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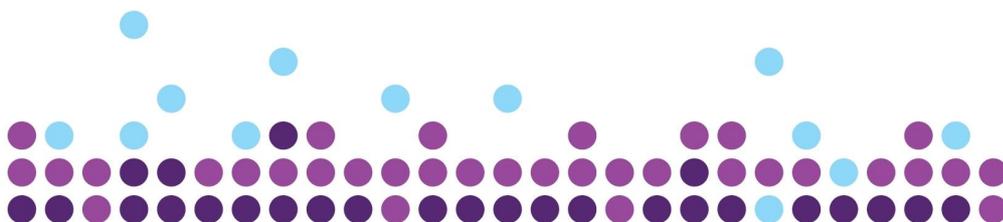
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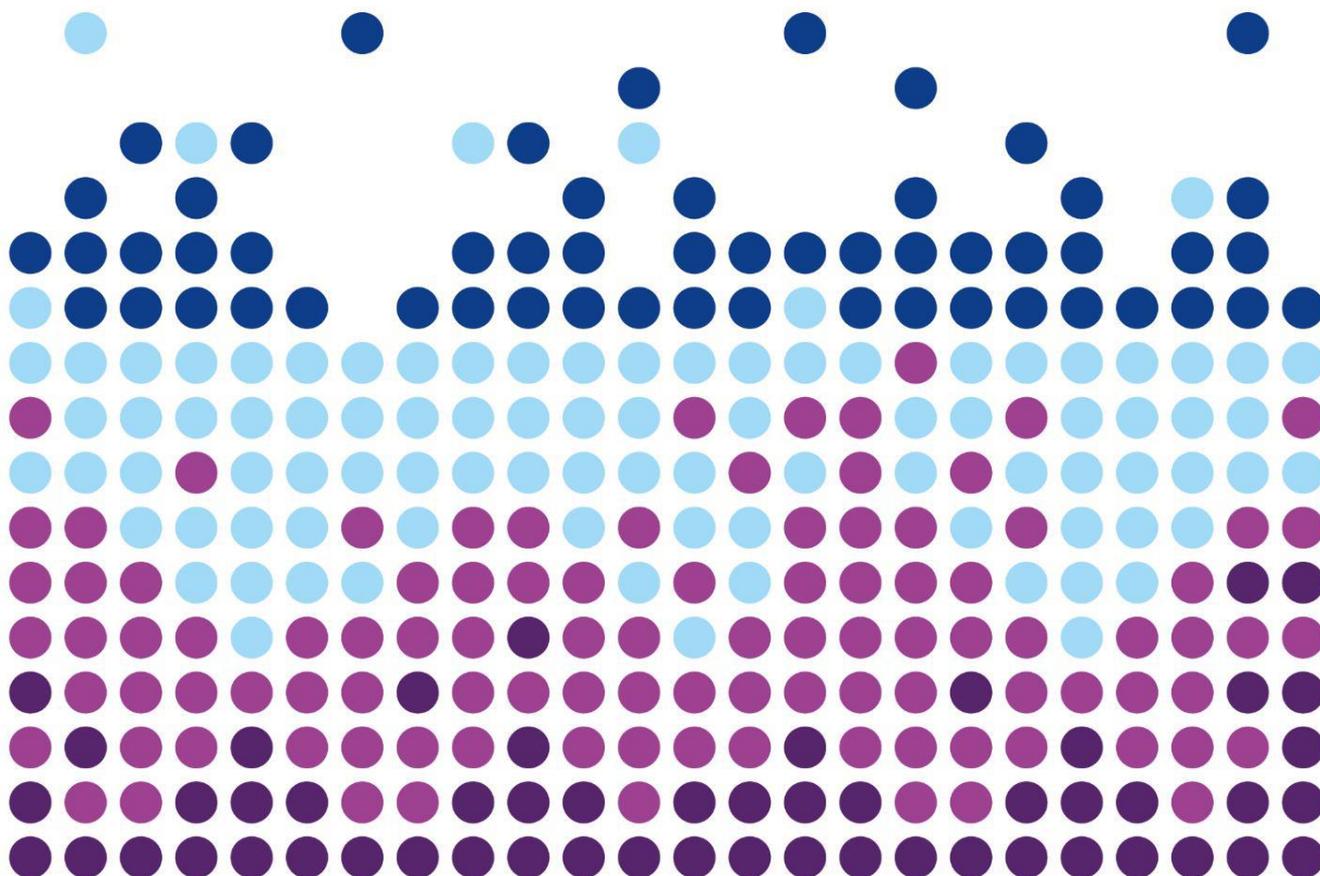
# Recovery of cesium and strontium isotopes

