

Physical chemical properties of geomaterials

Zharikov A.V.^{1,2}, Malkovsky V.I.^{1,3} New techniques for laboratory studies of rock permeability

¹Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, RAS

²Institute of Experimental Mineralogy, RAS

³D.I.Mendeleev University of Chemical Technology of Russia

Abstract. It is indicated that highly variable properties of a fluid in two-phase or near-critical domain of state parameters can exert an influence on fluid filtration through rocks. Thermodynamic similarity of CO₂ to water is shown what allows to use CO₂ for physical simulation of a flow of an aqueous fluid through a rock sample at p, T -parameters from the two-phase or near-critical domain. A schematic diagram of a modified apparatus for measurement of rock sample permeability for CO₂ is presented with estimated control parameters which specify conditions of the experiment.

Key words: rock, sample, permeability, fluid, supercritical parameters.

Citation: Zharikov A.V., V.I. Malkovsky (2014). New techniques for laboratory studies of rock permeability. *Experimental geochemistry*. V. 2. No.

Many experimental works are dedicated to studies of rock samples permeability [Shmonov et al., 2002; Shmonov et al., 2011; Malkovsky et al., 2013]. The authors of these publications considered permeability of both isotropic and anisotropic rocks as well as influence of p, T -parameters on the permeability. Available methods of rock permeability determination on samples are based on measurement of parameters of gaseous or liquid fluid filtration through the considered sample. Gas (e.g. argon or nitrogen) is often used as a fluid because its dynamic viscosity is lower than the dynamic viscosity of liquids. As a result, fluid velocity in experiments with the gaseous fluid is higher what reduces the measurement time. The measurements can be carried out with use of steady state method or pulse decay method with the regard for Klinkenberg effect [Collins, 1961]

Some applications, e.g. mathematical modeling of ore-bearing fluid flow, which forms hydrothermal ore deposits, calls for determination of transport properties of rocks for an aqueous fluid at near- and supercritical values of p, T -parameters. Both temperature dependence of rock permeability for a homogeneous fluid and substantial variability of thermophysical properties of the fluid near to its critical point can exert some influence on characteristics of the fluid filtration process in this case. As a result of relatively high values of the critical temperature (T_{cr}) and the critical pressure (p_{cr}) for an aqueous fluid, experimental determination of the rock permeability for the fluid in the near-critical domain of its state parameters is a matter of substantial difficulty. That is why it seems to be worthwhile to carry out the experiments on modeling liquids [Miropolsky, Soziev, 1990]. Substances are thermodynamically similar to each other for certain parameters (e.g. for density and dynamic viscosity) if ratio of corresponding parameters of the both substances at the same values of reduced pressure $\pi = p/p_{cr}$ and reduced temperature $\tau = T/T_{cr}$ are close

to constant values. It is obvious that process of fluid filtration in a porous medium depends on the dynamic viscosity of the fluid. Taking into account the Klinkenberg effect, one can expect that the fluid density exerts also an influence on the filtration nature. Therefore, it is reasonable to select such modeling substances for the experiment which are thermodynamically similar to H₂O from the viewpoint of density and dynamic viscosity. Carbon dioxide can be considered as such modeling substance. The critical values of pressure and temperature for H₂O and CO₂ are presented in Table 1.

Table 1. Critical parameters of H₂O and CO₂

Substance	p_{cr} , MPa	T_{cr} , K
H ₂ O	22.1	647.2
CO ₂	7.38	304.2

Therefore, if water and carbon dioxide are thermodynamically similar for density and dynamic viscosity the experiment for the same values π and τ at $\tau \geq 1$ can be carried out on CO₂ much simpler than on H₂O.

Plots of density and dynamic viscosity against reduced pressure and reduced temperature for water and carbon dioxide from [Miropolsky, Soziev, 1990] are presented below in Fig. 1–3.

