

Radioactive wastes

Kotova N.P., Ivanov I.P. Phase equilibria in the system (Na, Cs)₂O-SrO-Al₂O₃-P₂O₅-H₂O within the range of T=25-350°C and P_{sat} - 500 bar (in connection with the problem of deep radioactive waste repository).

key words [*Sr phosphates glass equilibrium solutions*]

The system (Na, Cs)₂O-SrO-Al₂O₃-P₂O₅-H₂O has been designed to model phase equilibria at leaching by underground waters of technological glass containing ra-



The T-P phase diagram of this system has been calculated for the range of T=25-350°C and P_{sat}=500 bar (fig.1). As follows from the figure equilibria of hydration reactions 1,9, and 4 realized in the T and P range in question are temperature-governed. Pressure is of minute effect for them. Reactions 1,4, and 9 partition the diagram into 4 divariant fields - I, II, II, and IV. Ternary phase associations within each field are illustrated on the composition - paragenesis diagrams. The hydration reactions have shown that in the range of T=25-350°C and P=P_{sat}-500 bar the completely stable phases are SAP, SPH, DSP. Variscite (VAR) is stable in the confines of field I at T<186°C. Above of 186°C VAR gets dehydrated (by reaction 1) and transforms to berlinite (BER). At the II=III fields boundary the association GO+SPH transforms to the association SAP+BER by reaction 2, at the III-IV fields boundary GO decomposes completely (following reaction 4) with formation of the association DSP+BER+SAP. At T>300°C 2 ternary associations are stable : DSP+BER+SAP and BER+SAP+SPH.

In the closed system SrO-Al₂O₃-P₂O₅-H₂O we have calculated the combined solubility of ternary parageneses of solid phases including SAP, GO, and SPH. With the

radioactive isotopes ⁹⁰Sr and ¹³⁷Cs under deep repository conditions.

It has been found that phosphates of Na and Cs are readily leached from glass. In the repository site there remain low-soluble phases: Sr-hydroxidapatite (SAP) - Sr₁₀(PO₄)₆(OH)₂, goyuzite (SO) - SrAl₃(PO₄)₂(OH)₅·H₂O, strontium hydrophosphate (SPH) - SrHPO₄, diaspore (DSP) - AlOOH, berlinite (BER) - AlPO₄, variscite (VAR) - AlPO₄·2H₂O that enter the system SrO-Al₂O₃-P₂O₅-H₂O. A thermodynamic database has been created for these phases concluding brine particles.

Fig.1. T-P phase diagram of the closed system 1-3 monovariant lines, I-IV - divariant fields, GL-figurative technological glass composition

phase ratios 1:1:1 the compositions of eutonic solutions have been calculated at 25, 186, 260 and 300°C and P_{sat} corresponding to phase transition boundaries VAR = BER, GO+SPH=BER+Sap and GO=BER+SAP+DSP on the T-P diagram of the system. It has been found that out of Sr-phases the minimal solubility is demonstrated by SAP ($n \cdot 10^{-7}$ mole/kg H₂O), the maximal one is demonstrated by SPH ($n \cdot 10^{-4}$ mole/kg H₂O), so is in the intermediate position between them. The results of calculation are listed in the table. On all the composition - parageneses diagrams the figurative technological glass (GL) composition is plotted. It appears to be shifted far from the region of compositions of low-soluble phases towards the readily soluble component P₂O₅. In the temperature range 25-186°C on the line of saturated water vapor the GL composition lies in the field of the triangle VAR-SPH-P₂O₅, above 186°C in the field of the triangle BER+SPH+P₂O₅. In either case no crystalline phase of P₂O₅ exists as it is dissolved in water once it is abundant. The concentration of Sr in the solution at the glass-water interaction is: at 186°C and P_{sat} - $1.3 \cdot 10^{-3}$ mole/kg H₂O, at T=260°C and P_{sat} - $1.3 \cdot 10^{-4}$ mole/kg H₂O, at T=300°C and P_{sat} - $2.4 \cdot 10^{-5}$ mole/kg H₂O.

