

APPLICATION OF MEMBRANE SORPTION REACTOR TECHNOLOGY FOR LRW MANAGEMENT

Yuri Glagolenko, Evgeny Dzekun
FSUE "Mayak", Russia

Boris Myasoedov
Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences

Vladimir Gelis, Evgeny Kozlitin and Vitaly Milyutin
Institute of Physical Chemistry of the Russian Academy of Sciences

Lev Trusov
Association "Aspect", Russia

Vadim Tarassov
"Aspect USA", USA

Mike Rengel, Stewart M. Mackay and Michael E. Johnson
CH2M HILL, USA

ABSTRACT

A new membrane-sorption technology has been recently developed and industrially implemented in Russia for the treatment of the Liquid (Low-Level) Radioactive Waste (LRW).

The first step of the technology is a precipitation of the radionuclides and/or their adsorption onto sorbents of small particle size. The second step is filtration of the precipitate/sorbent through the metal-ceramic membrane, Trumem™. The unique feature of the technology is a Membrane-Sorption Reactor (MSR), in which the precipitation / sorption and the filtration of the radionuclides occur simultaneously, in one stage. This results in high efficiency, high productivity and compactness of the equipment, which are the obvious advantages of the developed technology. Two types of MSR based on Flat Membranes device and Centrifugal Membrane device were developed. The advantages and disadvantages of application of each type of the reactors are discussed.

The MSR technology has been extensively tested and efficiently implemented at "Mayak" nuclear facility near Chelyabinsk, Russia as well as at other Russian sites. The results of this and other applications of the MSR technology at the different Russian nuclear facilities are discussed. The results of the first industrial applications of the MSR technology for radioactive waste treatment in Russia and analysis of the available information about LRW accumulated in other countries imply that this technology can be successfully used for the Low Level Radioactive Waste treatment in the USA and in other nuclear countries.

INTRODUCTION

Modern technologies for the reprocessing of spent nuclear fuel from power nuclear reactors generate substantial quantities of the liquid radioactive waste (LRW) of different radioactivity level and complex chemical composition. Taking into account the LRW accumulated up to date as a result of defense programs, the gross radionuclide

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quantity currently in storage at Russian nuclear complexes and abroad is about 10^9 Curies. The most toxic radionuclides contained in the waste are the long-lived ^{137}Cs , ^{90}Sr , ^{235}U , ^{239}Pu , and $^{241,243}\text{Am}$, with up to 80% of the radioactivity being accounted for by the ^{137}Cs radionuclide.

Several approaches used for the LRW treatment and conditioning are as follows:

- tank storage;
- deep injection;
- LRW treatment aimed at the separation of the long-lived radionuclides followed by conversion of the separated fractions into low soluble compounds.

Tank storage is the simplest way, however, it has the significant drawbacks associated with deterioration of the tank over time and possible release of radionuclides into the environment. In the case of deep injection of radioactive waste into the geological collector layers, the monitoring of the injected waste behavior is very complicated.

Long-lived radionuclide separation technology currently employs the following techniques and combinations thereof:

- extraction processes;
- sorption processes;
- precipitation processes.

An extraction technique using the chlorinated cobalt dicarbollide (CCD) followed by precipitation of rare earths and transuranic elements (TRU) elements as oxalates from the process raffinate is widely used in Russia for separation of ^{137}Cs , ^{90}Sr , and TRU elements from the high-level radioactive waste (HLRW) solutions. Full-scale implementation of this technology in Russia has allowed us to separate and convert into glass matrices over 50 million Curies of the long-lived radionuclides (1, 2). The principal flowsheet for this technology is shown in Fig. 1. An inorganic, potassium-copper ferrocyanide (FS-10 type sorbent) sorption technology was used for separation of ^{137}Cs from the acidic HLRW solutions (3). To date, this technology has been used to remove over 50 million Curies of ^{137}Cs from HLRW and either convert the ^{137}Cs into a glass form or sell the ^{137}Cs as a radiation source. The total quantity of the long-lived radionuclides vitrified to date at the Production Association Mayak exceeds 300, 000, 000 Curie.

