

Immobilization of Polonium on Natural Minerals and Rocks

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Abstract—Immobilization of ^{210}Po on natural minerals (magnetite, glauconite), rocks (basalt, dunite), and synthesized manganese dioxide of the composition $\text{MnO}_{1.97}$ was studied. Basic and ultrabasic rocks (basalts, dunites) widely occurring in the nature can be used for making artificial geochemical barriers for the removal of Po from weakly acidic and neutral liquid radioactive wastes. Dunite ensures the most efficient ^{210}Po immobilization from acidic solutions, and basalt, from neutral solutions. The degree of ^{210}Po removal upon 48-h interaction with dunite and basalt was 93 and 80% relative to its initial content in solutions with initial pH 3.0 and 7.0, respectively. With all the samples except $\text{MnO}_{1.97}$, the ^{210}Po immobilization in the initial step (0–5 h) is more efficient in the initially neutral solutions, but with time the degree of the ^{210}Po removal from the initially acidic solutions becomes higher. The rate of the ^{210}Po immobilization on $\text{MnO}_{1.97}$ does not appreciably depend on pH in the examined acidity range.

Keywords: polonium, immobilization, natural minerals, rocks, artificial geochemical barriers

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Polonium is an extremely hazardous element. All its isotopes, even on the level of natural background concentrations, pose serious hazards to human health [1]. The most abundant radionuclide, ^{210}Po , with a half-life of 138.4 days is the member of the ^{238}U decay series. It emits only α -particles and is highly toxic: The interference level for the ^{210}Po content in potable water is 0.11 Bq kg^{-1} , and the dose coefficient at peroral intake is $1.2\text{--}3 \text{ mSv Bq}^{-1}$ [2].

The sites of processing of uranium and polyelement radioactive ores and of production and utilization of polonium alloys are the most important sources of the environment pollution with polonium, and today there is acute need for the development of simple and cost-saving methods for immobilization (reduction of the migration mobility) of this element, allowing efficient localization of the corresponding radiogegeochemical anomalies.

One of the ways to reduce technogenic pollution of the environment and localize technogenic anomalies is making artificial geochemical barriers in the form of filtering media consisting of natural or synthesized materials [3, 4]. When these materials interact with

migrating flows of pollutants, the pollutants pass from the mobile dissolved state into weakly mobile forms: difficultly soluble compounds, adsorbed components, and admixtures in the newly formed solid phases.

In aerated aqueous solutions, Po is in the tetravalent state [5]. The solubility product of $\text{Po}(\text{OH})_4$ is $10^{-51.2}$, which is in the range of solubility products of hydroxides of such hydrolyzable tetravalent metals as Th, W, Zr, and U: $10^{-49.7}\text{--}10^{-54.2}$ [6]. These metals efficiently coprecipitate with Fe(III) and Al oxyhydroxides. This fact suggests the possibility of efficient immobilization of Po on basic and ultrabasic rocks that are unstable under the conditions of the earth surface and relatively rapidly decompose to form Fe(III) and Al oxyhydroxides and secondary clayey minerals exhibiting high sorption capacity. Acidic medium accelerates this process. Iron(II) oxides and carbonates in the hypergenesis zone also transform into Fe(III) oxyhydroxides and can participate in immobilization of Po by the coprecipitation mechanism.

This study deals with the Po immobilization from neutral and weakly acidic solution on basic and ultra-

basic rocks and minerals with high Fe(II) content.¹

EXPERIMENTAL

In our experiments we used monomineral fractions of magnetite $\text{Fe}(\text{FeO}_2)_2$, glauconite (complex iron-containing sheet silicate of hydromica group), and two types of rocks with high Fe(II) content: basalt and dunite, belonging to basic and ultrabasic rocks, respectively. The results of chemical analysis of glauconite, basalt, and dunite samples are given in Table 1. We also used in the experiments a synthesized sample of manganese(IV) oxide of the composition $\text{MnO}_{1.97}$, which is stable in the presence of O_2 in aqueous medium at pH in the range 3–12 [4] and can take up Po by the purely sorption mechanism.

