

EXPERIMENTAL STUDY OF SORPTION OF HEAVY METALS (CU, ZN, PB, CD, CO, NI, MN) BY ALUMINA-SILICATE GELS

A.V. Savenko

(Lomonosov Moscow State University, Geological Faculty, Moscow, Russia)

Key words: heavy metals, alumina-silicate gels, geochemical barriers

Construction of protective screens based on alumina-silicate gels is the very perspective technologic decision for the problem of localization of antropogenic sources of pollution. It was estimated by [1] that alumina-silicate gels possess of high sorption capacity with respect to heavy metals. But the method used by [1] was not completely correct, because the alumina-silicate gel used in experiments was not separated from the intermicellar solution, which contained oxalate- and sulfate-ions constituting poorly soluble compounds with heavy metals. These ions are capable to change the sorption equilibrium state due to formation of complex ionic forms. To specify the available information we have provided for thorough studies of sorption of heavy metals (Cu, Zn, Pb, Cd, Co, Ni, Mn) on alumina-silicate gels under extensive range of acid-base conditions of solutions.

Rather fast removal of dissolved compounds into environment takes place while exploiting protective alumina-silicate gel screens. Solid phase is the main factor to control the immobilization of pollutants. Therefore our experiments were focused on immobilization of pollutants onto a solid phase of pure alumina-silicate gel. The gel was washed many times from intermicellar solution with distilled water. The quality of removal of intermicellar solution was controlled by the absence of reaction with barium indicative for sulfate ion. Experiments were provided in addition to study an interaction between solutions of heavy metals and intermicellar liquid from alumina-silicate gels.

The alumina-silicate gel applied to experiments was prepared using the conventional method [1] by mixing the solution of sodium silicate (density 1.19 g/cm³) and the complex solvent, which contains 50 g/l of aluminum sulfate and 50 g/l of oxalic acid. Sorption of heavy metals on the washed alumina-silicate gel was studied in background solutions of 0.10M NaClO₄ and 0.05M CH₃COONa. Variable amounts of concentrated CH₃COOH were added to maintain the pH level inside the 3.9–6.5 ranges. The water content in gels was determined by drying under 110 °C as 90 %. The gel/solution ratio by weight was constant during the experiments (1 : 50 or 1 : 500 when calculating on dry substance of gel). Concentrations of heavy metals varied 33 μM to 290 μM in initial solutions. The procedure of experimental study of interaction between solutions of heavy metals and the intermicellar liquid from alumina-silicate gel was the follows: 10 ml of solution of heavy metals (the level of concentration of every heavy metal was about 11 mM) was added to 50 ml of mixture of intermicellar solution and distilled water. The initial concentration of heavy metals varied 1.5 mM to 2.1 mM in experiments, but the proportion of intermicellar liquid varied from 33 % to 83 %. Samples were stirred intensively for 7 days, and were filtered through the “blue ribbon” dense paper filter after that. The pH value in filtrate was measured by potentiometer, and residual concentrations of heavy metals were determined by AAS.

The study of sorption properties of pure alumina-silicate gel has shown that sorption isotherm is linear for entire range of equilibrium concentrations of heave metals applied to experiments, as follows:

$$\Gamma_i = K_d [i], \quad (1)$$

where Γ_i is the specific sorption capacity of element i in μmol/kg, $[i]$ is the concentration of element in equilibrium solution in μM, K_d is the distribution coefficient of metals between gel and solution in l/kg.

The experimental data was processed using the equation (1). As a result, average values were obtained of distribution coefficients of metals in seriated experiments with solutions of different acidity (table 1). One can see in the table, that parameters of sorption equilibrium is independent upon acid-base conditions for cobalt, nickel, and manganese, but sorption effectiveness increases with decrease in acidity of medium for copper, zinc, lead, and cadmium. There are linear equations of correspondence between the K_d logarithm and the pH value, as follows:

$$\lg K_d = a + b\text{pH}. \quad (2)$$

Values of coefficients a and b are listed in the table 2.

