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Konstantin E. German
A. N. Frumkin Institute of Physical Chemistry …

Alexey V. Safonov
Russian Academy of Sciences

E. A. Tyupina
Mendeleev Russian University of Chemical Te…

TECHNETIUM STABILIZATION FORMS FOR LONG-TERM STORAGE IN CEMENT COMPOUND

Kamornyi D.A., Tyupina E.A., Safonov A.V. * German K.E*
D. Mendeleev University of Chemical Technology of Russia, Moscow, Russia
*A.N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow, Russia

Cementing of radioactive waste is the simplest and cheapest method of curing radioactive waste. However, some radionuclides contained in RAW may not be included in the cement matrix, since they have a high degree of leachability and are therefore easily washed by groundwater. One such radionuclide is technetium. The purpose of this paper is to search for a stabilizing ligand. The following substances were selected as stabilizing ligands:
1) PGMH-hydrochloride (polyhexamethyleneguanidine hydrochloride, 2) TFF-chloride (tetraphenylphosphonium chloride), 3) Polyethylenimine (PEI), 4) Thiourea.
5) Chitosan is a polysaccharide. This procedure would form insoluble complexes with technetium and promote strong retention of technetium in the cement compound.
In the course of mechanical tests, an optimal water-cement ratio of 0.5 was chosen, which will be used later in the evaluation of leaching. The leachability assessment of the pertechnetate ion at the cement samples revealed that PGMH-HCL is the most efficient for retaintion the pertechnetate ion in the cement matrix.
***Key words**: cementing of radioactive waste, technetium, stabilizing ligand, leaching.*

Among the fission products produced in nuclear reactors, ^{99}Tc is the most environmentally hazardous. This is associated with a long half-life (213,000 years), a high content in irradiated nuclear fuel (0.8-1.0 kg in a ton of SNF), low sorption capacity and high mobility under aerobic conditions. More than 60 tons of ^{99}Tc has been accumulated to the present in a highly concentrated form. The radioactivity of technetium accumulated in radioactive waste is determined by the nuclides ^{99}Tc and ^{98}Tc and is less than 10^{-3}% of the total radioactivity of SNF at the present time. However, after 500 years, when the short-lived PD decays, the proportion of technetium in β-radioactivity will become one of the largest. The urgency of solving the problem of isolating 99Tc from the environment is obvious. A necessary link in the solution of this problem is the immobilization of technetium in a highly stable, hardly soluble matrix, which will ensure reliable isolation for thousands of years until it completely decays [1].

One of the possible methods of isolation of technetium from the biosphere is its cementing with the formation of matrices that are stable during storage. Unfortunately, technetium-containing cement matrixes are not stable during storage, since Tc in them is in the form of a highly water-soluble pertechnetate ion. The incorporation of technetium into such a cement-like matrix, like bentonite, also does not lead to the stabilization of Tc. For example, upon contact of the matrix with water, after 10 days, up to 40% of technetium is leached [1].

Technetium occupies a central place in the block of d-elements and, consequently, is prone to the formation of complex compounds [1]. Therefore, our goal was to search for ligands that form insoluble complexes with technetium and firmly retain it in the cement matrix.

The following substances were selected as stabilizing ligands:

1) PGMG-hydrochloride (polyhexamethyleneguanidine hydrochloride) is a cationic polyelectrolyte, which possesses a unique combination of physicochemical and biocidal properties, which allows this polymer to be used practically in all spheres of the national economy [2].

2) TFF-chloride (tetraphenylphosphonium chloride) - white crystals. The perrhenate ion forms a white crystalline precipitate with tetraphenylphosphonium chloride [3].

3) Polyethylenimine (PEI) - a synthetic polymer, a polymerization product of ethyleneimine; colorless viscous liquid. High affinity for metal ions informs polyethyleneimine of the ability to dissolve and retain hydroxide, oxides, carbonates and other insoluble compounds in the solution [4].

4) Thiourea-diamide of thioureous acid, thiourea, white crystals of bitter taste. It is capable of forming insoluble complexes with metals.

5) Chitosan is a polysaccharide. The molecule of chitosan contains a large number of free amino groups, which allows it to bind hydrogen ions and acquire an excessive positive charge. This also explains the ability of chitosan to bind and firmly hold ions of various metals (including radioactive isotopes, as well as toxic elements) [5]. With this form of ligand arose small difficulties due to the insolubility of these flakes in the water. Therefore, it was decided to transfer chitosan to a more convenient gel-form by dissolving it in 2M hydrochloric acid (HCl). Since the cement slurry has an alkaline medium reaction (pH> 7), to ensure the greatest affinity, the chitosan treated with hydrochloric acid was washed with 0.1 M NaOH solution until neutral reaction of the medium (pH=7).

Experimental part and results

Mechanical tests. GOST R 51883-2002 "Radioactive cement waste. General technical requirements" regulates a number of important parameters for a cement block containing radioactive waste, one of which is the compressive strength of 4.9 MPa. Therefore, prior to the leaching studies of technetium, it was decided to conduct tests to determine the effect of the inclusion of ligands on the mechanical strength of the cement compound. Three types of cement matrices with different water-cement ratios (0.4, 0.5, 0.9) were prepared, each of which included stabilizing ligands (5 total species) of different concentrations (0.1 wt%, 0,5% by weight, 1% by weight). Thus, 45 variations of cement compounds with sides 2x2x2 cm, with different water-cement ratio and ligand content, were obtained. A total of 90 matrices were made (2 replicates of each variation). In the same way, six "single" cubes with a water-cement ratio (0.4, 0.5, 0.9) were prepared in which stabilizing ligands were not added. They were necessary in order to further compare the mechanical properties of the "single" cubes and cubes with the included ligand.