ASOF deliverable D1.2.1

Authors: Ken Verguts and Karen Van Hecke

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## Introduction

The radioactive isotopes of cesium (*i.e.*  $^{137}\text{Cs}$  ( $t_{1/2} = 30$  years)) and strontium (*i.e.*  $^{90}\text{Sr}$  ( $t_{1/2} = 29$  years)) are synthetic radioisotopes that are not found in nature. However, they can be found in spent nuclear fuel (SNF), where they are formed by nuclear fission of uranium-235 during nuclear power plant operation. Valorization or partitioning of these isotopes can be achieved by treating irradiated fuel using solvent extraction techniques or separation on ion exchange columns.

Radionuclides can be recovered from SNF assemblies by selectively extracting them. In general, a specifically designed solvent is used to extract specific ions to an organic phase. In the best case, molecules that have an affinity to only the ions of interest are used. In a second step, the ions are back-extracted (or stripped) to a fresh aqueous phase. A well-known example is the recovery of uranium and plutonium (and neptunium), where liquid-liquid extraction is used in the so-called plutonium uranium reduction extraction (PUREX) process. Here, SNF is dissolved in a concentrated nitric acid solution. Next, tributyl phosphate (TBP) in kerosene is used as a solvent to selectively extract uranium, in the form of  $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$ . Meanwhile, plutonium is co-extracted as  $\text{Pu}(\text{NO}_3)_4(\text{TBP})_2$ . In the next steps, the organic phase is treated with reducing agents to further separate U from Pu and uranium is then stripped from the kerosene using 0.2 M nitric acid. The aqueous phase, the so-called HAR (highly active raffinate), consists of a mixture of minor actinides (*e.g.* Np, Am, Cm,...), fission products, corrosion products, protons and nitrate anions. Several solvent extraction systems have been developed earlier to separate the heat-generating fission products, Cs and Sr.

Although the separation of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  from High Level Liquid Wastes (HLLW) is one of the challenging subjects in the management of used nuclear fuel, reports concerning useful solvent extraction, column separation or precipitation methods for these fission products, especially from acidic HLLW which is typical for advanced partitioning scenarios, are rather limited. An overview of the existing processes is given in Figure 1 and the literature is described further in this manuscript.

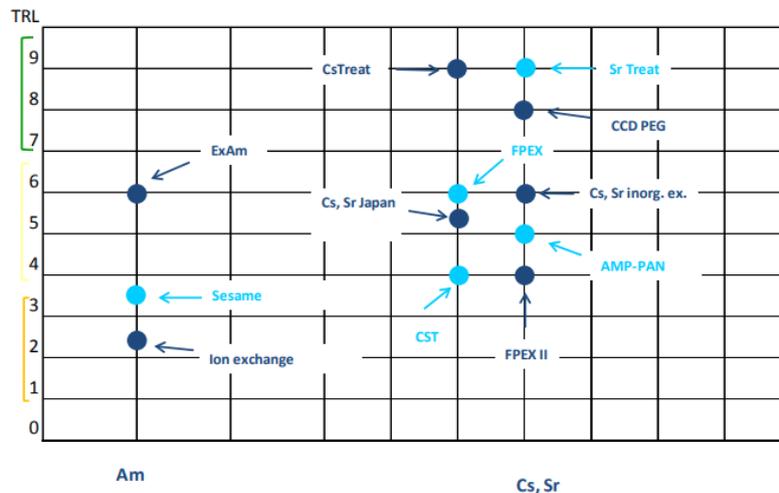


Figure 1: Overview of the technology readiness levels (TRL - 2018) of the processes related to (Am), Cs and Sr partitioning.<sup>1</sup>

