

INTERACTION BETWEEN DISSOLVED SILICA AND CALCITE

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In this work, we investigated the interaction between dissolved silica and calcite during adsorption and coprecipitation in connection with the problem of retardation of recrystallization process in oil chalk reservoirs.

To assessment the interaction a lot of attention was given to choose optimal experimental conditions: silica to calcite ratio ($\text{SiO}_2/\text{CaCO}_3$), concentration of calcite-forming reagents, calcite precipitation rate, etc. All experiments were performed in a glass jacked reaction vessel ($T=25^\circ\text{C}$) at different CO_2 partial pressures ($p\text{CO}_2=10^{-3.5}$ atm and 1 atm).

In the adsorption studies weighed amount of calcite powder (1-10 g) and 50 ml of 0.1 M NaCl solution were placed into the reaction vessel. When the equilibrium at given CO_2 partial pressure between calcite and the solution was reached (controlled by pH and Ca-electrodes) the aliquot of 0.1 M SiO_2 solution was added into the vessel. The calcite suspension concentration ranges from 20 to 200 g/L. The aqueous phase was periodically sampled, filtered with $0.2\ \mu\text{m}$ (Sartorius) and analyzed for silica. Simultaneously we ran blank experiments with the same silica concentration but without calcite in the system. To determine concentration of silica in the taken samples the colorimetric method was used. We could not see any difference between silica concentration in the samples and the blank samples even when the amount of placed calcite was high. We also analyzed silica concentration in solid phase. To do that, in the end of each experiment calcite was rinsed several times with calcite-saturated solution and dried at 60°C for 10-12 hours. A part of the solid sample was dissolved in 5 M HCl and analyzed for Si by colorimetric method. Results show small amounts of silica in calcite phase (less than 1.5 %), which increase with increasing SiO_2 concentration in the solution (fig. 1).

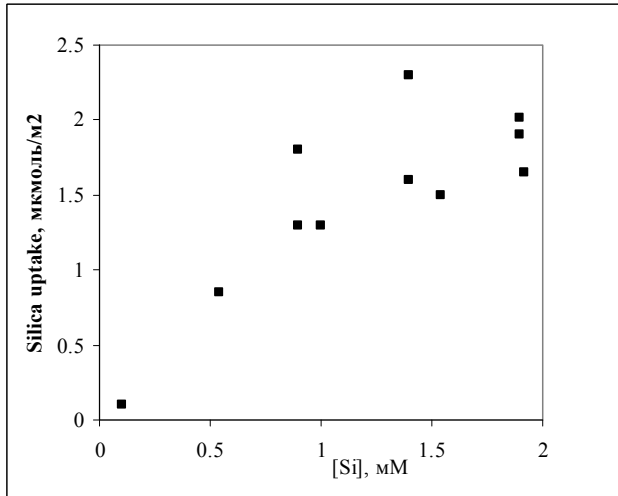


Fig.1. The dependence of silica uptake (mcmol/m²) on SiO_2 concentration in solution. CaCO_3 concentration consists 30 g/L

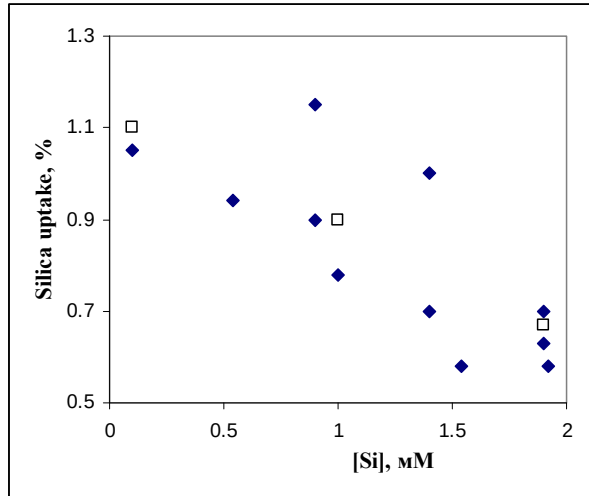


Fig.2. The dependence of silica uptake (%) on SiO_2 concentration in the solution for two solid to solution ratios (♦ - 30 g/L, □ - 150 g/L)

Fig. 2 shows the dependence of silica uptake (%) on SiO_2 concentration in the solution for two solid to solution ratios (♦ - 30 g/L, □ - 150 g/L).

