Engineering of experiment

Chevychelov* V.Y., Kotelnikov A.R. Methods of conducting experiments on the melting of carbonate-silicate rocks at elevated CO₂ partial pressure. *UDC* 550.42

Korzhinskii Institute of Experimental Mineralogy RAS; Russia, Chernogolovka, Moscow district <u>chev@iem.ac.ru</u>,

Abstract. To conduct experiments on low-pressure hightemperature melting of natural carbonate-silicate rock at conditions of elevated CO₂ partial pressure, a special methods was used to create such pressure inside capsules with the carbonate-silicate charge. The experiments were carried out at pressures from 7 to 17 MPa and temperatures of 1250-1300°C on a "gas bomb". At our experiments, external pressure on the capsule was created by the inert gas Ar. Inside the capsule pressure was created by CO₂ released as a result of the decomposition of silver oxalate at these experiments. The H₂O pressure was negligible due to its absence in the initial charge. After the experiment, the weight of the gas phase inside the capsule was determined.

Keywords: decomposition of silver oxalate; melting of carbonate-silicate rock; elevated CO₂ partial pressure; experiment

The chemical composition used in the experiments of carbonate-silicate rock (wt. %): 16.3 SiO_2 , 0.3 TiO_2 , 9.1 Al_2O_3 , 0.8 Fe_2O_3 , 0.4 FeO, 0.1 MnO, 1.9 MgO, 39.9 CaO, 2.6 Na₂O, 0.3 K₂O, 0.2

 P_2O_5 , 26.2 CO₂, 1.5 H_2O^+ , 0.5 H_2O^- , 0.2 S_{tot}, 0.2 SrO, 100.6 Σ. The mineral composition of this sample is as follows: calcite (≈ 59.5 wt. %), melilite + clinopyroxene + nepheline aggregates; quartz, albite-anorthoclase, plagioclase, zircon, etc. are less common (Peretyazhko et al., 2021).

The experiments were carried out at pressures from 7 to 17 MPa and temperatures of 1250–1300°C in platinum capsules (Table 1). Most experiments were carried out in two stages. For the experiments, the internally heated pressure vessel (gas bomb) was used. In this vessel, external pressure on the capsule was created by the inert gas Ar. The pressure inside the capsule was determined by the partial pressure of carbon dioxide released during the experiment. The pressure created inside the capsule by water was sharply subordinated due to its virtual absence, with the exception of two experiments PRT-1b and PRT-1c. The oxygen fugacity fO2 inside the capsule corresponded to approximately (Ni-NiO) + 3.5, according to the estimate given in (Berndt et al., 2005; Chevychelov, Korneeva, 2018). In addition to gas bomb, at the first stage in experiments PRT-3 and PRT-4, a laboratory drying oven was used, in which the capsules were kept at $T = 130-140^{\circ}$ C for 3 to 4.5 hours.

Table	1. Ez	knerimen	tal con	ditions	and	results	obtaine	ed
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		First stage of experiment ¹			Second stage of experiment ²				After the experiment ³		
Experi- ment number	Initial composition of the experiment (m _{charge} ; m _{Ag2C2O4(H2O)})	<i>T</i> °, C	$P_{\text{total}} = P_{\text{CO2}},$ MPa	Dura- tion, h	P, MPa ⁴ at T = 700°C , when out- put to mode	<i>T</i> °, C	$P_{\text{total}} = P_{\text{CO2}},$ MPa	Dura- tion, h	Weight of gas (mg) / liquid (ml) phases in capsule, mg	Amount of decom- posed calcite (Cal _{decomp} _{osed}) in the charge, mg	Amount of carbonate- contain-ing phases in products (Cal ₁), mg/wt. %
PRT-1a	Charge ⁵ (50.19 mg)	-	-	-	9.0	1300	9.8	5.9	10.7/0.1	24.4	5.5/18.3
PRT-1b	Charge ⁵ (50.54 mg); H ₂ O (5.42 mg)	-	-	-	9.0	1300	9.8	5.9	10.5/5.0	23.9	6.2/20.6
PRT- 1c ⁶	Charge ⁵ (50.44 mg); H ₂ C ₂ O ₄ ×2H ₂ O (24.67 mg)	-	-	-	9.5	1300	9.8	5.75	-	-	-
PRT-2a	Charge ⁵ (49.19 mg); Ag ₂ C ₂ O ₄ (30.78 mg)	150— 160	4.3	0.9	5.5	1300	7.0— 9.7	5.4	18.7/0.65	22.2	7.0/24.0
PRT-2b	Charge ⁵ (20.36	115—	7.75	1.4	9.4	1300	12.3	5.8	15.5/0.5	9.1	3.0/25.2