## PUREX raffinate composition

The composition of spent nuclear fuel was discussed in the ASOF deliverable D4.1. The elemental composition of the normal PUREX HAR is given in the table below. Here, the fission products and actinides in 5000 L of PUREX raffinate originating from the reprocessing of 1 tons of heavy metal (tHM) of spent UO<sub>2</sub> fuel, 4.2% <sup>235</sup>U enrichment and a burnup of 50 GWd tHM<sup>-1</sup> is presented.

Element	Conc (mg L <sup>-1</sup> )	Element	Conc (mg L <sup>-1</sup> )	Element	Conc (mg L <sup>-1</sup> )
Ag	2.35E+01	In	4.64E-01	Sb	3.31E+00
Am	1.80E+02	La	3.66E+02	Se	1.61E+01
Ba	5.49E+02	Mo	8.09E+02	Sm	2.45E+02
Br	6.21E+00	Nd	1.22E+03	Sn	1.79E+01
Cd	3.13E+01	Np	1.00E+00	<b>Sr</b>	<b>2.25E+02</b>
Ce	7.24E+02	Pd	3.59E+02	Tb	7.94E-01
Cm	1.57E+01	Pm	3.52E+00	Tc	1.06E+01
<b>Cs</b>	<b>7.17E+02</b>	Pr	3.33E+02	Te	1.47E+02
Dy	3.86E-01	Pu	1.00E+01	U	4.00E+01
Eu	3.90E+01	Rb	1.05E+02	Y	1.34E+02
Gd	4.86E+01	Rh	6.80E+01	Zn	8.46E-04
I	1.20E+00	Ru	3.44E+02	Zr	1.03E+03

The elements Cs and Sr, which are of interest for this manuscript, are highlighted in bold. When the major and minor actinides are partitioned from the spent nuclear fuel waste stream, the majority of heat generation is due to the <sup>137</sup>Cs and <sup>90</sup>Sr isotopes. Further partitioning of these isotopes is thus beneficial to decrease the gallery length for deep geological disposal.

## Solvent extraction of Cs and Sr

The first studies on Cs and Sr extraction were performed at the end of the 1960's by Czechoslovakian researchers and made use of dipicrylamine, tetraphenylborate or picrate as ligands. In addition to these ligands being very unsafe to handle, there was no selectivity, causing all alkali metals to be co-extracted together.<sup>2,3</sup> The obtained distribution coefficient ( $D$  values) were reported to be close to 1.<sup>2</sup> In a later phase, a selective cesium extraction system was developed by Rais *et al.* in 1975.<sup>3</sup> Here, a "sandwich" polyhedral complex of cobalt was proposed as Cs extractant. The structure of the anion  $[\pi-(3)-1,2-B_9C_2H_{11}]_2Co^-$  (also called cobalt dicarbollide - CD) had been described earlier by Hawthorne.<sup>4</sup> CD is well soluble in organic diluents. The best extraction results were found when nitrobenzene was used as a diluent, and the extraction system was later optimized by varying the nitric acid concentration. The highest  $D_{Cs}$  value of 102.6 was reported for 0.1 M  $HNO_3$ , with a ligand concentration of 0.01 M in nitrobenzene. In these conditions the  $D_{Sr}$  was very low: 0.041.<sup>3</sup>

