature 80 °C and atmosphere pressure the biggest indicators of dissolution belong to calcium (64 % of the clay powder content in the sample) and magnesium oxide (60%) and iron oxide (62%). The aluminium oxide is sustained only on 30% and silicon oxide is not dissolved at all. The pressure increasing from 0,1 to 15 MPa causes the partial (5-10%) decreasing of sustaining of calcium, magnesium and iron oxides and increasing 2-3% of the sustaining of silicon oxide at the excess of rock and 5-15% at the excess of acid (fig.3) and aluminium oxide on 3-15% of their content in the sandstone (fig.4). Such an increasing of the quantity of dissolved oxides Al₂O₃ and SiO₂ is connected with the improving of conditions of penetrating of both acids (but especially hydrofluoric which is shown on fig. 1) to the centre of silicon tetraedres where mainly ions of silicon and aluminium are located. The decreasing of temperature of interaction 80 to 40 °C causes the decreasing of quantity of all suspended oxides on 5-10%.

In the case of excess of rock the process of dissolution of aluminium oxide with increasing of pressure tends to increase (fig.4) which is intensified with increasing of temperature. At the same conditions during dissolution of iron oxide with increasing of pressure on the contrary we can observe the tendency for decreasing (fig.5) and the temperature increasing ensures the increasing of oxide dissolution.

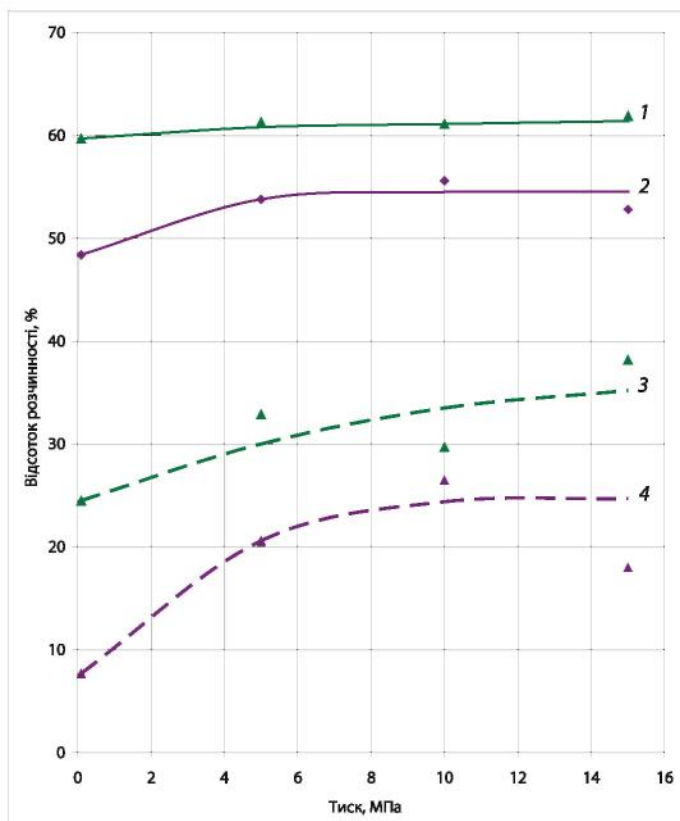


Fig. 4. Dependence of solubility of aluminium oxide from gorodyshchensky clay powder of the pressure and temperature: at 40 °C curves– 2, 4, at 80 °C –curves 1, 3; at curving time 15 min and excess of: 1, 2 – acid; 3, 4 – rock