Schematic diagram of apparatus of sample permeability measurement for CO₂ is presented in Fig. 4. A substantial difference of the diagrams in Fig. 4 and in [Malkovsky et al., 2013] is presence of the thermal press for carbon dioxide. The reason is that carbon dioxide in the gas-cylinder at subcritical pressures ($T_{cr} \approx 304.2$ K) is in two-phase state (liquid+gas). As a result, the pressure in the gas-cylinder is equal to the pressure of saturated vapor of CO₂ p_{sat} at the temperature of environment T_0 . If the first 4 valves between the gas-cylinder (1) and after the input volume are open liquid CO₂ flows from the gas-cylinder into the volume at the pressure of $p_{sat}(T_0)$. If it is necessary to study permeability of the sample for the fluid of supercritical parameters of the state, the pressure in the input volume (3) should be increased at least up to p_{cr} . This is carried out as follows. The liquid carbon dioxide flow by the action of pressure in the gas-cylinder from it and fills the volume of the thermal press (5) and the receiver below. For that, the gas-cylinder in operation state is mounted so that its valve is at the bottom. We denote volumes of the thermal press and the receiver as V_0 and V_1 respectively. Then the valves before the thermal press and after the receiver are closed. Electric heating leads to an increase of the temperature in the thermal press up to $T_1 > T_0$. As a result of thermal expansion of CO₂ in the thermal press, the pressure increases in the thermal press and in the receiver up to a value p_c . This value is controlled by variation of T_1 due to adjustment of electric heating of CO₂ in the volume of the thermal press. As the value of p_c reaches a prescribed value, the valve between the thermal press and the receiver is closed, and one can start the procedure of rock permeability measurement with use of the technique which is described in detail in [Shmonov et al., 2011; Malkovsky et al., 2013].

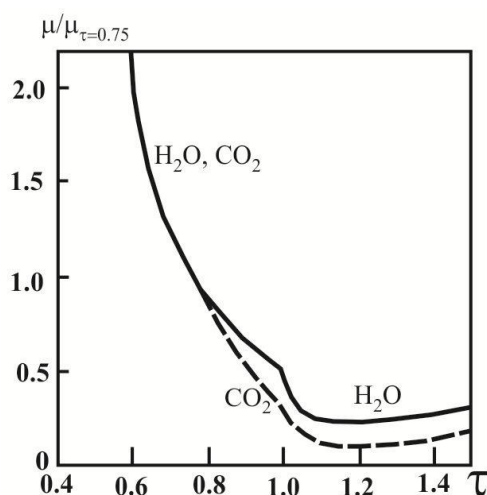


Fig.1. Dependence of dynamic viscosity on reduced temperature for water and carbon dioxide at $\pi = 1.1$.

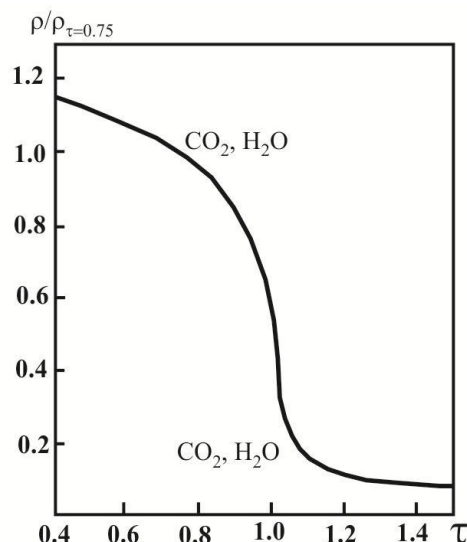


Fig.2. Dependence of density on reduced temperature for water and carbon dioxide at $\pi = 1.1$.

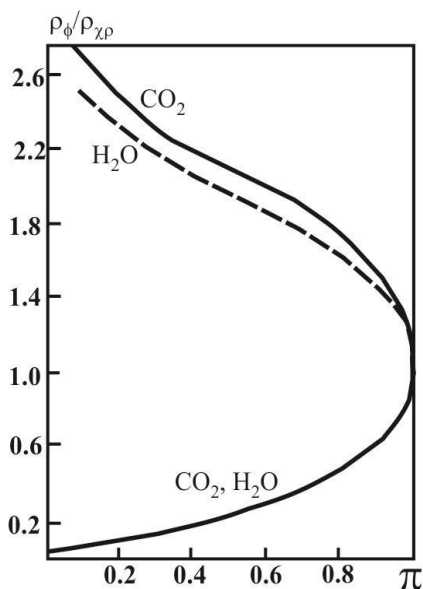


Fig.3. Dependence of liquid phase density on reduced pressure for water and carbon dioxide.