The experiments were performed at the solid phase : solution weight ratio of 1 : 100. Samples were preliminarily ground in an agate mortar to the powder state (approximately 95% of particles had the size smaller than 20 μm). The pH of the initial solution containing tracer amounts of ^{210}Po was 7.0. In a half of the experiments, the solution was acidified to pH 3.0 by adding a small amount of 0.1 M HCl. Upon filtration through a membrane filter with a pore diameter of 0.22 μm , we obtained a transparent solution without visible opalescence. To evaluate the polonium immobilization kinetics, small samples (1 mL) of the solution were taken 100 min, 300 min, 1 day, and 2 days after the start of the experiments, and the residual activity of ^{210}Po in these samples was measured.

RESULTS AND DISCUSSION

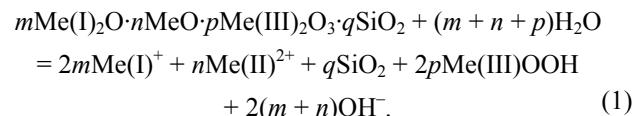
It follows from the experimental data presented in Table 2 that, in all the cases, ^{210}Po is removed from the solution and the process, except that with $\text{MnO}_{1.97}$, is accompanied by an increase in pH, which reaches a constant value within less than 24 h. For silicates (dunite, basalt, glauconite), an increase in pH, according to numerous studies, is caused by leaching of alkali

¹ In the case of radioactive contamination, at the end of operation of a geochemical barrier it is insulated from the environment by making shields of materials with very low filtration rate (bentonite clays, aluminosilicate gels), which ensures negligibly low mass exchange with the environment during the time sufficient for the radioactive decay of the accumulated radionuclides. When choosing materials for artificial geochemical barriers, this fact allows us to restrict the study to evaluating their performance and radionuclide absorption capacity, without considering the mobilization processes caused by desorption and dissolution of solid phases carrying the pollutants.

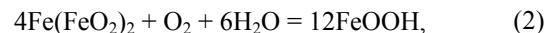
Table 1. Chemical composition of glauconite, basalt, and dunite samples used in the experiments, wt %

Component	Glauconite	Basalt	Dunite
SiO_2	52.03	53.18	40.71
TiO_2	0.07	0.24	0.03
Al_2O_3	8.10	4.24	1.92
FeO	19.61	8.04	14.33
MnO	0.01	0.20	0.20
MgO	3.67	26.77	41.37
CaO	0.65	3.61	1.23
Na_2O	0.01	0.44	0.15
K_2O	8.52	0.06	0.05
H_2O	7.38	—	—
Total	100.05	96.78	99.99

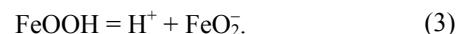
and alkaline earth elements in the course of incongruent dissolution with the formation of free silica and secondary oxyhydroxides of iron and aluminum:



In the experiments with magnetite, which in the presence of free oxygen transforms into iron(III) oxyhydroxide,



the final pH is apparently determined by the solubility of FeOOH (ferrous acid), dissociating in accordance with the scheme



For freshly precipitated and crystalline FeOOH , the standard free energy of formation differs by 4.4 kcal mol⁻¹: -112.67 and -117.04 kcal mol⁻¹, respectively [7]; for FeO_2^- , it is -88.00 kcal mol⁻¹ [8]. Hence, we obtain the range of the equilibrium constants of reaction (3): $K = 10^{-21.4} - 10^{-18.1}$. In the region of the minimal solubility of FeOOH , the concentrations of H^+ and FeO_2^- are equal. This fact allows calculation of the equilibrium pH value, $\text{pH} = 0.5\log K$, which, in accordance with the above-given estimates of K , should be in the range 9.0–10.7. This value is consistent with the experimental data.

Thus, all the minerals and rocks used, except manganese dioxide, are unstable in neutral and weakly

Table 2. Removal of ^{210}Po from aqueous solutions upon interaction with minerals and rocks, % of initial activity

Sample	pH		Exposure time, h			
	initial	equilibrium ^a	1.7	5	24	48
Magnetite	7.0	9.80 (6)	36.7	46.0	57.5	61.7
Magnetite	3.0	8.45 (6)	23.4	38.4	61.7	77.8
Glauconite	7.0	8.63 (22)	11.0	15.0	19.4	25.8
Glauconite	3.0	6.52 (22)	3.9	10.8	34.2	46.0
Basalt	7.0	9.37 (6)	65.5	70.6	74.9	80.1
Basalt	3.0	4.41 (22)	53.3	58.2	78.9	87.2
Dunite	7.0	9.57 (6)	54.1	58.0	61.8	67.7
Dunite	3.0	5.75 (22)	49.1	56.4	80.3	93.4
$\text{MnO}_{1.97}$	7.0	6.73 (2)	14.7	18.4	29.7	44.7
$\text{MnO}_{1.97}$	3.0	3.36 (2)	23.8	35.3	55.6	71.0