A first modification of the CD was made by replacing some of the hydrogen atoms by chloride atoms:  $[\pi-(3)-1,2-B_9C_2H_8Cl_3]_2Co^-$  (chlorinated cobalt dicarbollide – CCD).<sup>5</sup> Additionally EDTA and polyethylene glycol (PEG-400) were added.<sup>5,6</sup> Due to the addition of PEG, a selective extraction of Sr from Ca could be obtained. The  $D_{Sr}$  values increased to 708.8 with a  $SF_{Sr/Ca}$  of approx. 3900.<sup>5</sup> Furthermore, it was observed that the increase of  $Na^+$  concentrations decreases the  $D_{Sr}$  values, however, without affecting the  $SF_{Sr/Ca}$ . Also the presence of  $Li^+$  cations affected the extraction system by increasing the  $D_{Sr}$  values. Therefore, an adjustment of the desired  $D_{Sr}$  values could be obtained by varying the Li/Na ratio in the system.<sup>5</sup>

A collaboration between Czechoslovakian and Russian researchers of the Khlopin Radium Institute (KRI) led to a process running at industrial scale in the Mayak UE-35 facility.<sup>7-9</sup> CCD and PEG in fluorinated nitrobenzene (*m*-nitro trifluoromethyl benzene) were used as organic phase.<sup>10</sup> Here, approx. 800 m<sup>3</sup> of acidic high level waste were processed and approx. 444 PBq ( $4.44 \times 10^{17}$  Bq) of Cs and Sr isotopes were recovered. The results of these CCD/PEG testing were used to formulate a flowsheet for extended testing in the INEEL centrifugal contactor pilot plant. It was found that after extracting Cs and Sr from a simulated tank waste, 97.5% of the Cs and >99.992% of the Sr isotopes could be recovered in the stripping solution.<sup>9</sup>

At the end of the 1990s, a collaboration between Russian and American researchers reported the *Universal Extraction* (UNEX) process. Here a solvent was composed to co-extract cesium, strontium and the actinides from acidic radioactive waste.<sup>11</sup> This solvent consists of a mixture of CCD, PEG, carbamoylmethyl phosphine oxide (CMPO) and phenyltrifluoromethyl sulfone as a diluent. For recovery of all major radionuclides, the optimal ratio of [CCD]:[CMPO]:[PEG] was found to be 5:1:1. In addition, the extraction properties, combined with high radiation and chemical stability, explosion and fire-safety and minimal solubility in aqueous media makes the UNEX technically suitable for processing highly radioactive waste.<sup>11</sup>

The UNEX process has been demonstrated on actual INEEL acidic tank waste. Here, the solvent contains 0.08 M chlorinated cobalt dicarbollide, 0.5% polyethylene glycol-400 (PEG-400), and 0.02 M diphenyl-N,N-dibutylcarbamoyl phosphine oxide (Ph<sub>2</sub>Bu<sub>2</sub>CMPO) in a diluent consisting of phenyltrifluoromethyl sulfone. Twenty-four stages of shielded 2 cm diameter centrifugal contactors were used in a countercurrent flow. Removal efficiencies of 99.4%, 99.995%, and 99.96% were obtained for Cs-137, Sr-90, and alpha emitters, respectively.<sup>12</sup> The centrifugal contactors were operating at a calculated stage efficiency of 87%. Moreover, it was also reported that the Cs, Sr isotopes, Ln and An could be effectively removed from the solvent using 0.05 M DTPA (diethylene triamine pentaacetic acid) in 1.0 M guanidine carbonate,<sup>12</sup> which is much simpler than the existing process by eliminating a solvent wash section, and the secondary waste stream coming from this solvent washing.<sup>13</sup> It should be noted that the development of the UNEX process was mainly application driven, with little understanding of the fundamental chemistry behind the process.<sup>13</sup>