Table. Combined (eutonic) solubility of ternary association of solid phases in the system SrO-Al₂O₃-P₂O₅-H₂O at P=P_{sat}

Association	T°, C	Equilibrium solution mole/kg/H ₂ O			pH	Precipitation sequence
		Al _{tot}	Sr _{tot}	P _{tot}		
DSP+SAP+BER	350	4.94.10 ⁻⁶	4.54.10 ⁻⁷	1.99.10 ⁻⁵	5.093	SAP→DSP→BER
DSP+SAP+BER	300	3.56.10 ⁻⁶	6.56.10 ⁻⁶	4.04.10 ⁻⁵	4.746	SAP→DSP→BER
BER+SAP+SPH	350	9.28.10 ⁻⁸	2.20.10 ⁻⁶	6.10.10 ⁻⁴	4.264	SAP→BER→SPH
BER+SAP+SPH	300	1.74.10 ⁻⁷	2.39.10 ⁻⁵	3.10.10 ⁻⁴	4.101	SAP→.BER→SPH
BER+SAP+SPH	259	2.21.10 ⁻⁷	6.58.10 ⁻⁵	2.69.10 ⁻⁴	4.020	SAP→BER→SPH
GO+SAP+BER	299	3.34.10 ⁻⁶	6.97.10 ⁻⁶	4.24.10 ⁻⁵	4.732	SAP→GO→BER
GO+SAP+BER	259	2.27.10 ⁻⁷	6.51.10 ⁻⁵	6.66.10 ⁻⁴	4.208	SAP→GO→BER
DSP+SAP+GO	299	3.53.10 ⁻⁶	6.67.10 ⁻⁶	3.97.10 ⁻⁵	4.755	SAP→DSP→GO
DSP+SAP+GO	259	2.62.10 ⁻⁶	9.30.10 ⁻⁶	2.43.10 ⁻⁵	5.173	SAP→DSP→GO
DSP+SAP+GO	187	2.37.10 ⁻⁶	8.95.10 ⁻⁶	1.07.10 ⁻⁵	6.107	DSP→SAP→GO
DSP+SAP+GO	25	9.50.10 ⁻⁸	1.12.10 ⁻⁵	8.64.10 ⁻⁶	8.713	DSP→SAP→GO
DSP+GO+BER	299	3.51.10 ⁻⁶	6.49.10 ⁻⁶	4.07.10 ⁻⁵	4.734	DSP→GO→BER
DSP+GO+BER	259	1.76.10 ⁻⁶	2.82.10 ⁻⁶	5.21.10 ⁻⁵	4.434	DSP→GO→BER
DSP+GO+BER	187	3.70.10 ⁻⁷	1.87.10 ⁻⁷	8.15.10 ⁻⁵	4.141	DSP→GO→BER
BER+GO+SPH	258	2.13.10 ⁻⁷	6.77.10 ⁻⁵	2.75.10 ⁻⁴	4.196	BER→GO→SPH
BER+GO+SPH	187	5.06.10 ⁻⁹	5.75.10 ⁻⁴	2.30.10 ⁻³	3.445	BER→GO→SPH
DSP+GO+VAR	186	3.62.10 ⁻⁷	1.83.10 ⁻⁷	8.09.10 ⁻⁵	4.143	DSP→GO→VAR
DSP+GO+VAR	25	2.95.10 ⁻⁹	2.09.10 ⁻⁷	1.91.10 ⁻⁶	5.807	DSP→GO→VAR
VAR+GO+SPH	186	4.86.10 ⁻⁹	5.85.10 ⁻⁴	2.33.10 ⁻³	3.444	GO→SPH→VAR
VAR+GO+SPH	25	6.76.10 ⁻¹²	3.77.10 ⁻⁴	7.36.10 ⁻⁴	5.601	GO→SPH→VAR
GO+SAP+SPH	258	2.16.10 ⁻⁷	6.70.10 ⁻⁵	2.69.10 ⁻⁴	4.206	SAP→GO→SPH
GO+SAP+SPH	187	1.73.10 ⁻⁸	1.45.10 ⁻⁴	3.23.10 ⁻⁴	4.649	SAP→GO→SPH
GO+SAP+SPH	25	2.47.10 ⁻¹¹	1.16.10 ⁻⁴	1.74.10 ⁻⁴	6.870	GO→SAP→SPH