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		First stage of experiment ¹			Second stage of experiment ²				After the experiment ³		
Experi- ment number	Initial composition of the experiment (m _{charge} ; m _{Ag2C2O4(H2O)})	<i>T</i> °, C	$P_{\text{total}} = P_{\text{CO2}},$ MPa	Dura- tion, h	P, MPa ⁴ at T = 700°C , when out- put to mode	<i>T</i> °, C	$P_{\text{total}} = P_{\text{CO2}},$ MPa	Dura- tion, h	Weight of gas (mg) / liquid (ml) phases in capsule, mg	Amount of decom- posed calcite (Cal _{decomp} _{osed}) in the charge, mg	Amount of carbonate- contain-ing phases in products (Cal ₁), mg/wt. %
	mg); Ag ₂ C ₂ O ₄ (39.70 mg)	160									
PRT-3	Charge ⁵ (55.93 mg); Ag ₂ C ₂ O ₄ (50.65 mg)	130— 140 140— 180	4.3	4.5 1.9	5.5	1300	7.0	6.5	26.54/1.0	27.0	6.3/18.9
PRT-4	Charge ⁵ (21.33 mg); $Ag_2C_2O_4$ (42.13 mg)	130	-	3.3	15.0	1250	17.3	6.1	16.56/1.1	9.9	2.8/22.0

Notes.

¹ In experiments PRT-1a, PRT-1b and PRT-1c the first stage of experiment was absent. In experiments PRT-2a and PRT-2b, the first stage was carried out in internally heated pressure vessel (gas bomb) preceding the second stage. In experiment PRT-3, the first stage was carried out first in a drying oven and then in internally heated pressure vessel, and in experiment PRT-4 the first stage was carried out only in a drying oven.

² The second stage of all experiments was carried out in internally heated pressure vessel.

 3 (Cal₁) are all carbonate-containing phases identified in the experimental products, including preserved calcite and four carbonate and carbonate-silicate melts formed in the experiment. Detailed explanations are given below in the text of the article.

⁴ The pressure is according to the pressure gauge readings when output to mode of the experiments. The pressure values are given at $T = 700^{\circ}$ C, since, according to thermogravimetry of the charge sample, the decomposition of calcite into CaO and CO₂ occurs at a higher temperature of about 700-815°C. (see explanations in the text).

⁵ Powder of the studied carbonate-silicate rock.

⁶ The capsule of this experiment was opened without determining the contents of the gas and liquid phases inside.

The preparation of the experiments was carried out as follows. Into one small capsule (outer diameter 4 mm, wall thickness 0.2 mm and length 18–20 mm) the powder of the studied carbonate-silicate rock (charge, 20-56 mg) was placed, and freshly prepared silver oxalate (Ag₂C₂O₄, 31-51 mg) was loaded into another identical capsule (Table 1). Silver oxalate was preliminarily synthesized by the reaction $2AgNO_3 + Na_2C_2O_4 \rightarrow Ag_2C_2O_4 \downarrow + NaNO_3$ by draining together salt solutions and subsequent drying of the multiple washed precipitate. Then both small capsules were squeezed to 2/3 of their length, but not welded shut, and placed inside a large capsule (10 mm \times 0.2 mm \times 50 mm), which was welded shut. All operations were controlled by weighing with an accuracy of 10^{-4} – 10^{-5} g.