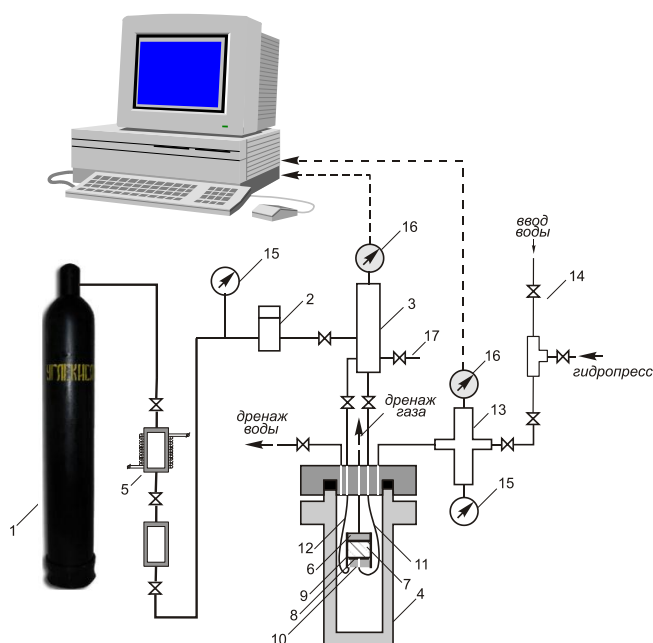


Fig. 4. Schematic diagram of apparatus for measurement of samples with use of carbon dioxide at near-critical parameters of state.

Dependence between p_c and T_1 is determined as follows. The mass of liquid CO_2 which flows initially from the gas-cylinder into apparatus is equal to $m = \rho'(p_{sat}(T_0), T_0)(V_1 + V_2)$, where $\rho'(p, T)$ is density of the liquid phase of CO_2 at the pressure p and temperature T .

The value of p_c is obtained through solution of the equation

$$\rho'(p_c, T_1)V_1 + \rho'(p_c, T_0)V_2 = m \quad (1)$$

The nonlinear equation (1) is solved numerically by the dichotomy method. The function $\rho'(p, T)$ is determined through approximating formulas from [Altunin, 1975].

The determined plots $p_c(T_1)$ at different $r = V_2/V_1$ from 0.1 to 0.5 are presented in Fig.5.

One can indicate that the supercritical pressure in the receiver can be obtained at relatively low heating of thermal press.

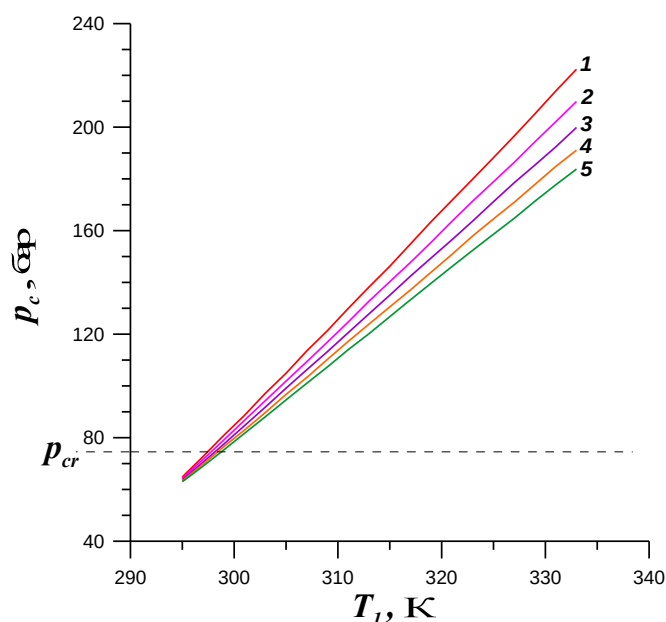


Fig.5. Dependences of pressure in the receiver on temperature in the thermal press. (1) $r=0.1$; (2) 0.2; (3) 0.3; (4) 0.4; (5) 0.5.

Acknowledgement The study is carried out with financial support of RFBR (project number № 14-05-00736).