References:

- Ivanov I.P., Kotova N.P., Plyasunov A.V. (1994) Investigation of phase equilibria of subsolidus and sunliquidus in the system (Na, Cs)₂O-SrO-Al₂O₃-P₂O₅-H₂O in connection with the problem of vitrification and deep radioactive waste repository. // *Geochim.* N.10, pp.1424-1436.
- Ivanov I.P., Kotova N.P. (1999) Stability study of Na-Al phosphate glass containing radioactive isotopes ⁹⁰Sr and ¹³⁷Cs in contact with water at T=25-350°C and P=P_{sat}-500 bar. // *Radiochemistry*, V.41, N.1, pp.90-94.

Dunaeva A.N. Sorption of ⁹⁰Sr on kaolinite, montmorillonite, and illite.

key words [*sorption Sr kaolinite illite*]

Clays and clay minerals are the important sorbents of heavy metals and radionuclides.

One of the major process of sorptive fixation of radionuclides by clay minerals is their ion exchange with macrocations of clay exchange complex.

It is found, that clay minerals retain their ability for ion exchange within the wide range of pH, from 4 to 10.

This interval includes the overwhelming majority of pH of natural waters.

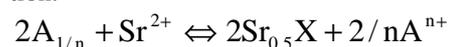
The purposes of the study:

1. To obtain the constants of binary ion exchange of ⁹⁰Sr and macrocations K⁺, Na⁺, Ca²⁺, Mg²⁺ on kaolinite, montmorillonite, and illite on the basis of treatment of published experimental isotherms of sorption of radionuclides on pure minerals.

2. To estimate the dependence of ion exchange sorption on pH.

3. On the basis of the obtained data to show the possibility of modeling Sr sorption from multicomponent aqueous solution by polymineral rocks.

Theoretical basis The process of Sr sorption by clay mineral can be described by the following chemical reaction:



where A - exchange cation of mineral-sorbent, n - cation charge, X - clay end-member.

It is suggested in the calculation of the ion exchange equilibria, that only the portion of mineral, which corresponds to its sorptive capacity, is able for reaction. In this case, the constant of reaction accounting for exhausting sorptive capacity, can be written

$$K_1 = \frac{x_{Sr^{2+}(s.ph.)} \cdot m_{A^{n+}(solut)}^{2/n}}{(C - x_{Sr^{2+}(s.ph.)})^{2/n} \cdot m_{Sr^{2+}(solut)}} \cdot \frac{\gamma_{Sr^{2+}(s.ph.)}^{2/n} \cdot \gamma_{A^{n+}(solut)}^{2/n}}{\gamma_{A^{n+}(s.ph.)}^{2/n} \cdot \gamma_{Sr^{2+}(solut)}}$$

where x , m , γ are mole fractions, molalities, and activity coefficients of components. C [eq/kg] - sorptive capacity of minerals, which characterizes the number of positions in sorbents, able for ion exchange. It is suggested, that the sorptive capacity, at which ion exchange occurs, is an ideal solution with respect to sorbed strontium ($\gamma_{Sr^{2+}(solid)} = \gamma_{An+(solid)} = 1$). The molalities of ions in an aqueous solution are calculated accounting for hydrolysis process and complex formation in an aqueous phase. Activity coefficient were calculated using the Debye-Hückel theory.



Fig.1. Strontium sorption by clays minerals as a function of pH.

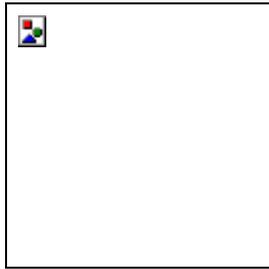


Fig.2. Experimental data of strontium sorption by nature clays [2,3] and sorption isotherms, calculated using K_1 , K_2 values, obtained from Wahlberg J.S. experimental work [1] • - exp. data; — - calculation curves