The structure of their three capsules assembled in this way was kept in the temperature range from 115° to 180° C for 1-6 hours (the first stage of the experiment) for the decomposition of silver oxalate according to the reaction Ag₂C₂O₄ \rightarrow 2Ag + 2CO₂↑. Subsequently, during the experiment, the pressure inside the capsule was created by the CO₂ released by the reaction. According to the pressure gauge readings when output to mode of the experiments in the second stage at $T = 700^{\circ}$ C, this pressure ranged from 5.5 to 15.0 MPa (Table 1). The pressure values are given at $T = 700^{\circ}$ C, since, according to thermogravimetry of the charge sample, the decomposition of calcite in the charge into CaO and CO₂ occurs at a higher temperature of about 700-815°C. Thus, when the calcite decomposition temperature was reached when output to mode of the experiment, the partial pressure of CO₂ inside the capsules was significant; in experiments PRT-2a and PRT-3 it exceeded 5.5 MPa, in experiment PRT-2b > 9.4 MPa, and in experiment PRT- 4 > 15.0 MPa.

For comparison, experiments PRT-1a, PRT-1b and PRT-1c were carried out without the addition of silver oxalate, the first at "dry" conditions, the second with the addition of water, the third with the addition of oxalic acid $H_2C_2O_4 \times 2H_2O$ (Table 1). These three experiments were immediately heated to temperature of 1300°C (the first stage was omitted). In all other experiments, the high-temperature second stage followed the first low-temperature stage. The duration of the second stage was 5.5–6.5 hours. The quenching of the experiments was carried out as follows: after turning off the heating of the furnace, as a result of constant cooling of the outer vessel of gas bomb by running cold water, a rapid drop in temperature and an associated decrease in pressure occurred. The initial rate of temperature decrease was no less than 70-80 degrees/min.

After the experiment, the large capsule was "bloated" due to the excess gas phase inside. The experiment was opened as follows: (1) the capsule was weighed, then it was frozen in liquid nitrogen for 3 minutes, then several holes were pierced in the capsule and kept in air for 3 minutes to warm up to room temperature, while excess gas phase was removed from the capsule through the holes , (2) then the capsule was weighed again, heated at 100°C in the drying oven for 3 minutes, while the liquid phase was removed from the capsule through the holes, then the capsule was kept in air for 3 minutes to cool to room temperature and weighed again. Table 1 shows the contents of the gas and liquid phases released from the capsules upon opening of each experiment. The use of the obtained data is discussed below.

After the experiment, the solid products extracted from small capsule with carbonate-silicate rock, when examined under binocular microscope, were an aggregate of light whitish-gray grains and their fragments with varying degrees of transparency and homogeneity. The other small capsule was empty, since the silver oxalate initially loaded into it completely decomposed at the experimental conditions. Small growths were observed on the inner walls of the second capsule, which we believe were accretion of silver, formed at the decomposition of oxalate.

The weight of the gas phase released from the capsule upon opening varied from 10.5 mg to 26.5 mg, depending on the weight of the initial charge and silver oxalate (Table 1). The excess gas (fluid) phase was represented by CO₂ released as a result of the decomposition of silver oxalate and calcite. The gas phase was partially formed during the first lowtemperature stage of the experiment due to the decomposition of silver oxalate, and the rest of the part at the second high-temperature stage due to the decomposition of calcite from the studied carbonatesilicate rock (charge). The weight of the liquid phase released from the capsule, represented by H₂O, as expected, was extremely small, from 0.1 to 1.1 mg, and only in experiment PRT-1b, containing about 5.4 mg of initial H₂O, 5.0 mg of liquid was released upon opening.

Knowing the weight of the gas (m_g) and liquid (m_l) phases released from the capsule upon opening each experiment, we can estimate the possible amount of both decomposed calcite (Cal_{decomposed}) and all carbonate-containing phases after the experiment (Cal₁), including preserved calcite and four carbonate and carbonate-silicate melts formed in the

experiment. The calculation was carried out as follows. The calcite content in the initial charge is approximately 59.47 wt. %, based on the fact that the CO_2 content in the charge is 26.15 wt. %, and calcite CaCO₃ contains 43.97 wt. % CO₂. In each experiment, knowing the mass of the charge (m_{charge}) (Table 1), we can calculate the mass of the initial calcite ($m_{charge} \times 0.5947$). For experiments with the initial silver oxalate, you can calculate the amount of CO₂ released during complete decomposition of the oxalate ($m_{Ag2C2O4} \times 0.29$). Then the possible amount of decomposed calcite is calculated using the formula $Cal_{decomposed} = (m_g - (m_{Ag2C2O4} \times 0.29)) : 0.4397$, and the amount of all carbonate-containing phases after the experiment is calculated using the following formula $Cal_1 = (m_{charge} \times 0.5947)$ - $Cal_{decomposed}$. In experiments PRT-1a and PRT-1b, which did not contain the initial silver oxalate, the entire gas phase released from the capsule was formed during the decomposition of the charge calcite.