One can see from fig. 2 that the amount of silica uptake for different calcite concentrations has similar values. This fact contradicts the idea of adsorption theory where the rising of the concentration of adsorption sites causes the increasing of decline of adsorbed component from solution. That is why in the experiments with high calcite concentrations (more than 150 g/L) the changes of SiO_2 concentration in the solution should be appreciable (at least more than 5%). But we did not observe it. The most plausible ex-

planation is that uptake is not correlated with adsorption of monomeric silica, as was interpreted by Klein and Walter (1995) [1], but rather that silica removal from solution depends on silica polymers precipitation, of which the amount depends on $\text{SiO}_{2(\text{aq})}$ concentration in solution.

A set of coprecipitation experiments was performed using the constant addition method which allows to synthesize solid phase of a constant composition at a given precipitation rate. An amount of calcite powder (0.5 g) was placed into the glass reaction vessel with 50 ml of NaCl solution at $P_{\text{CO}_2}=1$ or $10^{-3.5}$ atm. Precipitation was induced by injection at fixed rate (0.008-0.05 mL/min) of two separate solutions (CaCl_2 and Na_2CO_3) with the same molarity (0.2-0.7 M) with peristaltic pump. After steady-state was reached, where solution composition in the vessel became constant (controlled by pH and Ca-electrodes), aliquots of 0.1 M SiO_2 were added into the vessel and Na_2CO_3 solution to get equal silica concentrations in them. After that the solutions were continuously pumped with the same rate. The duration of experiments varied from 24 to 72 hours. In the end of run the determination of silica concentration in the solid phase was determined in the same way like for adsorption experiments.

The dependence of SiO_2 uptake ($\text{SiO}_{2(\text{uptake})}$) on calcite precipitation rate at $p\text{CO}_2 = 1$ and $10^{-3.5}$ atm is shown on fig. 3. The amount of coprecipitated silica is significant at $\text{pH}=8.3$ ($p\text{CO}_2 = 10^{-3.5}$ atm) and increases with increasing concentration of SiO_2 in the solution. At pH 6 silica uptake is minimum and does not depend on its concentration in the solution.

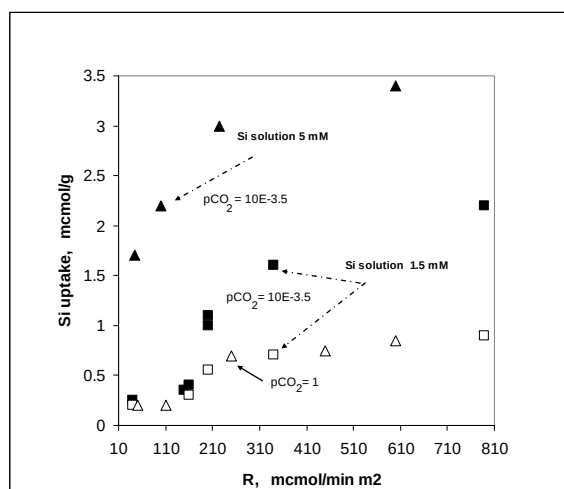


Fig.3. The dependence $\text{SiO}_{2(\text{uptake})}$ on calcite precipitation rate R (mcmol/min m²)

We also observed that $\text{SiO}_{2(\text{uptake})}$ increases with increasing calcite precipitation rate. Such behavior is similar to the behavior of other elements which distribution coefficient is less than 1. By equation 1 silica distribution coefficient was calculated to be about 10^{-3} .

$$K_d = \frac{[\text{silica}]_s}{[\text{carbonate}]_s} \times \frac{[\text{carbonate}]_{\text{aq}}}{[\text{silica}]_{\text{aq}}} \quad [1]$$

Reference

1. Klein & Walter // Chemical Geology. 1995. 125. P. 29-43.

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