Organic ion exchange resins, inorganic natural and synthetic sorbents are widely used for the low-level radioactive waste (LLRW) treatment. Those processes were extensively studied and reported. As an example, over 150000 m^3 of various LLRW were decontaminated at the Production Association "Mayak", Oziorsk, Russia using the inorganic ferrocyanide containing sorbent.

Precipitation techniques were extensively used at the earlier stages of the radiochemical technology (4). However, the complex problem of the liquid-solid phase separation was not solved until recently, and precipitation processes, although simple and straightforward, were losing their significance. Clarification of solutions by means of conventional batch filtration generated more secondary waste on account of the need for regenerating the filtering element. Organic polymer membranes widely used in water conditioning systems appeared to be not suitable for the purpose in most cases due to their low radiation stability.

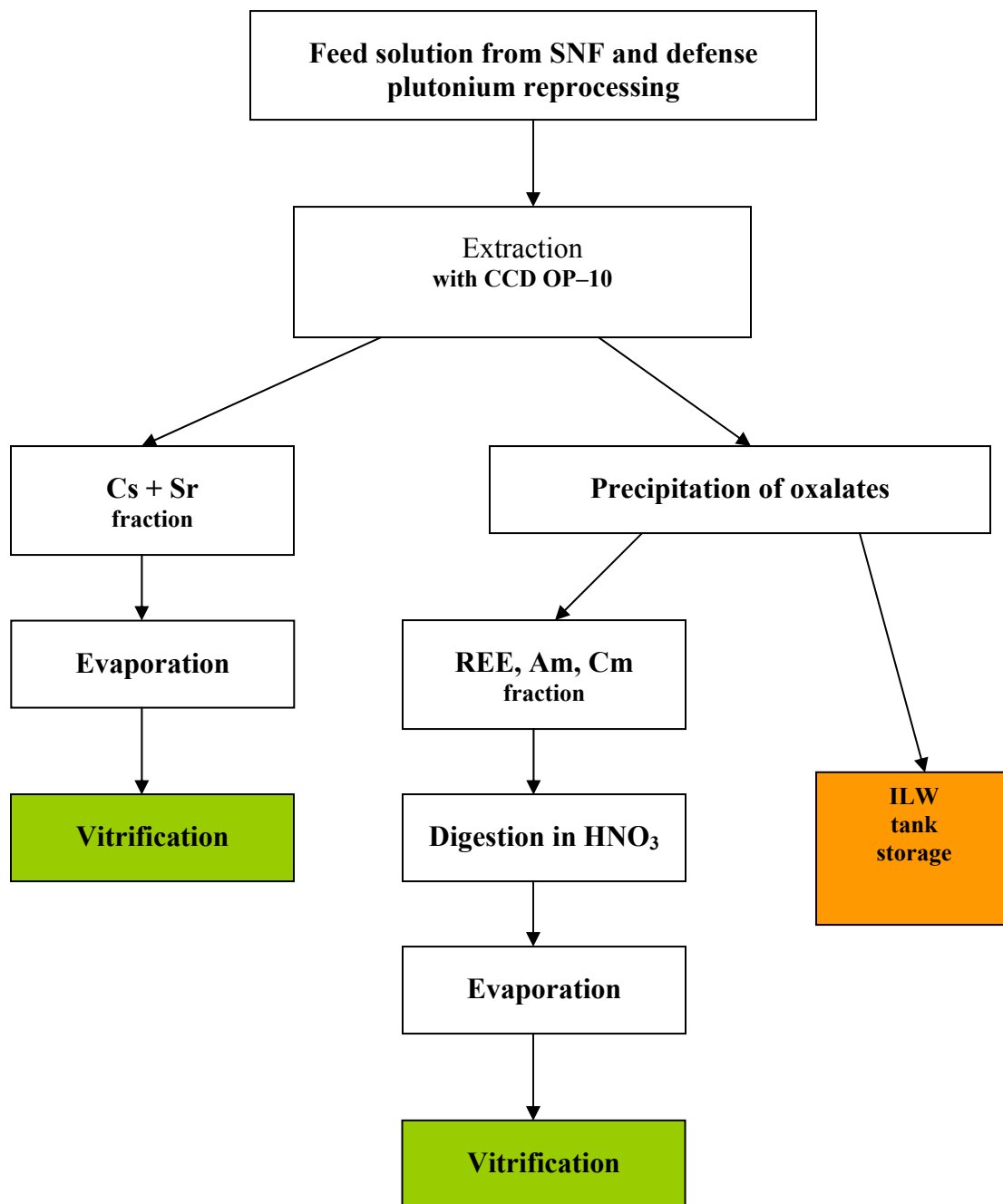


Fig. 1 Principal Flowsheet of the Separation Technology for LRW Separation

The primary goal of our work was to develop a high performance LRW decontamination technology using the combination of the old-fashioned precipitation processes with the state-of-the-art metal-ceramic “TruMem” membranes. These membranes were installed in centrifugal filtering units operating in the continuous mode in the Membrane Sorption Reactor (MSR) facility.

MEMBRANE SORPTION REACTOR DESIGN

The “TruMem” membrane is the main element of the MSR. It consists of three layers:

- support layer 200 micron thick, made of stainless steel;
- intermediate diffusion layer;
- separation layer made of the porous titanium or aluminum oxide-based ceramics (TiO_2 or Al_2O_3) with available pore size of 0.03 to 0.4 micron.

Separation characteristics of the “TruMem” membranes are given in the Table 1 using the LRW decontamination as an example.

Table 1. Separation Characteristics of the “TruMem” Membranes

| Radionuclide | Feed Solution, Bq | Membrane porosity | | |
|-------------------------|-------------------|-------------------|------------|------------|
| | | 0.05 micron | 0.1 micron | 0.4 micron |
| Gross β -activity | 19150 | 13180 | 13420 | 13140 |
| ^{144}Ce | 550 | < 2.3 | < 2.3 | < 2.3 |
| ^{154}Eu | 7030 | < 2.0 | < 2.0 | < 2.0 |
| ^{241}Am | 1620 | < 0.79 | < 0.79 | < 0.79 |
| ^{243}Am | 30 | < 0.36 | < 0.36 | < 0.36 |
| ^{137}Cs | 1840 | 1670 | 1850 | 1870 |

The data in Table 1 demonstrates the ability of the TruMem membranes to retain the readily hydrolyzed radionuclide species. Obviously, the membranes would effectively retain any fine dispersed particles as well. High hardness of the ceramics provides for low abrasive wear.

Different layouts of the continuously operated filtration process are shown in Fig. 2. As shown in Fig. 2 the concentration polarization, i.e. the deposit formed on the membrane surface could be removed either by high tangent flow velocity (flat membrane unit) or by the impact of the centrifugal force and high shear stress (centrifugal membrane unit).