In all six experiments conducted under different conditions (varying the weight of the charge, silver oxalate and the ratios of these weights, using and without using silver oxalate, changing the temperature from 1300° to 1250°C, total pressure from 7 to 17 MPa, etc.) the same amount of all carbonate-containing phases was obtained after the experiment (Cal₁) approximately 18–25 wt. % (Table 1). The difference between experiments with an increased CO₂ pressure previously created in the capsule and without it is very small: in the first case 19-25 wt. %, and in the second case 18.3-20.6 wt. %. This shows that the technique we used for preliminary creation of increased CO₂ pressure in the capsule due to the decomposition of silver oxalate, unfortunately, does not prevent the decomposition of calcite in the charge during the experiments and most of the initial calcite (75-82 wt. %) decomposes. Moreover, such decomposition of calcite occurred at different conditions of output to mode the experiment, namely at $T > 700^{\circ}$ C in experiments PRT-2a and PRT-3 at $P_{\text{total}} = P_{\text{CO2}} > 5.5$ MPa, in experiment PRT-2b at $P_{\text{total}} = P_{\text{CO2}} > 9.4$ MPa, and in experiment PRT-4 at $P_{\text{total}} = P_{\text{CO2}} > 15.0$ MPa.

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References

Berndt J., Koepke J., Holtz Fr. An experimental investigation of the influence of water and oxygen fugacity on differentiation of MORB at 200 MPa // J. Petrol. — 2005. — V. 46. № 1. — P. 135—167.
Chevychelov V.Yu., Korneeva A.A. Evaluation of the oxygen fugacity (f₀₂) in experiments in internally

heated pressure vessel (IHPV) // Experiment in Geosciences. — 2018. — V. 24. № 1. — P. 215— 216.

Peretyazhko I.S., Savina E.A., Khromova E.A Lowpressure (> 4 MPa) and high-temperature (> 1250°C) incongruent melting of marly limestone: formation of carbonate melt and melilite-nepheline paralava in the Khramaryn-Khural-Khiid combustion metamorphic complex, East Mongolia // Contrib. Mineral. Petrol. — 2021. — V. 176 : 38. — P. 1—28.

Zharikov A.V., Malkovsky V.I., Yudintsev S.V. A new method for studying the transport properties of rock samples - application for the assessment of radionuclides colloidal migration. *UDC 621.039.7*

IGEM RAS, Moscow (vil@igem.ru)

We have developed a new method that allows to simultaneously determine, in the course of a single experiment, the values of the permeability of rock samples and the Klinkenberg parameter characterizing the properties of the rock pore space, and then, based on them, to estimate the distribution parameters of the effective diameters of the pore channels (mathematical expectation and standard deviation).Such measurements were carried out on the samples of the Nizhnekansky massif, which is currently considered as a perspective site for building a federal underground HLW depository. It is shown that the part of the actinide-containing colloidal particles mechanically retarded by rocks exceeds 99%. Taking into account the fact that a significant part of the actinides from the aged Al-P glass matrix enters the groundwater in the form of colloids, this result is of great practical importance for assessing the safety of the HLW disposal.

Keywords: high-level radioactive waste; glassy matrix; groundwater; radionuclides; colloids; migration; gneiss; granitogneiss; permeability; mechanical retardation

According to the legislation of the Russian Federation solid high-level radioactive waste (HLW) must be stored in deep underground depositories. The underground research laboratory, which in case of positive results of HLW safe isolation, will be expanded and transformed into a depository, is currently under constraction at the Yeniseisky site in the environment of the Nizhnekansky massif. This site was selected as a result of long-term comprehensive geological and geophysical studies of the Nizhnekansky massif, as well as an analysis of the entire set of geological, geographical and economic conditions (Kochkin et al., 2017). A number of alternatives sites were considered during the study, including the Itatsky and Kamenny (Fig.1).