References:

1. Altunin V.V. (1975). Thermophysical properties of carbon dioxide. M.: *Izdatelstvo standartov*. 552 p. (in Russian)
2. Collins R.E. (1961). Flow of fluids through porous materials. New York: *Reinhold Pub. Corp.* 270 p.
3. Malkovsky V.I., Zharikov A.V., Shmonov V.M. (2013). Use of Argon for measurement of rock permeability. Argon. Production, characteristics and applications. Ed. by Bogos Nubar Sismanoglu, Homero Santiago Maciel, Marija Radmilovic-Radjenovic, Rodrigo Savio Pessoa. N.Y.: Nova Science Publishers. P. 17–36
4. Miropolsky Z.L., Soziev R.I. (1990). Fluid dynamics and heat transfer in superconducting equipment. New York: *Hemisphere Pub. Corp.* 315 p.
5. Shmonov V.M., Vitovtova V.M., Zharikov A.V. (2002). Fluid permeability of Earth's crust rocks. M.: *Nauchniy mir*. 216 p. (in Russian)
6. Shmonov V. M., Mal'kovskii V. I., and Zharikov A. V. (2011). A technique for measuring permeability of samples of anisotropic rocks for water and gas. *Instruments and Experimental Techniques*. V. 54. №5, P.722–728.

Shchekina T.I., Kurbyko T.A., Batanova A.M., Alferyeva Ya.O., Gramenitskiy E.N. Changes of spinels composition in the interaction columns between refractories and melts of nickel production at 1600°C and 1 atm

M. V. Lomonosov Moscow State University, Department of Geology, Moscow

Abstract. Nickel-bearing spinels were obtained in laboratory conditions at interaction between chromite-periclase, periclase-carbon refractories and the melts of nickel production at 1600 °C and 1 atm. Spinel form a wide variety of solid solutions between both divalent (Mg, Ni), and trivalent cations (Cr, Al, Fe). Spinel composition is changing in zoning column due to the mutual diffusion of the components of the interacting media.

Key words: chromite-periclase and periclase-carbon refractories, melts of nickel and slag, spinel, interaction, reactionary columns, zoning.

Citation: Shchekina T.I., T.A. Kurbyko, A.M.Batanova, Ya.O. Alferyeva, E.N. Gramenitskiy E.N. (2014). Changes of spinels composition in the interaction columns between refractories and melts of nickel production at 1600°C and 1 atm. *Experimental geochemistry*. V.2. No.

The interaction columns with a clear zoning were obtained in studies of the slag- and metal stability of periclase-chromite and periclase-carbon refractories in laboratory conditions at atmospheric pressure and temperature of 1600 °C [Shchekina T.I., Gramenitskii E.N., et al., 2011]. Spinel is one of the main mineral of reaction zones in reactionary columns appeared in both types of refractories. Spinel composition observed in periclase-carbon refractory conforms to ideal formula $MgAl_2O_4$. Spinel formed as a result of interaction processes between refractory and melts manifest itself as the diffusion of alumina from slag to refractory.

Spinel of periclase-chromite refractory are the characteristic minerals as in the source material both in all reaction zones of interaction column. Spinel of starting refractory makes up large grains of size up to 0.5–0.7 mm and is presented by magnesia, most of the chromium rich and poor iron species. There are also porous grains with inclusions of silicates. The composition of this spinel is characterized by greater contents of Al, Fe and less one of Cr as compared with large grains. The chemical composition of phases was studied by electron-probe energy dispersive microanalyzer based on scanning electron microscope Jeol JSM-6480LV (spectrometer X-Max N-50, Oxford Instruments) of Department of Petrology, Moscow State University.

The spinel composition in the first zone the farthest removed from contact with molten slag and nickel varies as compared to composition of the original refractory towards a substantial increase of the iron and aluminum and decrease of chromium. The same trend can be seen in the changes from the center of the grain to their edge. In the second zone the relict large spinel grains undergo further changes. They continue to decline chromium. The more ferruginous, aluminous but less chromium margin appear around them, but they contain impurities of Ni and Co. Fine grains are subjected to recrystallization and corrosion. Mg and Cr are carried out from primary chromite, Ni and a Co are introduced from metallurgical melts. The numerous new growth spinel grains formed in