^a The time of attainment of the constant pH value, h, is given in parentheses.

acidic solution, and the ^{210}Po removal from the solution occurs against the background of formation of secondary mineral phases, which can act not only as sorbents, but also as carrier phases in the course of coprecipitation. In the case of manganese dioxide, the pH changes insignificantly, which indicates that $\text{MnO}_{1.97}$ is stable in the examined range of acidity. Therefore, ap-

parently, manganese dioxide takes up ^{210}Po only by the sorption mechanism.

The maximal ^{210}Po immobilization from a neutral solution (initial pH 7.0) is observed with basalt, and from an acidic solution (initial pH 3.0), with dunite. Both these minerals show high performance in the whole examined pH range. The ^{210}Po activity in the solution decreased after 48-h contact with basalt and dunite by 80 and 68% at initial pH 7.0 and by 87 and 93% at initial pH 3.0, respectively.

Notably, with all the sorbents except $\text{MnO}_{1.97}$, the degree of the ^{210}Po removal in the first 5 h was higher in the initially neutral solution, but then it remained higher in the initially weakly acidic solution (Fig. 1). This trend is probably caused by the fact that all the examined silicates and magnetite are unstable even in dilute solutions of strong acids and partially dissolve with the formation of free silica and of iron and aluminum oxyhydroxides. These oxyhydroxides, having high specific surface area in the freshly precipitated state, can, on the one hand, adsorb the dissolved ^{210}Po and, on the other hand, take it up by the coprecipitation mechanism. Apparently, the amount of the newly formed secondary phases and the degree of the ^{210}Po removal will be the higher, the higher is the initial solution acidity and the longer was the time for the solution neutralization.

The equilibrium between ^{210}Po -containing solutions and the samples studied (magnetite, glauconite, basalt, dunite, $\text{MnO}_{1.97}$) is not attained in 2 days. In all the experiments, except those with $\text{MnO}_{1.97}$, after a short initial period (about 5 h) the rate of the ^{210}Po immobilization from the initially acidic solution exceeded that

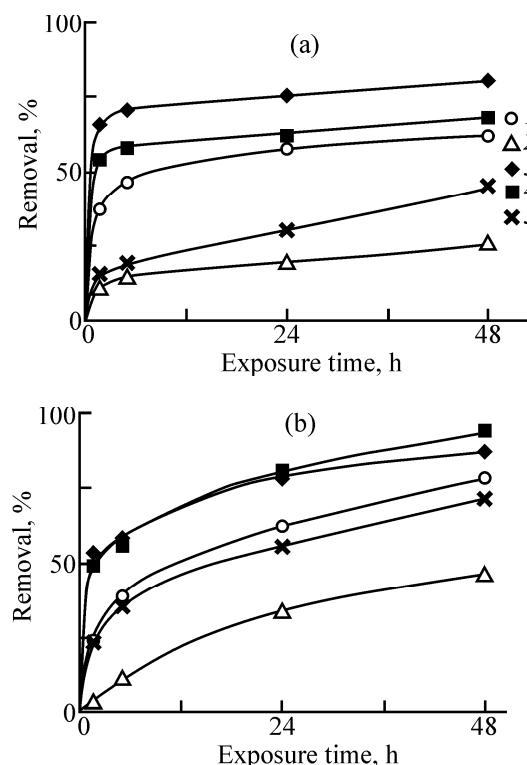


Fig. 1. Kinetics of ^{210}Po removal from aqueous solutions with natural minerals [(1) magnetite and (2) glauconite], rocks [(3) basalt and (4) dunite], and manganese dioxide (5). Initial solution acidity: (a) pH 7.0 and (b) pH 3.0.

from the initially neutral solution. Thus, in the initial steps of the interaction of solutions with silicates and magnetite, the ^{210}Po immobilization is more efficient in neutral solution, but with time the degree of the ^{210}Po removal from the initially acidic solutions becomes higher than from neutral solutions.

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