Values of sorption capacity of alumina-silicate gels with respect to studied elements differ significantly (table 1). The highest sorption capacity under entire range of acid-base conditions is characteristic for lead. Sorption capacity for copper is also high enough, but it is approximately two

fold less. Removal of zinc cadmium, cobalt, nickel, and manganese by sorption is insignificant: K_d values are less than 6 l/kg for these elements.

Table 1.

Distribution coefficients of heavy metals (K_d , l/kg) between solution and gel

Metals pH	Cu	Zn	Pb	Cd	Co	Ni	Mn
6.43 ± 0.05	26.7 ± 3.6	5.7 ± 0.3	54.6 ± 2.4	4.9 ± 0.4	4.0 ± 0.7	3.1 ± 0.4	3.2 ± 0.6
4.98 ± 0.01	7.1 ± 1.6	2.0 ± 0.3	11.0 ± 2.6	3.0 ± 0.7	4.4 ± 0.9	2.6 ± 0.5	2.9 ± 1.0
3.92 ± 0.01	2.4 ± 0.4	1.7 ± 0.4	4.4 ± 1.1	1.7 ± 0.8	3.9 ± 1.2	2.3 ± 0.4	3.3 ± 1.2

Table 2.

Values of parameters and correlation coefficients for equation (2)

Metals	a	b	r
Cu	-1.220	0.416	0.998
Zn	-0.673	0.218	0.960
Pb	-1.086	0.440	0.999
Cd	-0.449	0.181	0.988

When solutions interact with intermicellar liquid of alumina-silicate gels, poorly soluble oxalates and sulfates of heavy metals originate. This may enforce the protective capacity of gel screens at the early stage of their exploitation. The experiments have shown that the mixture with 33 % to 83 % of intermicellar liquid removes 96.1–98.6 % of lead, 83.8–98.2 % of cadmium, 60.9–92.7 % of zinc, and 23.9–91.1 % of manganese. Nevertheless the removal of copper, cobalt, and nickel was insignificant due to precipitation of their own mineral species (4.5–51.3 %, 8.6–27.7 %, and 1.1–4.8 %, correspondingly).

Hence in general rather high effectiveness of immobilization of heavy metals is characteristic for alumina-silicate gel barriers. Formation of poorly soluble compounds of heavy metals with oxalate- and sulfate-ions plays an important role during the period of diffusion removal of dissolved solids from intermicellar liquid. This allows to enforce the process of immobilization of pollutants by introducing dissolved compounds, which are inert with respect to alumina-silicate phase but are capable to produce poorly soluble compounds with poorly sorbed elements, into gel-forming mixtures.

The results obtained allow to make the following conclusions:

1. Alumina-silicate gels washed from intermicellar liquid possess a high sorption capacity with respect to lead and copper, but of low sorption capacity with respect to zinc, cadmium, cobalt, nickel, and manganese.
2. The effectiveness of sorption of copper, zinc, lead, and cadmium increases with decrease in acidity of medium in accordance with linear regression equations between logarithm of distribution coefficient of metals K_d and pH value. Parameters of sorption equilibrium are independent upon acid-base conditions for cobalt, nickel, and manganese.
3. Formation of poorly soluble compounds of lead, cadmium, zinc, and manganese with oxalate- and sulfate-ions contained in intermicellar liquid of alumina-silicate gels results in immobilization of essential amounts of these metals even under high proportion of distilled water in mixture. Precipitation of own mineral phases is less effective for copper, cobalt, and nickel.

The research was supported by the RFBR, grant 01-05-64668.

Reference:

1. The underground water protection from pollution in regions of projecting and operated waste reservoirs (by edition of V.I. Sergeev). M.: MSU Press, 1992. 168 p.

*Electronic Scientific Information Journal "Herald of the Department of Earth Sciences RAS" № 1(21) 2003
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2003
URL: http://www.segis.ru/russian/cp1251/h_dgggms/1-2003/informbul-1_2003/hydroterm-20e.pdf
Published on July 15, 2003*

© Department of the Earth Sciences RAS, 1997-2003
All rights reserved