

APPLICATION OF CROWN-ETHERS AND FERROCYANIDE-BASED INORGANIC MATERIAL FOR CESIUM AND STRONTIUM RECOVERY FROM HIGH-LEVEL RADIOACTIVE WASTES

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ABSTRACT

Safe handling and disposal of high-level radioactive wastes (HLRW) is the indispensable condition for further development of nuclear power engineering. The most efficient approach to the problem of issue assumes the removal of especially hazardous long-lived radionuclides (namely, ^{90}Sr , ^{134}Cs , ^{137}Cs , transplutonium elements) from HLRW, thus transferring the latter into the intermediate-level radioactive waste (ILRW) category (1).

This paper presents the results obtained during the bench and pilot-plant scale tests of the crown-ether-based extraction process for ^{90}Sr and ferrocyanide-containing inorganic ion exchanger-based adsorption process for $^{134,137}\text{Cs}$ removal from HLRW. The data on the HLRW immobilization technique comprising the adsorption of HLRW on an inorganic adsorbent particles at elevated temperature followed by firing them at 800-1000°C are also reported.

RECOVERY OF STRONTIUM-90

In recent years, the extremely high selective capacity of macrocyclic polyesters (crown-ethers) (2) with respect to ^{90}Sr attracted the attention of research groups developing the method for recovery of ^{90}Sr from HLRW. However, to implement such a process into industrial scale the following factors should be considered:

- commercial availability of the exotic reagents;
- unsatisfactory re-extraction;
- the radiolytical formation of corrosive chloride ions;
- the lack of tests on the real HLRW.

Bearing the above challenges in mind, the extraction technique based upon dicyclohexyl-18-crown-6 (DCC-6) for selective recovery, concentrating, and decontamination of ^{90}Sr has been elaborated. The bench-scale and pilot-plant "hot cell" tests with Purex waste have been performed.

General Features of the Technique

The technique provides the recovery of high chemical and radiochemical grade ^{90}Sr eminently suited for use in radioisotope heat sources, etc. The process is rather flexible for different types of HLRW including waste with high salt content; no pre-adjustment of a feed solution composition is required. The only reagent used is distilled water which facilitates strontium concentrates handling and prevents the accumulation of metal salts in radwaste. The process can be implemented in different types of equipment - both mixer-settler and centrifugal extractors can be utilized.

Technical specifications of the technique are listed below:

1. Three-component mixture including 0.01 mole/l DCC-6 is used as an extractant. The extraction system capacity with respect to strontium makes up 10+15 g/l. The composition of the diluent is a commercial secret;
2. Extraction cycle comprising the isolation, concentration and decontamination of ^{90}Sr is performed at 14-15 stages of extraction, stripping, and re-extraction. Dis-

tilled water is used as a stripping and re-extracting solution;

3. No adjustment of nitric acid concentration in a feed solution is required; the pre-treatment includes only clarification by settling;
4. The extraction system possesses high radiation stability and is not corrosive to the equipment thereof. Actually no corrosion of stainless steel was observed at the total irradiation dose up to 10^7 Gray;
5. Expert assessment within the current regulations in Russia proved the process to be fire and explosion safe;
6. Extraction system contains no toxic components.

PILOT-PLANT TESTS

The pilot-plant included 9 extraction stages, 2 stages of stripping organic extract by acidified water, and 11 re-extraction stages. According to the technique, 5-6 re-extraction stages are sufficient, the extra stages being involved due to the design of the installation available. The flow rate of the feed was maintained at 100-200, 50-100, and 50-100 l/hr in the 1st, 2nd and 3rd extraction cycle, respectively; the flow rate of the stripping solution was maintained at 15-25 l/hr and that of the re-extracting solution at 15-20 l/hr in all cycles. In order to ensure the reliable monitoring of the flow rate (based on the solution conductivity measurement), distilled water was substituted for 1-3 g/l HNO_3 solution.

During the 1st extraction cycle 85.5 m³ of high-radioactive raffinate arisen from the Purex reprocessing of irradiated WWER fuel elements have been treated. The feed solution and resulting product composition along with the decontamination factors of ^{90}Sr (D_f) are listed in Table I.

As a result of the 1st cycle, 540000 Ci of ^{90}Sr contained in 12.5 m³ of strontium re-extract and 100 m³ of the raffinate have been obtained. Average loss of ^{90}Sr with the raffinate amounted 0.32 Ci/l (ranged from 0.014 to 0.87 Ci/l) or 4.3% of strontium content in the feed. The average concentration factor of ^{90}Sr per extraction cycle reached 5.8, maximum concentration factor being 18.3 at the loss of ^{90}Sr with the raffinate not more than 5%.