Fig. 1. Geological map of the Krasnoyarsk Mining and Chemical Combine (MCC) area and the position of the Yeniseisky and alternative sites: Itatsky and Kamenny

- 1 gneiss complex;
- 2 gneiss-shale complex with amphibolites, marbles and guartzites;
- 3 granitoids of the Nizhnekansky complex;
- 4 sedimentary rocks;
- 5 Quaternary sedimentary deposits.

The main requirement for the site selected for the underground HLW repository is to minimize the risk of radionuclide leakage with groundwater flow into the biosphere. In this regard, it is important to perform the detailed studies of transport properties of rocks and first of all of their permeability as one of the key factors that determine the fluid dynamics both for natural and artificial fluids in the geological media.

Solid HLW accumulated in Russia are incorporated into a preservation matrix based on alumophosphate glass. During heating caused by radioactive decay, the glasses crystallize, and their stability in groundwater decreases. As a result, primary colloids capable to radionuclides transport over long distances enter into solution due to watermatrix interaction (Malkovsky et al., 2022).

During the experimental study of glass crystallization it was heated in the presence of water vapor with a humidity of ~ 70% for 1-2 days at temperatures of 200, 250, and 300 °C. The experiments were carried out with radionuclides simulators (Ce and Nd) – instead of transuranic actinides (Pu, Am and Cm), U – instead of Np and Pu).

Solid phases were studied by scanning and transmission electron microscopy, while solutions were analyzed by inductively coupled plasma mass spectrometry (ICP-MS). The first slight glass changes were observed at 200 °C, at 250 °C the crystallization rate increased to 0.05 mm per hour, and at 300 °C it increased by more than one order of magnitude. As a result, the glass of the cube-shaped sample with an edge size of 10 mm was completely replaced by the association of four crystalline Na-Al-

Fe phosphates including Sr-Ln-U phosphate with the monazite structure and aqueous Cs-U phosphate, probably with the otenite structure (only on the sample surface).

Leaching of pre-crystallized glass matrices in water was carried out in a quasi-dynamic mode at 90 °C. The sample was placed in a Ti autoclave filled with distilled water and in a thermostat. After 1, 3, 10 and 30 days, the solution was drained, the autoclave was filled with distilled water and was placed again in the thermostat. The ICP-MS method was then used to study the composition of the initial solution – and after filtration through membranes with decreasing pore diameters (450, 200, 100 and 25 nm) (Fig. 2). In the case of a dissolved form, the element content should not change after filtration. The content of actinide imitators (Ln and U) decreases after filtration; therefore, it can be concluded that they are mostly in the form of colloids (Fig.3).



Fig.2. Scheme of experiments with filtration of solutions obtained by leaching of Al-P glass sample with distilled water.







Fig.3. The high-resolution transmission electron microscope image of colloid particles from the leaching product of crystallized sample of the Na–Al–P-glassmatrix: (*a*) Sr–REE–U phosphate, (*b*) Na–Al–Fe phosphate.Scale marks are 100 nm.



Fig. 4. Permeability (a) and porosity (b) of the samples collected in the wells drilled at the Itatsky and Kamenny sites, Nizhnekansky massif.

Table 1. Permeability	and Klinkenberg parameter	of the main rock types.
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Sample	Rock	k_{w}, m^2	b, MPa
К 560,8	granodiorite	1.488.10 ⁻¹⁸	0.334
К 613.1	adamellite	3.307.10 ⁻¹⁸	0.238
I 142.6	granite gneiss	3.712.10 ⁻²⁰	0.652
I 491.7	gneiss	8.201.10 ⁻¹⁹	0.275
I 357.2	quartz diorite	3.092.10 ⁻¹⁹	0.6 6
I 504.6	quartz diorite	9.595.10 ⁻¹⁹	0.243