In parallel with the UNEX process, the fission products extraction (FPEX) process was developed. Here, researchers from Argonne National Lab (ANL) created a mixture of a Cs extractant and a Sr extractant in the same solvent. The respective individual extraction processes, named CSSX (cesium solvent extraction process or also known as caustic-side solvent extraction process) and SREX (strontium extraction process), were developed separately. The main difference between FPEX and UNEX processes is the use of different types of extractants. In FPEX, crown ethers and calixarenes are used instead of dicarbollides as described earlier for UNEX. The basic dicarbollides present drawbacks since they need to be diluted in a polar solvent such as nitrobenzene. Also, their efficiency strongly decreases as the acidity of liquid waste increases. On the other hand, crown ethers and

calixarenes enable cesium and strontium to be extracted if the concentration of sodium or the acidity of the solutions are not too high.<sup>14</sup>

Studies in the early 1990s report the use of several crown ethers for strontium extraction.<sup>15</sup> Horwitz *et al.* studied the extraction of strontium using dicyclohexano-18-crown-6 (DCH18C6) and 4',4'(5'')-di(tert-butylcyclohexano)-18-crown-6 (DtBuCH18C6) in different solvents –alcohols, carboxylic acids, ketones and esters,<sup>15</sup> the latter being more hydrophobic to reduce its solubility in the aqueous phase.<sup>15,16</sup> The values of  $D_{Sr}$ , obtained with 0.2 - 0.4 M solutions of DtBuCH18C6 in *n*-octanol in the range of 3 to 6 M HNO<sub>3</sub> are *approx.* 10 to 50, which permits the efficient extraction of strontium. Similar tests using DCH18C6 were performed in Russia, where fluorinated alcohols were employed to increase the distribution coefficients.<sup>17,18</sup> Later, Wood *et al.*<sup>19</sup> showed that *n*-octanol could be effectively replaced by 1.2 M tributyl phosphate in Isopar L® when high concentrations of interfering alkali metal ions (Na<sup>+</sup> and K<sup>+</sup>) were present. Despite the  $D_{Sr}$  values being one order of magnitude lower compared to the *n*-octanol experiments, the authors believed to have found a suitable solvent to achieve efficient decontamination of <sup>90</sup>Sr in waste treatment processes.<sup>19</sup> Also the coextraction of Pb<sup>2+</sup> by this solvent system was highly efficient, thus a simultaneous removal of these compounds from acidic high-level waste is feasible.<sup>19</sup> In addition to conventional solvents, mixtures with novel ionic liquids were studied.<sup>20-22</sup> The presence of tri-*n*-octylphosphine oxide (TOPO) and dicyclohexano-18-crown-6 (DC18C6) showed a unique synergistic effect in ion-pair extraction of Sr into cyclohexane using bis(trifluoromethanesulfonyl)imide (NTf<sub>2</sub>).<sup>23</sup> Wei *et al.* studied the extraction behavior of Sr<sup>2+</sup> using DCH18C6 as an extractant in C<sub>n</sub>mimNTf<sub>2</sub> (with n = 2, 4 or 6) diluents. It was observed that at a concentration of 15 mM DCH18C6, the  $D_{Sr}$  increased drastically for shorter carbon chain lengths to a maximum of 1600 for C<sub>2</sub>mimNTf<sub>2</sub>.<sup>20</sup> The influence of the carbon chain length was also observed by Takahashi *et al.*, who performed similar extraction studies using DtBuCH18C6 as a strontium extractant.<sup>24</sup> It was reported that the Sr<sup>2+</sup> was extracted in the organic phase by the ion exchange with [C<sub>2</sub>mim]<sup>+</sup>. A shorter carbon chain length leads to higher hydrophilicity of the compounds.<sup>20</sup> Radiolysis studies of these extraction systems revealed a reduction in extraction ability of DCH18C6–[C<sub>4</sub>mim][NTf<sub>2</sub>] and DtBuCH18C6–[C<sub>4</sub>mim][NTf<sub>2</sub>] systems revealed a reduction in extraction ability for Sr<sup>2+</sup> by 14.4% and 18.2% at 500 kGy respectively, which makes them promising systems for Sr<sup>2+</sup> extraction in SNF reprocessing.<sup>21</sup> Strontium stripping can be readily achieved using diluted nitric acid or deionized water.<sup>15,25</sup> However, despite being reasonable extractants for Cs<sup>+</sup> or Sr<sup>2+</sup> cations, the main disadvantages of the crown ethers have been their chemical and radiolytic instability. Moreover, the crown ethers also tend to form a third phase and are costly.<sup>8,18</sup>