Physical chemical properties of geomaterials

the following third zone. There are dominated by crystals with a high content of Al. Numerous newly formed spinel grains of third zone have zoning. In the center of the grain becomes more Al. Spinel composition expressed by the formula - $(\text{Mg}_{0,95}\text{Ni}_{0,09}\text{Co}_{0,02})_{1,06}(\text{Al}_{1,20}\text{Fe}_{0,18}\text{Cr}_{0,63})_{2,01}\text{O}_4$. The edges of the spinel grains contain significantly more of Fe and Ni and less Al and Cr. Their composition is expressed by the formula - $(\text{Mg}_{0,83}\text{Ni}_{0,19}\text{Co}_{0,04})_{1,06}(\text{Al}_{0,50}\text{Fe}_{0,97}\text{Cr}_{0,37})_{1,84}\text{O}_4$. Both types of spine crystals overgrow with the phase corresponding to bunsenite with a small content of Mg (0.1 formula unit-f.u.) and the impurities of Al, Fe, Cr and Co. In the fourth zone spinel and bunsenite are presented in roughly equal amounts, and are the main phases make up about 85% of the material. Periclase disappears completely, only about 8 % nickel containing olivine remains and 5-7% aluminosilicate glass appears in the fourth zone. Spinel grains have zoning due to the formation of rims of 2–10 microns thickness. Spinels form zoned crystals of two types. In the first type the center grains compose from more alumina, edge - less alumina, but more nickel spinel. Thus the Cr contents in both zones are almost the same. Feature of the second type is a high chrome spinel composition in the center of the grain and twice increasing alumina content - on the edge of the grain. Ni and Fe content in the center of the spinel grains are similar to those in the first type. Crystals of both types of spinel overgrow by phase rich of NiO. However in the boundary parts of the spinel grains of the first type indicated increasing of concentrations of Ni (from 0.18 to, 0.62 f.u.), whereas in the edge portions of the second type spinel grains its are slightly lowered from 0.21 to 0.13 f.u.. All the more intensively transformed spinel (Ni-Spl) is found in the fourth zone. It is characterized by high nickel contents still exceeding the concentration of magnesium in the 2nd-valence position of the cations. Another important phase in the fourth zone called magnesium containing bunzenite (Mg-Buns). It fills in the gaps between the crystals of spinel. It contains nearly 0.8 f.u. of Ni and about 0.2 f.u. of Mg. Other elements (Cr, Fe, Al) are contained in small amounts, that this can be attributed not to the spinel phase, and the oxides. Such behavior of the elements reflects the mutual diffusion of the components - removal of Mg and Cr of refractory and brings nickel, iron and aluminum from melts at the border of the solid and liquid media. In this case occurs their recrystallization, followed by redistribution of elements in phases.

Thus, it is shown that the composition of spinel in the products of experiments extremely diverse: from the starting magnesia chromite to the ferroalumino-chromite in zones close to the contact with the melts. There is isomorphism between trivalent metals Fe^{3+} , Al^{3+} , Cr^{3+} in spinel with the trend of substitution of chromium by iron and especially by aluminum as it approaches the contact with the melt. This is consistent with the known data about the wide isomorphism between minals: chromite, hercynite, magnetite. The main feature of composition changing of the original magnesia spinel in this experiment is the gradual replacement of magnesium by divalent cations of Ni^{2+} and to a lesser extent of Fe^{2+} and Co^{2+} . In the first column zones away from the contact the content of nickel and cobalt are less than 0.01 f.u; in the zone closest to the melts they are – to 0.8 and 0.1 f.u., respectively. In direct contact of melts with the refractory

Ni-containing spinel is converted to bunsenite with small impurities of Mg, Al, Cr and Fe. These facts are confirmed with the data on the existence of a continuous series of solid solutions in a number of MgAl_2O_4 – NiAl_2O_4 and indicate the possibility of isomorphism between the more complex compositions MgCr_2O_4 –Ni (Al, Fe) $_2\text{O}_4$ at 1600 ° C.

References

1. Shchekina T.I., Gramenitskii E.N., Batanova A.M., et al. 2011. Phase formation and structural changes in chromite-periclase refractories used during nikel production. *Refractories and Industrial Ceramics*, Kluwer Academic/Plenum Publishers (United States), V. 52, № 5, c. 363-376