Use of Iron Sulfide for Removing Polonium from Liquid Radioactive Waste

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Abstract—Immobilization of polonium from low-level liquid radioactive waste (LRW) on iron monosulfide in batch and dynamic modes was studied. In batch experiments, the Po immobilization on FeS increases with increasing pH. At the solid phase : solution weight ratio of 1 : 100, the degree of ^{210}Po removal from the solution in 2 days is 72.6% at pH 5.45 and 92.8% at pH 6.20. In filtration of LRW with pH 3–4 through a bulk filter of iron monosulfide dispersed in aluminosilicate gel and quartz sand, more than 99.4% of ^{210}Po is removed from the LRW volume exceeding the volume of the sulfide gel material by a factor of approximately 700. Iron monosulfide can be used for efficient removal of Po from low-level LRW.

Keywords: polonium, immobilization, iron sulfide

Removal of polonium from liquid radioactive waste (LRW) is a difficult problem, because polonium can occur in different valence states and can form stable complex species [1]. For practical purposes, it is important to find polonium immobilization methods ensuring high degree of its concentration and hence small amount of residual products to be isolated and disposed of for the time sufficient for practically complete radioactive decay (the most widely occurring polonium isotope, ^{210}Po, has a half-life of 138.4 days [2]). This study deals with the polonium immobilization on iron sulfide and is aimed at evaluating the possibility of using this process for polonium removal from low-level LRW.

In the presence of dissolved oxygen, polonium occurs in aqueous solutions in the tetravalent state. At pH in the range 4–7, the prevalent species is the hydroxo complex $Po(OH)_4^0$; at lower and higher pH values, the complexes $Po(OH)_3^+$ and $Po(OH)_5^-$, respectively, prevail [3]. In the presence of hydrogen sulfide, Po(IV) is reduced to bivalent Po^{2+},

$$Po(OH)_4^0 + H_2S + 2H^+ = Po^{2+} + S^0 + 4H_2O, \quad (1)$$
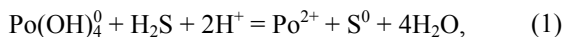
with the subsequent formation of difficultly soluble sulfide:

$$Po^{2+} + H_2S = PoS + 2H^+. \quad (2)$$
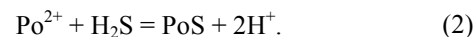
The solubility product (*L*) of PoS ($10^{-28.3}$) is close to that of cadmium ($10^{-27.8}$) and lead ($10^{-26.6}$) sulfides and is lower by 4–8 orders of magnitude than that of cobalt, nickel, and zinc sulfides [4]. Only silver, copper, mercury, and bismuth sulfides are less soluble. It is important that the solubility product of FeS ($10^{-17.3}$ [4]) exceeds that of PoS by a factor of 10^{11}, which suggests high efficiency of the sorption immobilization of Po on FeS:

$$\overline{FeS} + Po^{2+} = \overline{PoS} + Fe^{2+}, \quad (3)$$
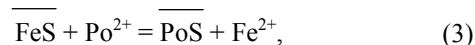
where the overscore denotes the surface adsorption complex. The coprecipitation of Po with FeS should probably be still more efficient, because in this case the impurity is captured by the whole volume of the carrier phase and not only by its surface.

BATCH EXPERIMENTS

To confirm the possibility of efficient immobilization of Po on FeS, we performed experiments on the ^{210}Po sorption onto analytically pure grade FeS ground in an agate mortar to the powder state (approximately

95% of particles had the size smaller than 20 μm). The solid phase : solution weight ratio in the experiments was 1 : 100. In the first series of experiments, pH of the initial solution containing tracer amounts of ^{210}Po was 7.0, and in the second series the initial solution was acidified to pH 3.0 by adding a small amount of 0.1 M HCl. A constant pH value was attained within approximately 4 h: pH 6.20 in the initially neutral solution and pH 5.45 in the solution with the initial pH 3.0. The solution aliquots for measuring the activity (1 mL) were taken four times: 100 min, 300 min, 1 day, and 2 days after the start of the interaction. The results of the experiments are given in Table 1.