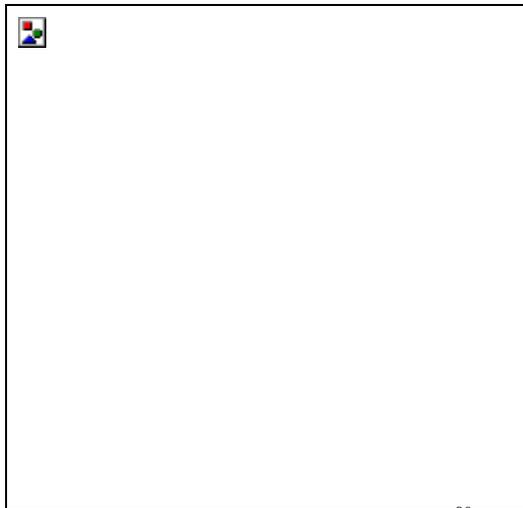


Fig.3. Thermodynamic modeling of ^{90}Sr sorption from multicomponent solution by polymineral soil fraction

Along with the binary ion exchange sorption of Sr^{2+} , the competing sorption of proton by clay minerals becomes significant in acid solutions:
 $nA_nX + nH \rightleftharpoons nHX_nA^{n+}$

$$K_2 = \frac{(C - x_{A^{n+}(s.ph.)} - x_{Sr^{2+}(s.ph.)})^n \cdot m_{A^{n+}} \cdot \gamma_{A^{n+}}}{x_{A^{n+}(s.ph.)} \cdot m_{H^+}^{n+} \cdot \gamma_{H^+}^{n+}}$$

Combination of the equations for K_1 and K_2 gives the equation for dependence of concentration of sorbed strontium on its content in a solution for each i -point on

the experimental isotherms. In case of the heterovalent sorption such equation turns to:

$$x_{Sr^{2+}(s.ph.)} = \frac{C \cdot K_1}{(K_2 \cdot m_{H^+} + m_{A^+})^2 \cdot \gamma}, \text{ where } \gamma = \frac{\gamma_{A^+}^2}{\gamma_{Sr^{2+}}}$$

Equation (1) approximates the experimental isotherm of sorption. The function

$$F = \sum_1^N (f_i - x_{Sr^{2+}(s.ph.)})^2$$

where N - number of experiments, f_i - concentration of the sorbed Sr in a experiment, is minimized with respect to two unknown parameters, K_1 and K_2 . Sorptive capacity is taken equal to its experimentally obtained value [1].

The experimental isotherms of ^{90}Sr sorption from K, Na, Ca, Mg-chloride solutions by kaolinite, montmorillonite, and illite, saturated with these components, were treated by the described method. Electrolyte concentration varied from 0.001 to 0.2 N, the interval of ^{90}Sr was 10^{-10} - 0.1 N. Size of clay particles did not exceed 1 mkm. Water : rock ratio was equal to 100 : 1.

In case of the heterovalent sorption the experiments were performed in acid solutions (pH = 3). It allowed to estimate the constants for ion exchange H-Na, H-K, and, subsequently, to calculate the constant for H-Ca and H-Mg for above minerals according to the Gess law.

Calculations of sorption equilibria by the program SlgSol (Mironenko, 1992) performed on the basis of the obtained thermodynamic information on constants of binary ion exchange sorption, i.e. K_1 and K_2 , allowed:

1) to numerically reproduce the initial experimental data [1] with accuracy up to 10 %;

2) to show, that at $\text{pH} > 4$ Sr sorption does not depend on pH of a solution (Fig. 1); therefore, absence of correction for the competing proton sorption does not appreciably influence thermodynamic modeling of ^{90}Sr behavior in surface and ground waters;

3) by constants K_1 and K_2 , calculated from experimental data [1], to reproduce the ^{90}Sr sorption in other model systems, including natural minerals and multicomponent aqueous solutions (Fig. 2);

4) to show the possibility of modeling radionuclide sorption from multicomponent solution on polymineral soil (Fig. 3).

References:

1. Wahlberg J.S. et al (1965) Exchange adsorption of strontium on caly minerals // U.S. Geological Survey Bulletin. V.1140-C.
2. Erthen H.N., et al (1988) Sorption of cesium and strontium on montmorillonite and kaolinite. // Radiochim. Acta, V.44/45, pp.147-151.
3. Hatipoglu S., Eylem C., Göktürk H., Erten H.N. (1990) Sorption of strontium and barium on clays and soil fractions // Sci.Geol. Mem, N.86, pp.79-86.