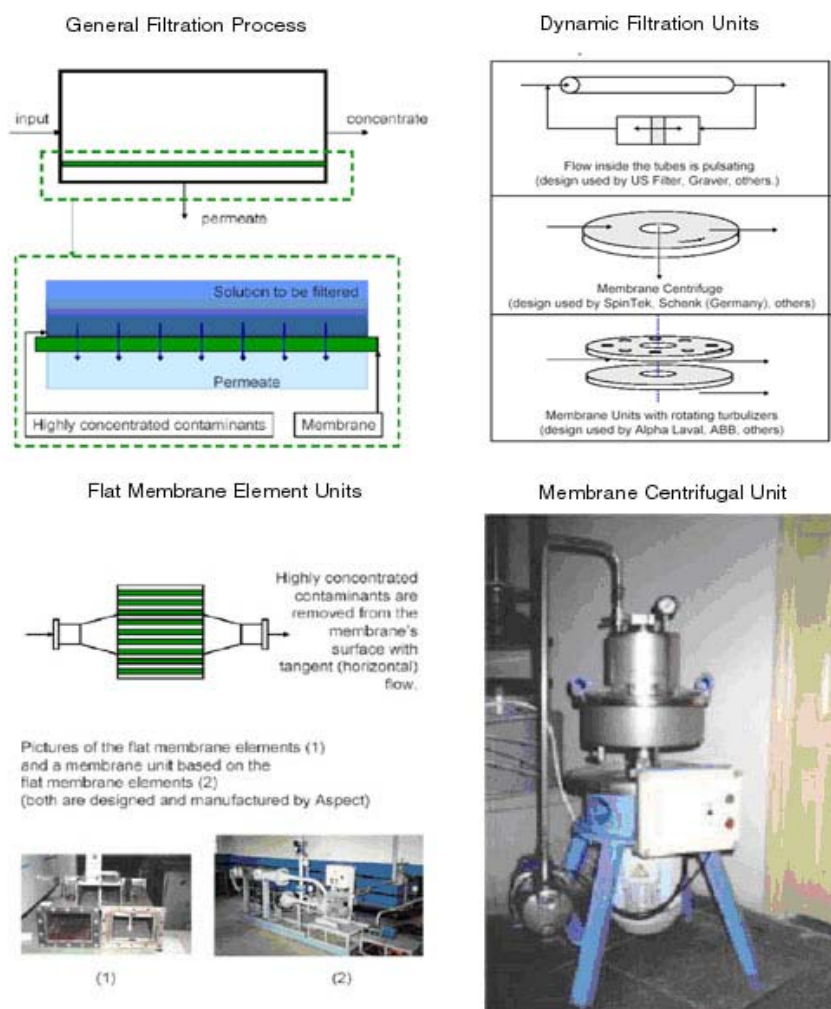
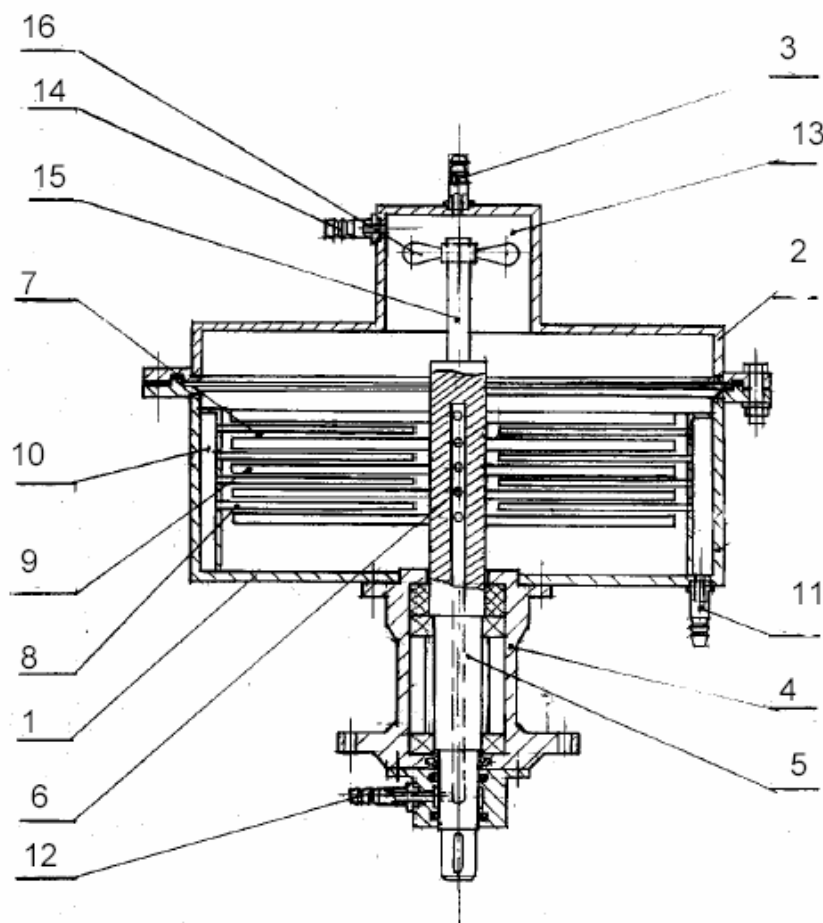


Fig. 2. Different process layout with the membrane filtering elements

In our work, the simultaneous processes of the radionuclide concentrating by means of sorption on a fine dispersed selective sorbent or co-precipitation with a special reagent additives and the continuous filtration to achieve the liquid - solid phase separation were combined in the Membrane Sorption Reactor unit (see Fig. 3).