TABLE I

The Recovery of ^{90}Sr From the Purex Raffinate (1st cycle) and the Concentrating ^{90}Sr From the 1st Cycle Re-Extract (2nd Cycle)

| Components | Purex Raffinate Composition | 1st Extraction Cycle | | 2nd Extraction Cycle | |
|---|-----------------------------|------------------------|---------------------------------|------------------------|---------------------------------|
| | | Re-Extract Composition | ^{90}Sr D _f | Re-Extract Composition | ^{90}Sr D _f |
| ^{90}Sr , Ci/l | 7.35 | 43.3 | | 88.6 | |
| HNO ₃ , mole/l | 3.0 | 0.09 | | 0.18 | |
| EDR, $\mu\text{R/s}\cdot 1$ | 2750 | 60.8 | | 14.8 | |
| Non-Radioactive Impurities, g/l | | | | | |
| Fe | 0.32 | 0.03 | 60 | 0.03 | 10 |
| Cr | 0.04 | 0.01 | 20 | 0.01 | 3 |
| Ni | 0.13 | 0.01 | 75 | 0.01 | 9 |
| Ca | 0.06 | 0.03 | 12 | 0.03 | 6 |
| Pb | 0.01 | 0.01 | 6 | 0.01 | 9 |
| Ba | 0.20 | 0.50 | 2 | 0.30 | 3 |
| Na | 0.62 | 0.03 | 120 | 0.03 | 40 |
| Al | 0.34 | 0.01 | 200 | 0.01 | 9 |
| Gamma-Spectrum, % | | | 615* | < 0.015** | 13* |
| ^{144}Ce | 6.9 | 2.7 | 80 | - | |
| ^{106}Ru | 11.7 | 3.0 | 125 | 45.8 | 10 |
| ^{154}Eu | 2.3 | 0.3 | 200 | - | 270 |
| ^{134}Cs | 15.6 | 3.5 | 145 | 44.3 | 80 |
| ^{137}Cs | 63.5 | 90.5 | 22 | 9.9 | 85 |
| * The decontamination factor from total γ -activity. | | | | | |
| ** Total γ -activity in the re-extract, Ci/l. | | | | | |

The solubility of DCC-6 in the raffinate reached 300 mg/l, nitric acid concentration in the raffinate was equal to 2.58 mole/l.

Gamma-spectrometry of 50% re-extract samples did not detect cerium and europium radionuclides.

The equivalent dose rate (EDR) of the extractant in the course of tests was within the range of $0.8 + 1.7 \mu\text{R/s}\cdot 1$ due to the presence of ruthenium and cesium radioisotopes. It is worth to mention that no intra-cycle washing of the extraction mixture was conducted.

During the 2nd extraction cycle the concentrating of ^{90}Sr has been performed. Strontium re-extract from the 1st cycle was acidified up to 3.5 mole/l with respect to HNO₃ and used as a feed solution; the addition of acid resulted in 1.43-fold dilution of the re-extract. The feed amount of 8.5 m³ have been treated; 2.45 m³ of strontium re-extract and 11.6 m³ of the raffinate have been obtained. The loss of ^{90}Sr with the

raffinate amounted 0.78 Ci/l (2.5% of strontium content in the feed). The re-extract composition along with the decontamination factors of ^{90}Sr are listed in the Table I. The 2nd extraction cycle provided additional decontamination and 3-fold concentrating of ^{90}Sr , the yield of the latter reached 97.5%.

In the 3rd extraction cycle the recovery of ^{90}Sr from the ≈ 20 -fold concentrated Purex raffinate have been performed. The solution was fed into the installation without pre-clarification on the reason below. The high activity of the feed solution caused self-heating, and required cooling was conducted by means of a jacketed vessel where the temperature of the fee batch was lowered to $15 + 20^\circ\text{C}$ followed by the mixing and agitating the cooled batch with the bulk of the feed raffinate in the tank. Preventing settling in the feed tank the above procedure maintained the marked suspension content

in the feed which hindered the normal operation by deteriorating the process hydrodynamics.

The feed amount of 20.92 m³ has been treated; above 1000000 Ci of ⁹⁰Sr contained in 5.84 m³ of the re-extract and 25.93 m³ of the raffinate have been obtained. Average loss of ⁹⁰Sr with the raffinate amounted 5.0 Ci/l or 6.9% of strontium content in the feed. The feed solution and resulting product composition along with the decontamination factors of ⁹⁰Sr are listed in Table II.

The extractant in the 3rd cycle contained the marked amount of suspensions, EDR of the re-cycling extractant reached 10 μR/s•l. After filtration of an extractant sample the value of EDR was reduced by 25 + 30% and was defined by almost equal shares of ruthenium and cesium radionuclides.