As can be seen, Po is removed most efficiently from a neutral solution (93% in 48 h) in which the FeS solubility and hence the Fe(II) concentration is approximately 7000 times lower than at pH 3.0. In accordance with Eq. (3), a decrease in the Fe^{2+} concentration leads to a shift of the equilibrium of the ^{210}Po uptake to the right, i.e., to enhancement of its sorption. However, even in acidic solutions the degree of the Po immobilization is relatively high and reaches 73% in 48 h, i.e., FeS can be efficiently used in the entire examined pH range.

DYNAMIC EXPERIMENTS

Because of relatively high solubility product, FeS dissolves in acid solution,

$$FeS + 2H^+ = Fe^{2+} + H_2S, \qquad (4)$$
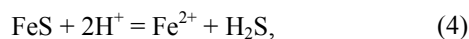
which leads to partial neutralization of the acid solution being filtered and to the precipitation of the previously dissolved FeS. The new portions of the acid solutions again dissolve the FeS precipitate formed, and these dissolution–precipitation cycles occur repeatedly until FeS is completely dissolved.

In each cycle of FeS dissolution–precipitation, the concentration (activity) of Po in the reaction zone increases. This process will continue until a steady state will be attained, at which the FeS sorption capacity will be saturated and further increase in the Po concentration will not be accompanied by an increase in its amount in the reprecipitated carrier phase. Apparently, attainment of the steady state corresponds to the condition when the Po concentrations at the inlet and outlet of the geochemical barrier are equal. The total specific capacity of the Po immobilization (E_{Po}, Bq g^{-1} FeS) can be estimated by the equation

Table 1. Removal of ^{210}Po from aqueous solutions via interaction with FeS, % of the initial activity

pH		Exposure time, h			
initial	equilibrium	1.7	5	24	48
7.0	6.20	68.9	75.0	84.5	92.8
3.0	5.45	32.5	43.6	56.4	72.6

$$E_{Po} = (m_{FeS})^{-1}\int_V (I_0 - I)dV, \qquad (5)$$

where I_0 and I are the Po activities in the initial sample and in the volume dV after passing through the FeS bed, Bq L^{-1}; m_{FeS} is the FeS weight, g.

Sulfide sulfur is present in aqueous solutions in the form of nondissociated H_2S molecules and of HS^- and S^{2-} ions:

$$[\textstyle\sum S^{2-}] = [H_2S] + [HS^-] + [S^{2-}] = [S^{2-}][a_{H^+}^2/(K_1K_2) + a_{H^+}/K_2 + 1], \qquad (6)$$

where $[\sum S^{2-}]$ is the total concentration of sulfide sulfur in solution; K_1 and K_2 are first and second step dissociation constants of hydrogen sulfide, and a_{H^+} is the activity of hydrogen ions. Because in the course of FeS dissolution the total concentrations of iron and sulfide sulfur are equal to each other,

$$[\textstyle\sum Fe^{2+}] = [\textstyle\sum S^{2-}], \qquad (7)$$

then, expressing the S^{2-} concentration in (6) via the FeS solubility product (L_{FeS}) and neglecting the presence of a small amount of Fe(II) hydrosulfide complexes,

$$[S^{2-}] = L_{FeS}/[Fe^{2+}] \approx L_{FeS}/[\textstyle\sum Fe^{2+}], \qquad (8)$$

we obtain an equation for the dependence of the iron sulfide solubility (R_{FeS}) on the activity of H$^+$ ions:

$$R_{FeS} = [\textstyle\sum Fe^{2+}] = [\textstyle\sum S^{2-}] = \{L_{FeS}[a_{H^+}^2/(K_1K_2) + a_{H^+}/K_2 + 1]\}^{0.5}. \qquad (9)$$

Calculations by Eq. (9), performed using the numerical values of L_{FeS}, K_1, and K_2, which are equal to $10^{-17.3}$, $10^{-6.99}$, and $10^{-12.60}$, respectively [4], show that, at pH < 5, the Fe(II) concentration in the solution in equilibrium with FeS reaches noticeable values: >10 mg L^{-1} (Table 2). Increasing acidity will certainly lead to an increase in the FeS solubility and in the mass of the reprecipitated carrier phase, but the dissolution rate of this phase will increase also and, hence, the time of its existence will decrease. Therefore, the