After 28 days (the term is regulated by GOST), cement compounds were sent to mechanical tests for the press of the PWG-1-10.

All samples with a water-cement ratio of 0.4 have passed the required strength threshold of 4.9 MPa. Samples containing PGMG; 0.1% by weight PEI; 0.5, 1 wt.% Thiourea demonstrated a greater margin of safety than the "blank" sample (22.3 MPa). It can be assumed that these additives in a certain ratio increase the safety margin of the cement compound. Samples containing 1% by weight of TFP; 0.1% by weight of thiourea and 1% by weight of chitosan, showing a tensile strength close to the limiting one, raise some doubts, since under severe conditions of groundwater and, under the radiation load, there is a doubt that the required mechanical parameters will be provided.

All samples with a water-cement ratio of 0.5 passed the required strength threshold of 4.9 MPa. A cement matrix containing 0.5% by weight of PGMG has a greater margin of safety than a "blank" sample (28.7 MPa). All samples are suitable for further study and work.

Compared to previous experiments, experiments with compounds of a water-cement ratio of 0.9 showed negative results. Many samples did not pass the threshold required by GOST. Those samples that have passed the threshold of strength in 4.9 MPa, are on the verge and cause doubts. Therefore, it was decided in the future experiments that compounds with a water-cement ratio of 0.9 should not be used.

Cement compounds with a water-cement ratio of 0.4 have also been decided not to be used in leaching experiments. this ratio is not enough convenient for work.

Leaching experiments. Within the leaching experiment samples (cubes) with a water-cement ratio of 0.5 containing potassium pertechnetate (KTcO4) of 10^{-3} M, 10^{-4} M, 10^{-5} M in pertechnetate ion were prepared. Also, these cubes contain a stabilizing ligand of different concentrations (0.1 wt%, 0.5 wt%, 1 wt%). Thus, 45 variations of cement compounds with sides 2x2x2 cm, with different concentration of pertechnitate ion and ligand content, were obtained. A total of 90 matrices were made (2 replicates of each variation).

According to GOST, leaching of pertechnitate ion is carried out after 30, 90, 180 days, therefore 6 more variations of compounds with potassium perrhenate were prepared in the same way for a more accurate presentation of leaching dynamics (since rhenium is a chemical analogue of technetium with no radioactive).

A total of 12 samples were prepared: 2 blank samples with potassium perrhenate of 10^{-3} M concentration, 2 samples containing 0.5% by weight of PGMG hydrochloride and potassium perrhenate 10^{-3} M, 2 samples containing 0.5% by weight of TFP -chloride and 10^{-3} M potassium perrhenate, 2 samples containing 0.5% by weight PEI and 10^{-3} M potassium perrhenate, 2 samples containing 0.5% by weight of thiourea and 10^{-3} M potassium perrhenate, 2 samples with a content of 0.5% by weight of chitosan and 10^{-3} M potassium perrhenate.

After 28 days of solidification, all the samples were placed in individual boxes and filled with a model solution of "Tomsk surface water." The composition of this solution is shown in the following table:

Table 1. Composition of model solution "Tomsk surface water"

$NaHCO_3$, mg/l	$MgSO_4*7H_2O$, mg/l	$CaCl_2*6H_2O$, mg/l	$MgCO_3$, mg/l
25,2	36,6	223,9	3,2

Samples containing potassium pertechnetate have not yet reached the 30-day mark when the first leach analysis can be carried out. But we obtained the first result on the leaching of perrhenate ions. After 10 days by the method of ion selective potentiometry, the following data were obtained:

Table 2. Results of potentiometric measurements of model solutions after 10 days

Sample	Content of the stabilizing ligand in the cement compound	Concentration [ReO4] - in the cement compound, g / l	Concentration of $[ReO_4]^-$in the model solution after 10 days of leaching, g / l	Leaching $[ReO4]^-$, %
1	-	0,1826	0,0368	20
2	0.5% by weight of PGMG hydrochloride	0,1826	0,0153	8
3	0.5% by weight of TPP-chloride	0,1826	0,0157	9
4	0.5% by weight PEI	0,1826	0,0194	11
5	0.5% by weight of thiourea	0,1826	0,0241	13
6	0.5% by weight Chitosan	0,1826	0,0217	12

It can be seen that from the samples with stabilizing ligands leaching of potassium perrhenate was less over the same period of time than from samples that did not contain stabilizing ligands. It is expected that after a while the difference in leachability between blank samples and samples containing stabilizing ligands will increase.

Conclusion

In the course of mechanical tests, an optimal water-cement ratio of 0.5 was selected, which will be used later in the evaluation of leaching. This research work is in an active stage. The leachability assessment of the pertechnetate ion will soon show which of the stabilizing ligands is most strongly retained by the pertechnetate ion in the cement matrix. The expectations are quite optimistic, because a preliminary estimate of the perrhenate ion leach has shown how strongly the addition of a stabilizing ligand affects the leachability within 10 days.

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