Glass and ceramics properties, applied mineralogy

#Kuryaeva R.G., Kirkinskii V.A. Refractive index and density of obsidian at pressures to 5.0 GPa from the measurement data in a diamond anvil apparatus.

key words [*obsidian refractive index contractability of obsidian high pressure diamond anvils*]

Silicate glasses are used as structural models of magmatic melts, and a high pressure study of their behaviour gives an insight into particular properties of deep-seated magmas, important for petrography, geochemistry, and geodynamics. We have shown earlier [1-4] that silicate glasses with silica content ≥ 50 wt% are characterized by a nonlinear increase of the refractive index and density with growing pressure, the pressure coefficient of these quantities initially increase, goes through the maximum and then slowly decreases herewith.

In order to have a more complete pattern of a change in the properties of glasses under pressure as a function of silica content in them, we have studied in this work rhyolite obsidian glass containing $\sim 75\%$ silica of density $\rho = 2.340 \pm 0.005$ g/cm³ (the density was measured by a hydrostatic weighing method). As suggested by the RSMA Camebax-micro data, the chemical composition of the glass in question (wt%) was as follows: SiO₂ 75.32, K₂O 4.13, CaO 0.941, Na₂O 3.43, MgO 0.182, Al₂O₃ 14.16, FeO 0.719, MnO 0.08, TiO₂ 0.173, Cr₂O₃ 0.006.

The measurement of the refractive index under high hydrostatic pressures was carried out by our technique [5] using a polarizing interference microscope and an apparatus with diamond anvils. The sample was pressurized in a stainless steel gasket. The diameter of the working area of the anvils was 800 μm , the sealing gasket opening diameter was ~ 300 μm . The pressure transmitting liquid being, simultaneously, optical medium was a standard alcohol mixture: methanol-ethanol (4:1). The pressure in the range of 0-2.0 GPa was determined by the technique of [6] using a polarizing interference microscope, and in the range of 2.0-5.0 GPa by the shift of the R₁-line of ruby luminescence. The luminescence was excited by a helium-neon laser radiation LG-79-1 ($\lambda = 630$ nm). The pressure uncertainty was $\sigma_P = \pm 0.05$ GPa.

The pressure dependence of the refractive index (fig.1) and the density of obsidian (fig.2) calculated from the obtained experimental data and photoelasticity theory [7], grow nonlinearly with increasing pressure with an inflection in the region of 2.5-3 GPa.

Such anomalous behaviour is analogous to the behaviour of silica [1] tholeiite basalt [2], and diopside [3] glasses (see fig.2) and is indicative of structural reorganizations under high pressures. The contractability of silicate glasses grows with silica concentration in the glass and the corresponding increase of the degree of binding of the silicoxygen carcass.

The work has been sponsored by the RFBR (Grant N 98-05-65247)



Fig.1. Refractive index n of rhyolite obsidian glass as a function of the pressure P .

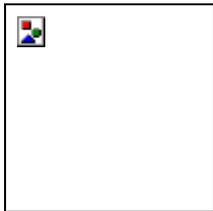


Fig.2. Relative density changes $(d-d_0)/d$ vs the pressure P for silicate glasses. 1- obsidian, 2 -tholeiite basalt glass, 3 - diopside glass, 4 - silica glass.

References:

1. Kuryaeva R.G., Kirkinskii V.A. (1995a) // Phys. and chem. of glass, V.4, pp.373-382.
2. Kuryaeva R.G., Kirkinskii V.A. (1997b) // Phys. and chem. of glass. V.25, pp.48-54.
3. Kuryaeva R.G., Kirkinskii V.A. // Geochim (to be published)
4. Kuryaeva R.G., Kirkinskii V.A. (1996) // Terra Nova, Abstracts Supplement, V.8, p.38.
5. Kuryaeva R.G., Kirkinskii V.A. (1994) // Instr. and Exp. Technique, V.6, pp.166-172.
6. Kuryaeva R.G., Kirkinskii V.A. (1998) // Instr. and Exp. Technique, V.3, pp.145-148.
7. Mueller H. (1935a) // Physics, V.6, pp.179-184.