- | | | | |
|---|--|----|--|
| 1 | Housing | 9 | Separator element (or vice versa) |
| 2 | Lid | 10 | Peripheral collector for the 1 st product |
| 3 | Inlet nipple – feed solution | 11 | Outlet nipple – 1 st product |
| 4 | Shaft seal | 12 | Outlet nipple – 2 nd product |
| 5 | Central shaft | 13 | Reaction chamber |
| 6 | Wall perforation of the shaft internal cavity | 14 | Inlet nipple – modifying additives – chemical reagents and nano-sorbents |
| 7 | Membrane and separator elements – complete set | 15 | Mixer shaft |
| 8 | Membrane element | | |

Fig. 3. Schematic Drawing of the Membrane Sorption Reactor

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Our MSR design provides the possibility for the sorption or co-precipitation processes to occur directly in the reactor chamber, thus allowing for efficient reagent utilization, prompt removal of the radionuclide concentrate from the system, and high precipitate concentrating factors.

Basic parameters of the MSR unit were determined using the results of from processing alkaline LRW to remove ^{137}Cs by precipitation with sodium tetraphenylborate (Na-TPB) additive. The data from processing the LRW to remove ^{137}Cs are given in Tables 2 – 5.

Table 2. Precipitation of Cesium with NaTPB from High-Level Radioactive Waste Solutions with Different Na Concentration

$[^{137}\text{Cs}]_{\text{feed}} = 3.7 \text{ g/L}$. Precipitating agent additive in excess of Cs/NaTPB < 1/20

| | [Na], mole/L | Precipitation factor, % |
|---|-------------------|-------------------------|
| 1 | $1 \cdot 10^{-9}$ | > 99.9 |
| 2 | 0.2 | > 99.9 |
| 3 | 0.5 | > 99.9 |
| 4 | 1.0 | > 99.9 |
| 5 | 1.5 | > 99.9 |
| 6 | 20. | > 99.9 |
| | | |

Table 3. Precipitation of Cesium with Na TPB from High-Level Radioactive Waste Solutions with Different Na Concentration

$[^{137}\text{Cs}]_{\text{feed}} = 30 \text{ mg/L}$. Precipitating agent additive in excess of Cs/NaTPB = 1/5

| | [Na], mole/L | Precipitation factor, % |
|---|--------------|-------------------------|
| 1 | 0.5 | 99.2 |
| 2 | 2.0 | 97.9 |
| 3 | 4.0 | 94.8 |
| 4 | 6.0 | 92.0 |

Table 4. Effect of Added TPB Quantity on the Precipitation Factor of Cesium

| [Na]=2 mole/L | Cs/Na TPB ratio, mole/mole | Cs precipitation factor, % |
|---------------|----------------------------|----------------------------|
| 1 | 1/5 | 99.94 |
| 2 | 1/4 | 99.94 |
| 3 | 1/3 | 99.95 |
| 4 | 1/2 | 99.9 |
| 5 | 1/1.5 | 99.8 |