TABLE II

The Recovery of ⁹⁰Sr From the Concentrated Purex Raffinate (3rd Cycle)

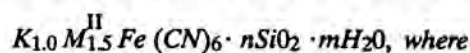
| Components | Concentrated Purex Raffinate Composition | 3rd Extraction Cycle | |
|---------------------------------|--|------------------------|---------------------------------|
| | | Re-Extract Composition | ⁹⁰ Sr D _f |
| ⁹⁰ Sr, Ci/l | 71.6 | 178.3 | |
| HNO ₃ , mole/l | 3.3 | 0.12 | |
| EDR, μR/s•l | 19600 | 305 | |
| Non-Radioactive Impurities, g/l | | | |
| Fe | 4.0 | 0.05 | 200 |
| Cr | 0.4 | 0.015 | 70 |
| Ni | 1.5 | 0.02 | 190 |
| Ca | 0.2 | 0.04 | 12 |
| Pb | 0.01 | 0.01 | 2.5 |
| Ba | 0.8 | 0.60 | 3 |
| Na | 7.0 | 0.30 | 60 |
| Al | 6.0 | 0.04 | 375 |
| Gamma Spectrum, % | | | 160* |
| ¹⁴⁴ Ce | 8.3 | 5.7 | 110 |
| ¹⁰⁶ Ru | 6.8 | 6.1 | 80 |
| ¹⁵⁴ Eu | 3.1 | 1.8 | 125 |
| ¹³⁴ Cs | 13.4 | 15.3 | 65 |
| ¹³⁷ Cs | 68.4 | 71.1 | 70 |

*The decontamination factor from total γ-activity.

RECOVERY OF CESIUM-134,137

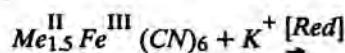
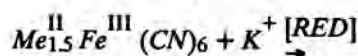
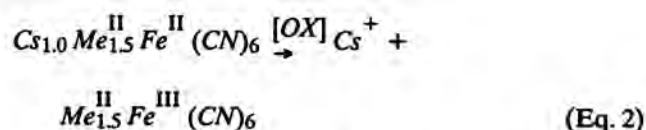
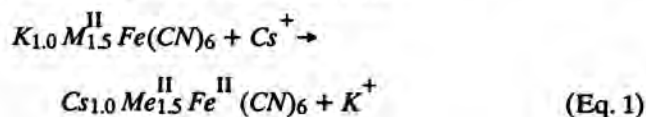
Among the various techniques employed for the recovery of cesium from HLRW the important place belongs to the methods based upon the application of inorganic ion exchangers containing the transition metal ferrocyanides. Those ion exchangers possess high selectivity to cesium and increased thermal, chemical, and radiation stability (3-5). Different types of ferrocyanide adsorbents are manufactured in Russia nowadays (6), thus allowing both bench and pilot-plant scale tests.

In this paper, the results of studying composite silica gelferrocyanide adsorbents containing zinc-potassium (registered trade mark FS-3), nickel-potassium (FS-7), and copper-potassium (FS-10) ferrocyanides are reported. The brutto-formula of the adsorbents said is the following:



Me^{II} denotes Ni, Cu, or Zn, n = 3-6, m = 4-8

The adsorption of Cs occurs due to the exchange of K ions in the solid for Cs ions in the fluid phase. The processes of desorption and regeneration proceed in oxidative media (oxidative desorption) and reductive media (reductive regeneration) according to the equations (1-3):



where [Ox], [Red] denote the oxidant and the reductant, respectively.

Various strong oxidants, namely, the solutions of nitric acid, potassium permanganate, cerium (IV) sulphate can be used for Cs desorption, and regeneration stage may be conducted by treating the oxidized adsorbent form with the solution of alkali metal sulphites, thiosulphates, nitrites, ascorbic acid, etc.

Laboratory Studies

The adsorption of Cs was studied using the solution of cesium nitrate ([Cs] = 2 g/l, pH = 6) and the simulated Purex raffinate of the following composition, g/l: Fe-10, Ni-1.0, Cr-1.0, Mn-1.0, Al-1.0, La-25, Ca-2.0, Sr-1.0, Ba-1.0, Cs-2.0, HNO₃-3 mole/l. The flow rate in column experiments was maintained at 3 b.v./hr (bed volumes per hour). The solutions and filtrates were analyzed for Cs content by means of radiometry using ¹³⁷Cs as a tracer.

The total dynamic capacity (TDC) values determined in the experiments are given in Table III.