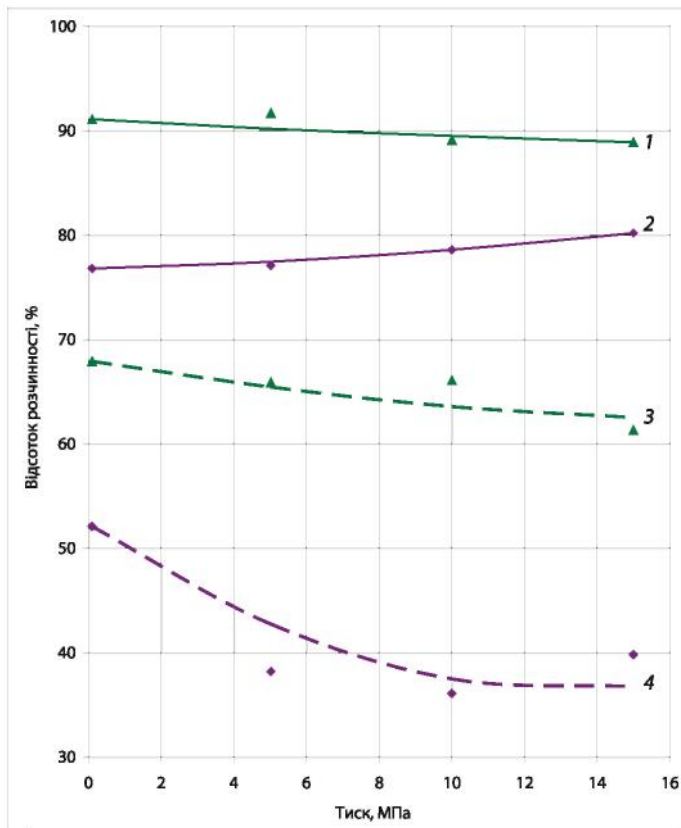


Fig.5. Dependence of solubility of iron oxide from gorodyshchensky clay powder of the pressure and temperature: at 40 °C curves– 2, 4, at 80 °C –curves 1, 3; at curving time 15 min and excess of: 1, 2 – acid; 3, 4 – rock

In the case of excess of the rock the dissolution of calcium oxide (fig.6) and magnesium oxide (fig.7) with the increasing of pressure tends to decrease and the increasing of temperature ensures the increasing of oxides solubility.

The acid excess (conditions created following the front of movement of first portions of acid and specific for the majority of acid and clay mud) promotes more complete suspension of researched oxides especially silicon oxide. For silicon oxide such an increasing is 7-10 times and for the other oxides – only 1.5-2 times in comparison with indicators specific for the condition of excess of rock over the acid. At this it is also necessary to consider that in case if excess of acid for short time (15 min) of interaction almost all oxides of two and three valent metals are dissolved and partially silicon oxides which are the components of silicate mineral (silicon oxides in the form of quartz do not undergo the acid action). The power increase from 0,1 to 15 MPa causes partial (5-15%) decrease of sustaining of calcium, magnesium and aluminium oxides, slight change of quantity of iron oxide and the increase of sustaining of silicon oxide for 5-15% of their content in the rock. Id est the pressure increase in the case of excess of acid works as the factor of decrease of solubility of most oxides of silicate minerals. In case of excess of the acid the process of dissolution of aluminium oxide with increase of pressure tends to increase (fig. 4). Excess of acid during the dissolution of iron oxide with the pressure increase tends to decrease (fig.5) except the case of short-time curing of the solution with the rock under the temperature 40 °C. In the case of excess of acid the dissolution of calcium oxide (fig.6) and magnesium oxide (fig.7) with increase of pressure tends to decrease. As the main part during the dissolution of betonite is the oxides of aluminium and iron, and less – oxides of calcium and magnesium then

when increasing the pressure we can observe either the decrease of sample solubility of the clay powder or the stabilization of solutability at certain level (id est increase of solutability of silicon oxide does not compensate the decrease of solutability of basic oxides of clay powder).

The carried out researches of solutability of gorodyshchensky bentonite clay powder in the mixture of 10% hydrochloride and 1% of hydrofluoride acids at the increased pressures testify that increase of pressure of interaction from the atmosphere to 15 MPa results either decrease of solutability of clay powder sample, or to the stabilization of solutability at certain level in the case of using of 10% HCl and 1 % HF. In the case of independent using of 3% solution HF with the increase of pressure on the contrary we can observe increase of solutability of bentonite clay powder. Such a difficult character of dependence of solutability of silicate rocks and minerals by acids of the pressure of interaction can be explained only the dependence of quantitative composition of carbonate and silicate components in the terrigene rock. At this when increasing the pressure of interaction the silicon oxides and aluminium oxides ensure increase of solutability of samples of terrigene rocks and the oxides of iron, calcium and magnium – on the contrary, decrease of samples solutability.