Table 5. Dynamics of Cs-TPB Precipitation from Solutions of Different Composition

| [Na] = 2 mole/L (NaOH/NaNO ₃ =2/1) | | | [Na] = 2 mole/L (NaOH/NaNO ₃ =2/1) | | |
|--|----------------------------|-------------------------------|--|-------------------------|-------------------------------|
| | Precipitation time, min | Cs precipitation factor, % | | Precipitation time, min | Cs precipitation factor, % |
| 1 | 1.0 | 99.94 | 1 | 1.0 | 99.58 |
| 2 | 3.0 | 99.93 | 2 | 2.0 | 98.88 |
| 3 | 5.0 | 99.93 | 3 | 3.0 | 98.57 |
| 4 | 60 | 99.85 | | | |
| 5 | 180 | 99.75 | | | |
| 6 | 360 | 99.65 | | | |
| 7 | 960 | 99.5 | | | |

Using the data from Tables 2 – 5 for guidance, we selected the optimum conditions for the precipitation of cesium, the time of contact for the feed solution and the reagent additives to determine the optimal volume of the reaction chamber. Taking into account the filtering capacity of the “TruMem” membranes for the solutions of different composition, we determined the surface area of the membranes to be installed in the unit to provide the throughput needed. The desired precipitate concentrating factor is established by varying the ratio of the feed flow rate and the concentrate removal rate. In Fig. 4, the general view of the semi-large scale MSR facility with capacity of 150 L/hr is shown.



Fig. 4. General View of the Semi-Large Scale 150 L/hr MSR Facility

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The Membrane Sorption Reactor was used for decontamination of low-level LRW of different chemical and radiochemical composition. The results are summarized in Table 5. The data prove the high efficiency of the MSR facility for decontamination of radioactive waste.

Table 5. LRW Decontamination With the Membrane Sorption Reactor

| | Firm, enterprise | Volume and composition and of the solution | Results |
|---|---|---|---|
| 1 | NPP “Ekoatom” Nuclear powered submarine decommissioning solutions | Waste volume – 50 m ³ Suspensions 980 mg/L Petroleum products 230 mg/l ¹³⁷ Cs – 10 ³ Bq/L ⁹⁰ Sr – 10 ³ Bq/L ⁶⁰ Co – 10 ² Bq/L | Suspensions < 3 mg/L Petroleum products < 0.05 mg/l ¹³⁷ Cs < 0.3 Bq/L ⁹⁰ Sr < 0.3 Bq/L ⁶⁰ Co < 0.3 Bq/L |
| 2 | MosNPO “Radon” Technological solutions | Waste volume – 120 m ³ ¹³⁷ Cs – 3 · 10 ³ Bq/L ⁹⁰ Sr – 2 · 10 ² Bq/L ²³⁹ Pu – 2.5 · 10 ³ Bq/L | Suspensions < 3 mg/L Petroleum products < 0.05 mg/l ¹³⁷ Cs < 0.3 Bq/L ⁹⁰ Sr < 0.3 Bq/L ²³⁹ Pu < 0.3 Bq/L |
| 3 | RTP “Atomflot” Murmansk Shipping Co. Decontamination solutions | Waste volume – 75 m ³ Suspensions 10 g/L Salt bearing 4.0 g/l ¹³⁷ Cs – 10 ³ Bq/L ⁹⁰ Sr – 10 ² Bq/L | Suspensions < 3 mg/L Hardness salts < 0.05 mg/l ¹³⁷ Cs < 0.3 Bq/L ⁹⁰ Sr < 0.3 Bq/L |
| 4 | Hydrometallurgy plant waste V = 120 m ³ /year Radionuclides ²³⁹ Pu, ²⁴¹ Am, ^{235,238} U □□ = 10 ³ – 10 ⁴ Bq/L pH = 7 – 14 Salt bearing 900 – 2000 mg/L | Σ ²³⁹ Pu, ²⁴¹ Am, ^{235,238} U α < 1 Bq/L | |
| 5 | Low-level RW of PA “Mayak” V = 20 m ³ /year Radionuclides ¹³⁷ Cs, ⁹⁰ Sr, FP, ²⁴¹ Am, ²⁴⁴ Cm □□ = 10 ² Bq/L □□ = 10 ³ Bq/L pH = 7 – 9 Suspensions 1000 – 2000 mg/L | Σα < 0.1 Bq/L Σβ < 1 Bq/L Suspensions 3 mg/L | |

The MSR was used as the baseline technology for the facilities currently being designed for decontamination of large LRW quantities at the Production Association “Mayak”. The design parameters for the waste type and quantity to be treated are given in Table 6.