TABLE III

The TDC Values of Inorganic Composite Silica Gel-Ferrocyanide Ion Exchangers With Respect to Cesium

| Solution Type | TDC w/r to Cesium mg/g, on Adsorbents | | |
|--|---------------------------------------|------|-------|
| | FS-3 | FS-7 | FS-10 |
| CsNO ₃ Solution, pH = 6 | 150 | 90 | 160 |
| Simulated Purex Raffinate, [HN ₃] = 3 mole/l | 7 | 3 | 5 |
| Neutralized Simulated Purex Raffinate, [HN ₃] = 0, 3mole/l | 115 | 30 | 100 |

As it is seen, TDC values for the simulated Purex raffinate are lower as compared to those for pure cesium nitrate solution and for the neutralized to 0.3 mole/l HNO₃ simulated Purex raffinate. It is explained by the oxidative effect of nitric acid on ferrocyanide functional groups.

Adsorbents saturated with Cs were treated by 8 mole/l nitric acid solution under dynamic conditions. The desorption in 10 b.v. yielded 80, 40 and 98% of adsorbed Cs for FS-3, FS-7, and FS-10, respectively. Observed deterioration of the exchange reversibility can be attributed to the change in adsorbent chemical composition under contact with the simulated solution. The FS-10 sample showed the best performance and provided its suitability for ¹³⁷Cs recovery for HLRW in a multi-cycle mode.

The regeneration of FS-10 was conducted by treating it with the solution containing sodium sulphite and potassium chloride followed by washing the column bed with water. Regenerated adsorbent was ready to use in the next cycle of cesium recovery.

Pilot-Plant Tests

The tests were performed using a stainless steel column of operating volume 120 l. To increase the ion exchanger capacity with respect to cesium ions, the pre-treatment of the feed Purex raffinate was conducted. So far as neutralization of the feed would increase the waste salt content, the special procedure comprising the addition of a reductant to the feed raffinate has been developed. The reductant composition is a commercial secret.

The yield of ^{134,137}Cs at the adsorption stage reached 98%, the desorption stage yielded 96-98% of ^{134,137}Cs. The concentration factor of cesium made up ≈ 100 . Above 10 million curies of ^{134,137}Cs have been produced on the installation since the tests commenced. During 15 cycles of operation no change in FS-10 performance has been detected.

After evaporation to dryness the ¹³⁷Cs nitrate product has been vitrified or used for γ -sources production.

ADSORPTIVE HLRW IMMOBILIZATION TECHNIQUE

The technique comprising the adsorption of radionuclides at elevated temperature on inorganic adsorbents has been developed for immobilization of HLRW in a solid waste form suitable for long-term safe storage.

The technique includes the adsorption of HLRW at 100+130°C on an inorganic adsorbent, e.g. silica gel, followed by firing the saturated adsorbent granules at 850-1000°C. Interaction of a certain HLRW volume (corresponding to 30-50% metal loading in the final solid waste) with an adsorbent results in complete adsorption of HLRW. Further firing converts adsorbed metal salts into metal oxides and metals dispersed within the silica gel matrix. It was found that above 850°C the dehydroxygenation of silica gel results in the formation of a stable structure (stressed Si-O-Si bridge) incapable of water adsorption.

Bench-Scale Tests

The process developed has been tested both on simulated solutions and on the Purex raffinate. No pre-adjustment of the feed Purex waste was required. The samples of saturated fired silica gel have been obtained; the samples were of fluidized fused surface granules 0.25+0.5 mm size. The metal loading reached 470 mg per 1 g of silica gel.

The radionuclide loss with off-gases did not exceed $2.6 \cdot 10^{-2}\%$ and $0.2 \pm 0.1\%$ of the radionuclide content in the feed HLRW on the adsorption and firing stage, respectively. The bulk of the off-gas adsorption and firing stage, respectively. The bulk of the off-gas activity has been trapped with four aerosol filters FMS and two gas filters MAI. The radioactivity of the filters originated by 90% from ¹⁰⁶Ru and ^{134,137}Cs radioisotopes.

The resistance of product granules to leaching made up $1.3 \cdot 10^{-5}$ $2.0 \cdot 10^{-4}$ g/cm²·d during the 1st day and $2.7 \cdot 10^{-8}$ $3.8 \cdot 10^{-6}$ g/cm²·d during the 2nd week of leaching.

A drum-type furnace with magnetic drive has been designed for the pilot-plant tests of the elaborated technique. The tests are supposed to commence in 1992.

CONCLUSIONS

The techniques based upon macrocyclic crown ether DCC-6 and ferrocyanide inorganic ion exchanger FS-10 have been developed for the recovery of ⁹⁰Sr and ^{134,137}Cs from HLRW. The bench and pilot-plant scale tests revealed good performance of the processes elaborated, high chemical and radiochemical grade strontium and cesium products have been produced. Almost 100% yields of the said radionuclides into the final product make the processes an option to convert the HLRW into the ILRW category.

The newly developed adsorptive HLRW immobilization technique is at the early development stage. The pilot-plant tests planned for 1992 followed by the evaluation of the solidified waste forms should prove the efficiency of the technique offered.

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