Table 2. FeS solubility (R_{FeS}) as a function of pH

pH	R_{FeS}, mM	R_{FeS}, mg L^{-1}	pH	R_{FeS}, mM	R_{FeS}, mg L^{-1}
2.0	140	12 300	6.0	0.015	1.32
3.0	14	1230	7.0	0.0020	0.18
4.0	1.4	123	8.0	0.00047	0.04
5.0	0.14	12.3	9.0	0.00014	0.01

Table 3. Polonium removal from LRW by filtration through the sulfide gel material[a]
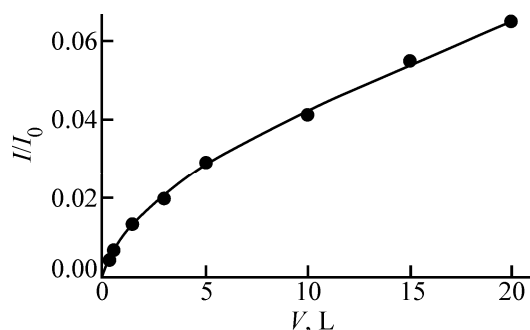
V, L	I, Bq L^{-1}	I/I_0	V, L	I, Bq L^{-1}	I/I_0
0.3	0.02	0.0004	5	0.13	0.028
0.5	0.03	0.006	10	0.19	0.041
1.5	0.06	0.013	15	0.25	0.054
3	0.09	0.019	20	0.30	0.065

[a] (V) Volume of filtered LRW; (I) Po activity in the filtrate, Bq L^{-1}; (I/I_0) Po activity in the filtrate relative to the initial solution.

optimum acidity of the initial solutions for the dynamic immobilization mode is, apparently, pH 3–4, when the Po precipitation occurs against the background of a relatively high FeS concentration in the solution, 0.1–1.2 g L^{-1}.

The validity of this conclusion was checked in the course of dynamic experiments on the filtration of ^{210}Po-containing untreated waste from a special production shop through a sulfide gel material.

The sulfide gel material was aluminosilicate gel with additions of finely dispersed FeS as active component and of quartz sand for enhancing the filtration ability. The aluminosilicate gel was prepared by the standard procedure, by mixing a solution of sodium silicate (density 1.19 g cm^{-3}) and a complex hardener containing 50 g L^{-1} aluminum sulfate $Al_2(SO_4)_3 \cdot 18H_2O$ and the same amount of oxalic acid $H_2C_2O_4 \cdot 2H_2O$ [5]. To 100 g of the unhardened aluminosilicate gel, 100 g of pulverized FeS (analytically pure grade)

and 300 g of pure quartz sand were added with mixing. After hardening, the sulfide gel material was thoroughly mixed once more, dried to the air-dry state, and used in this form in the experiments. The experimentally determined filtration coefficient for the material obtained was 22 m day^{-1}.

The filtration of LRW with pH 3.5 and initial Po activity I_0 4.63 Bq L^{-1} was performed through a column packed with the sulfide gel material (bed height 5 cm, total volume 30 cm^3). The filtration velocity was 0.86 m day^{-1}, or 3.6 cm h^{-1}. The residual Po activity was determined in successively taken portions of the filtrate on a Tri-Carb 3110 liquid scintillation spectrometer.

The results of the experiments showed (Table 3) that, even after filtration of 20 L of LRW, i.e., of the volume exceeding that of the sulfide gel material by a factor of ~700, the Po activity at the column outlet was only 6.5% of the initial value. After passing of the first portions of the solution, the dependence of the outlet activity on the volume of the filtered LRW became linear (see figure), which is typical of the early step of the adsorption saturation of the solid phase or of immobilization as a result of the above-described coprecipitation on the moving front of the interaction of LRW with FeS. The experimental data show that the sulfide gel material exhibits high ability to take up Po and can be efficiently used for removing Po from low-level LRW.

Ratio of the Po activity at the outlet and inlet of the column with the sulfide gel material as a function of the volume of the filtered LRW.

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