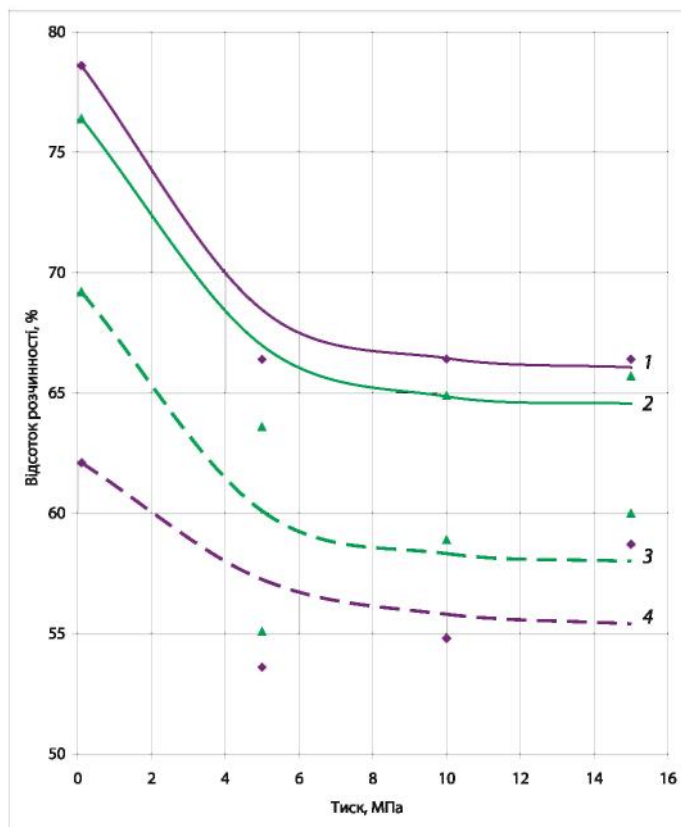


Fig. 6. Dependence of solubility of calcium oxide from gorodyshchensky clay powder of the pressure and temperature: at 40 °C curves– 2, 4, at 80 °C –curves 1, 3; at curving time 15 min and excess of: 1, 2 – acid; 3, 4 – rock

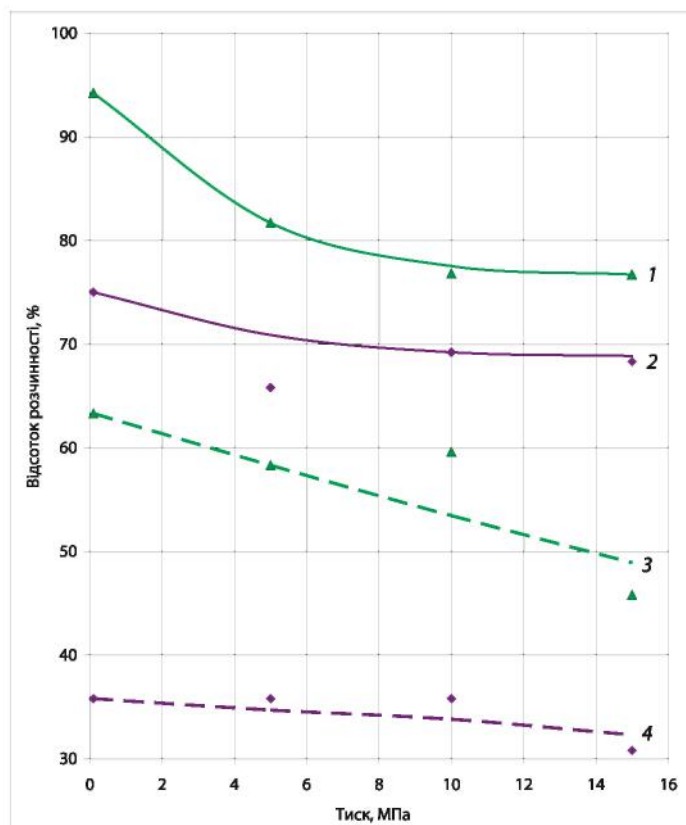


Fig. 7. Dependence of solubility of magnesium oxide from gorodyshchensky clay powder of the pressure and temperature: at 40 °C curves– 2, 4, at 80 °C –curves 1, 3; at curving time 15 min and excess of: 1, 2 – acid; 3, 4 – rock

Thus, during the interaction of any sample of silicate mineral with acid solution of the diverse composition, its solubility is the sum of the solubility of all basic oxides of metals of this sample. Consequently, dependence of the general indicator of solubility of various factors will depend on their influence on the solubility of each particular oxide and its part in the total amount of dissolved material. This interaction mechanism can be explained by the previously obtained results concerning the influence of pressure on the solubility of different rock samples. So, if the hydrochloric acid is used independently, the carbonate components are dissolved primarily and partially oxides of iron and aluminum. In connection with the dissolution of three of four oxides with slowed character with increasing of pressure for a general increase of pressure of bentonite clay powder one can observe the decrease of level of neutralization of hydrochloric acid by 30 %.