Table 6. MSR Facilities Under Design

| | Composition and volume of the feed | Results |
|---|--|--|
| 1 | Hydrometallurgy plant waste V = 120 000 m ³ /year Radionuclides ²³⁹ Pu, ²⁴¹ Am, ^{235,238} U □□ = 10 ³ – 10 ⁴ Bq/L pH = 7 – 14 Salt bearing 900 – 2000 mg/L | Σ ²³⁹ Pu, ²⁴¹ Am, ^{235,238} U $\alpha < 1$ Bq/L |
| 2 | Low-level RW of PA “Mayak” V = 400 000 m ³ /year Radionuclides ¹³⁷ Cs, ⁹⁰ Sr, FP, ²⁴¹ Am, ²⁴⁴ Cm □□ = 10 ² Bq/L □□ = 10 ³ Bq/L pH = 7 – 9 Suspensions 1000 – 2000 mg/L | $\Sigma\alpha < 0.1$ Bq/L $\Sigma\beta < 1$ Bq/L Suspensions 3 mg/L |
| 3 | Solution after VVER fuel element digestion 600 m ³ /y ¹³⁷ Cs – up to 2 g/L Suspensions up to 1 g/L | ¹³⁷ Cs < 0.01 g/L Suspensions 1-2 mg/L |

POTENTIAL APPLICATIONS FOR TREATING ALKALINE RADIOACTIVE WASTE IN THE UNITED STATES

While there are numerous potential applications of the Membrane Sorption Reactor technology for treatment of low-level radioactive wastes in the United States, the following are two specific examples where this technology could be used during treatment of wastes stored at Department of Energy facilities. The Department of Energy currently manages approximately 206 million liters of alkaline radioactive wastes at the Hanford Site in Washington and an additional 140 million liters of alkaline radioactive wastes at the Savannah River Site in South Carolina. The alkaline radioactive wastes are stored in underground tanks at these sites and are comprised of salt cake, sludges, and supernatant phases.

The Savannah River Site (SRS) currently plans to dissolve a portion of the saltcake waste and solidify a low curies fraction in a cementitious waste form (SaltStone). Another fraction of dissolved saltcake waste may also be solidified in SaltStone following removal of transuranic elements and ⁹⁰Sr by adsorption using monosodium titanate. The SRS currently plans to separate the monosodium titanate sorbent from the alkaline waste solution using sintered metal, crossflow filter units. The high curie fraction of dissolved saltcake and supernatants would also be processed to separate transuranic elements and ⁹⁰Sr by adsorption using monosodium titanate, followed by ¹³⁷Cs separation using a solvent extraction process. The pretreated supernatants would then be solidified in SaltStone. Alternative reagents (e.g., sodium permanganate) are being evaluated for removal of transuranic elements and ⁹⁰Sr from the supernatant and dissolved saltcake wastes.

SRS personnel have tested a centrifugal membrane separations unit (no reactor chamber) similar to the Membrane Sorption Reactor and demonstrated that the centrifugal solid-liquid separation unit achieves four to six times the throughput per area of filter media as a crossflow filter system. The Membrane Sorption Reactor combines the chemical reaction chamber with the solid-liquid separation step, which offers the advantages of relatively high throughput and small footprint for the radioactive equipment.

Another potential application for the MSR technology is in the treatment of sludges stored in the underground tanks at the Hanford Site. The Department of Energy is evaluating whether some of these sludges are transuranic wastes that could be packaged and shipped to the Waste Isolation Pilot Plant (WIPP) for disposal. The MSR could be used to separate supernatants, remove soluble analytes and radionuclides by washing and dewater the potentially transuranic sludges. Again, the Membrane Sorption Reactor offers the advantage of a compact processing unit with relatively high throughput when compared to crossflow filtration or other solid-liquid separation devices.

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