In order to assess the safety of the underground depository for vitrified HLW, it is necessary to study the possibility of radiocolloids retardation by its near-field rocks. The mobility of colloidal particles in the underground media depends on the water flow velocity, and the possibility of its mechanical retardation which is determined by the cross-section of the filtration channels. In turn, the dynamics of natural and artificial fluids flow in the geological media is governed by rock permeability. In order to assess the possibility of mechanical retardation of primary colloids using the original method developed by the authors (Malkovsky et al., 2009), the values of water permeability (k_w) and the Klinkenberg parameter (b) were determined on core samples taken from boreholes drilled at the Itatsky and Kamenny sites of the Nizhnekansky massif from the depths of 450-500 m corresponding to the probable depths of HLW disposal (Zharikov et al., 2014). It was found that the rocks of the Nizhnekansky massif, mainly represented by gneisses and granitogneisses, are characterized by very low values of permeability (10⁻

 $^{18}-10^{-20}\ m^2)$ and porosity (0.14 - 0.95 %) (Fig. 4, Table 1).

In order to determine the values of the filtration channels diameters, we have developed a new method for the theoretical analysis of fluid flow using the Kozeni-Karman model. It was convenient to approximate a probability density function for the diameters of the cross sections of the filtration channels with a single maximum by a log-normal distribution function

$$f(d_c) = \frac{1}{d_c \sigma \sqrt{2\pi}} \exp\left[-\frac{(\ln d_c - L_c)^2}{2\sigma^2}\right], \text{ where } \sigma \text{ and } L_c \text{ are }$$

distribution parameters.

These parameters are related to the values of $k_{\rm w}$ and b through the following equations

$$\begin{cases} 2L_{c} + 6\sigma^{2} = \ln(8k_{w}/\varphi), \\ L_{c} + \frac{7}{2}\sigma^{2} = \ln\left(\frac{16}{3\pi\sqrt{2}}\frac{k_{B}T}{bd^{2}}\right). \end{cases}$$
(1)

Where φ is the rock effective porosity (0.003), k_B is the Boltzmann constant, *T* is the temperature (K), *d* is the kinetic diameter of the argon molecule, equal to

0.36 nm.

Taking into account the data on the size distribution of the radiocolloid (Fig. 4), the mass fraction γ of the colloidal particles retarded by rocks is determined by the ratio

$$\gamma \ge \frac{1}{2} \left\{ \frac{C_0 - C_1}{C_0} \left[1 + \operatorname{erf}\left(\frac{\ln D_1 - L_c}{\sigma\sqrt{2}}\right) \right] + \sum_{n=1}^3 \frac{C_n - C_{n+1}}{C_0} \left[1 + \operatorname{erf}\left(\frac{\ln D_{n+1} - L_c}{\sigma\sqrt{2}}\right) \right] \right\}$$
(2)

Where C_n is the concentration of Ce or Nd in solution after a membrane with a pore diameter of Dn (n = 1, ..., 4).

The system of equations (1) is linear in L_c and σ^2 . From the solution, the value of γ was calculated according to the formula (2). The obtained results showed that more than 99% of the actinide colloidal fraction appearing in solution after interaction with crystallized Na-Al-P glass was mechanically retained in the studied samples.

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References

- 1 Kochkin, B.T., Malkovsky, V.I., Yudintsev, S.V. Scientific basis for safety assessment of geological isolation of long-lived radioactive waste. 2017. IGEM RAS, Moscow (in Russian).
- 2 Malkovsky V.I., Yudintsev S.V., Zharikov A.V. Radiocolloid Retention in the Nizhnekanskii Rock Massif // Doklady Earth Sciences. 2022. V. 503. P. 226–231. DOI: 10.1134/S1028334X22040109.
- 3 Malkovsky V.I., Zharikov A.V., Shmonov V.M. New Methods for Measuring the Permeability of Rock Samples for a Single-Phase Fluid // Izvestiya, Physics of the Solid Earth. 2009. V. 45. No. 2. P. 89–100.
- 4 Zharikov A.V., Velichkin V.I., Malkovsky V.I., Shmonov V.M. Experimental study of crystalline rock permeability: implications for underground radioactive waste disposal. // Water Resources. 2014. V.41. P. 881–895. doi:10.1134/S0097807814070136