Sorption of Long-Lived Technetium from Radioactive Wastes and Ground Water by Sulfides and Sulfide Rocks

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INTRODUCTION

Technetium-99 is one of the long - lived fission products formed with the highest yeld of 6 - 6.3% in irradiated nuclear fuel. Its high mobility under oxic conditions is due to the high thermodinamic stability of $[TcO_4]^-$ which is weakly sorbed by the basic silicate and alumosilicate minerals [1-4]. This mobility determines the increasing danger of the constantly accumulating technetium amounts for the environment. It is worth recalling andizols which are supposed to be better sorbents for anions like Tc and I in natural conditions [5]. To our mind its application is limited by life-time of these metastable minerals (approx. one thousand years) in comparison with the Tc half-life ~212000 years. More perspective to our opinion is the possibility of Tc fixation on sulfide minerals discussed [6-9]. As there is some confusion in the data on the nature of the sulfide sorbents for Tc, we made an attempt to redetermine some values of distribution coefficients for some previously studied minerals and also to study some more minerals from Russian deposites with respect to Tc sorption.

RESULTS AND DISCUSSION

The tracers of 8000 Bq Tc-99 were injected for each sorption test to preequilibrated solutions. Experimental did not differ from those discribed in [3, 11]. The liquid phase was obtained by equilibrating simulated waste solution or natural water with the appropriate mineral for 10 days. Table 1 presents the typical results of batch experiments on $[TcO_4]^-$ absorption by sulfide minerals and sulfide rocks from simulated low-level alkali wastes and natural water. Autoradiography of rock polished sections, accompanied by micro X-ray diffraction analyses, was also used.

Table 1. Technetium sorption by fine grain fraction of sulfide minerals (0.05 mm < d < 0.1 mm) from 0.5 M NaOH + 1.5 $NaNO_3$ solution, exp.time - 1 month, and natural water

No	MINERAL	CHEMICAL COMPOSITION	K_d,ml/g	
			simulated wastes	natural water
1	Pyrite	FeS_2	0.3 ± 0.2	0.4 ± 0.2
2	Pyrrhotite (25%, $Fe_{1-x}S$)	Fe_7S_8	720 ± 20	20 ± 2
3	Wurtzite	ZnS	5 ± 0.3	1.0 ± 0.3
4	Cinnabar	HgS	17 ± 2	1.0 ± 0.5
5	Chalcocite	Cu_2S	0.2 ± 0.1	0.2 ± 0.1
6	Geocronite	$Pb_{28}(As,Sb)_{12}S_{46}$	0.2 ± 0.1	0.2 ± 0.1
7	Bismuthinite	Bi_2S_3	1.5 ± 0.2	1.0 ± 0.2
8	Arsenopyrite	FeAsS	110 ± 2	2.2 ± 0.5
9	Molybdenite	MoS_2	2 ± 0.2	1.2 ± 0.2
10	Chalcopyrite	$FeCuS_2$	2 ± 0.2	2.1 ± 0.2
11	Galena	PbS	3 ± 0.2	1.2 ± 0.2
12	Millerite	β-NiS	3 ± 0.2	5.5 ± 0.2
13	Antimonite	Sb_2S_3	307 ± 20	460 ± 45
14	Covellite	CuS	0.2 ± 0.1	6.0 ± 0.3
15	Alabandite	MnS	13 ± 2	14 ± 3
16	Germanite	$Cu_3(Ge,Ga,Fe)(S,As)_4$	15 ± 3	17 ± 3

It was obviously confirmed that pyrite in oxygen atmosphere is a very weak sorbent with respect to technetium (K_d = 0.3 ml/g). Similar behavior was noticed for chalcopyrite, chalcocite, wurtzite, geocronite, bismuthinite, molybdenite, galena, millerite, covellite. For Tc sorption by these minerals reversible physical adsorption mechanism is suggested, K_d being decreased with the increasing the dispersity of solid phase.

Germanite and alabandite were found to be better sorbents for Tc(VII).

The best sorbents for Tc were found to be pyrrhotine (25% $Fe_{1-x}S$, Olimpiadinsk deposit) sorption being irreversible with R_s= 720, antimonite and arsenopyrite.

We found R_s= 307 from simulated waste and R_s= 460 from natural water for Tc sorption on the samples of antimonite free from senarmonite Sb_2O_3. The latter mineral

Two sulfide rocks radioactive by Tc(VII) sorption

was shown to be more powerful sorbent for technetium then antimonite due to its pronounced reductive properties. Sorption by arsenopyrite, antimonite and pyrrhotite was irreversible as no desorption on washing with nonspiked preequilibrated natural water could be detected.

As the possibility of technetium sulfide precipitation was considered in [7] to be the probable explanation of technetium-99 sorption by sulfide minerals we made an attempt to compare the distribution coefficients obtained in our study and the known solubility products of the minerals but no correlation has been obtained. It is also worth recalling that technetium heptasulfide has a considerably high value of solubility product [9] if compared to the solubilities of the natural minerals under study.

The influence of mineral micro impurities and crystallografic defects in rocks on technetium uptake by composite minerals and rocks has been studied autoradiographically. The autoradiographs have shown selective sorption patterns of technetium-99, with drastically higher sorption on pyrrhotite impurities in pyrite and somewhat higher sorption on senarmonite impurities in antimonite. In both cases sorption on quartz regions was negligible.

Olimpyadinsk deposits pyrrhotite rock could be considered as usefull backfill material for the maintainance of trench stoppers for Tc migration.

CONCLUSIONS

Technetium is strongly absorbed from alkali waste solutions on pyrrhotite, antimonite, arsenopyrite, cinnabar, alabandite and germanite. Its sorption from natural waters is somewhat lower. Sorption of Tc by natural rocks is affected by the presence of several sulfide and oxide impurities. Pyrrhotite rock could be useful for the maintainance of trench stoppers for Tc migration.

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