With the increase of part of carbonate components in the rock (for example, in the carbonate sandstone up to 15 %) the rate of dissolution slows in 1,5-2 times [3]. In the case of independent use of hydrofluoric acid the dissolution of oxides of silicon iron and aluminium prevails. In connection with the dissolution of two of three basic oxides with accelerated character with increasing pressure for the general solubility of bentonite clay powder the increase in the degree of neutralization of HF by 20 % is observed.

If we use CAM, we can observe the dissolution of all five oxides of bentonite clay powder, so the total solubility sample is defined as their sum. As the total solubility of bentonite decreases with increasing pressure, then this suggests that the solubility of iron calcium and magnesium oxides prevails the solubility of silicon and aluminium oxides. Consequently the general solubility of bentonite in such conditions is insignificant and amounts to a maximum of 10 %. Under certain conditions (short interaction time, the excess of the rock over acid) the growth of solubility of silicon and aluminium oxides is comparable with the decrease of solubility of iron oxides, calcium and magnesium, therefore, the general sample solubility with increasing pressure is stabilized at a certain level. The received results of experimental

researches of solubility of bentonite clay powder from gorodyschensky mine in the acid solutions of various content give an opportunity to make such conclusions. The modeling of conditions of passing of interaction of acid solutions with silicate rock is first carried out at the correlation of the volume of acid to the rock surface which corresponds pore channels with the size 40–620 mcm, in dynamic (during the mixing) and thermobaric (temperature 40–80 °C, pressure from 0,1 to 15 MPa) formation conditions as well as at excess and lack of acid. This helped to study the mechanism of interaction of acid solution with rock in different parts of the bottomhole formation zone: from the wellbore to the front of the movement of the active acid, where the value of the acidity of a solution is enough high (from 99 % to 10%), and at the front of movement of the first portions of acid, where the value of the acidity of a solution does not exceed 10 % or the solution is completely neutralized, and consequently the conditions of rock excess are created in the formation and there is the possibility of loss of low-soluble products of neutralization.

The solubility of bentonite clay powder under the increased pressures depends significantly of the composition of acid solution. Thus, in the case of use of hydrochloric acid as for the carbonate rocks the solubility of clay powder slows down with increase of pressure. If the hydrofluoric acid is used the solubility of clay powder on the contrary increases with pressure increase. In the case of applying of acid clay mud at the base of 10 % HCl and 1 % HF the solubility of clay powder with pressure increase for the short time of interaction either does not change or slows down. Consequently the experimental researches concerning the study of solubility of bentonites in acid solutions of various content can be carried out according the simplified methods – at the atmosphere pressure because it simplifies the carrying out of the researches themselves and gives an opportunity to receive meanings specific for the formation conditions.

The order of dissolution of oxides at the absolute meaning from the composition of bentonite clay powder in conditions of excess of acid for 15 min of curing at pressures from 0,1 to 15 MPa actually corresponds their initial distribution in the rock sample (almost all oxides R_2O_3 and RO are soluble and partially RO_2). In conditions of rock excess the selective dissolution of oxides occurs ($R_2O_3 > RO > RO_2$).

It is found out that the solubility of any silicate sample by the acid solution of various composition at increased pressure is the sum of solubility of all its basic metal oxides. At this silicon and aluminium oxides with the increase of pressure of interaction ensure the increase of solubility of samples of terrigenous rocks and iron, calcium and magnesium oxides with increase of pressure – decrease of samples solubility. As the mineralogic composition of silicate minerals is various then the dependence of their solubility in clay and acid muds at thermobaric conditions may differ from the received dependence for aluminium silicate (bentonite clay powder). Therefore the indicated researches must be continued at least for the main classes of silicate minerals.

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