In the CSSX process, the coordinating agents (*e.g.* crown ethers and calixarenes) have attracted great attention to extract Cs from alkaline waste.<sup>26</sup> Despite being several reports available on Cs extraction by crown ethers, a feasible process based on only crown ethers has not yet been successfully proved.<sup>27,28</sup> However, by appending crown ethers to calixarenes, a much higher selectivity for cesium ions was shown. Moreover, the calixcrown ether are stable in acidic media.<sup>28,29</sup> However, despite being more performant, the calixcrown ether molecules are currently quite expensive, and further work should be done to develop environmental friendlier diluents.<sup>28</sup>

As mentioned before, the fission products extraction process (FPEX) combines aforementioned CSSX and SREX processes. The extraction solvent consists of 4,4',(5')-di-(*t*-butyldicyclo-hexano)-18-crown-6 (DtBuCH18C6), calix[4]arene-bis-(*tert*-octylbenzo-crown-6) (BOBCalixC6), 1-(2,2,3,3-tetrafluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol, and trioctylamine in a branched aliphatic kerosene (Isopar® L).<sup>30,31</sup> This combination extracts Cs and Sr simultaneously from 1 M nitric acid solutions with a distribution ration of 7.7 and 8.8 respectively, at ambient temperature. The process was demonstrated at ANL with 2-cm centrifugal contactors and at ORNL with mixer-settlers. More than 99.99% of Cs and 99.8% of Sr were recovered in ANL, whereas 99.94% of Cs and 99.99% of Sr were recovered at ORNL. Later, the Cs extractant was replaced by 1,3-dioctyloxycalix[4]arene-crown-6 (CC6) in *n*-dodecane and isodecyl alcohol resulting in a  $D_{Cs}$  of 5.3 in 3.5 M HNO<sub>3</sub>, with a high selectivity for cesium extraction.<sup>32</sup> In the meantime, INL developed an optimized Cs extractant to overcome the limited solubility of BOBCalixC6 in the FPEX solvent (< 0.007 M). In the FPEX II process, the solvent consists of 0.020 M 1,3-Alternate-25,27-Di(2,7-dimethyl-1-octyl)calix[4]arenebenzocrown-6 (MaxCalix), 0.090 M di-*tert*-butyl-dicyclohexano-18-crown-6, and 1.5 M Exxal-8 dissolved in Isopar L. Proof-of-principle experiments demonstrated an improved stability and increased solubility of the Cs extractant as compared to the FPEX process.<sup>33</sup>

## Precipitation and column separations of Cs and Sr

Partitioning of cesium and strontium in nuclear chemistry can be achieved by column separation methods *e.g.* the preparation of environmental assay and bioassay samples. Since the accident at the Fukushima Daiichi nuclear power plant in 2011, removal of Sr and Cs from contaminated seawater has been another implementation of these methods. Regardless of the application and scale (large-scale or analytical scale), these column separation methods make generally use of an ion exchanger (inorganic or organic) or a Solid Phase Extraction (SPE) material.

Because of the wide variety of  $^{137}\text{Cs}$ - and  $^{90}\text{Sr}$ -bearing radioactive waste solutions (*e.g.* acidic, alkaline, sludge) and samples (*e.g.* sea water, digested soil), Cs and Sr separation is an extremely difficult task. A separation method suitable for one kind of matrix could be completely inappropriate for another kind of matrix. This is the reason why so many separation methods have been developed and tested. Particularly, elaborate research was performed in the U.S. in the 1990s on the isolation of Cs from radioactive waste solutions by means of ion exchange.<sup>34–37</sup> However, the focus of that research was on the separation of Cs and Sr from highly alkaline solutions. As a by-product of the nuclear weapons production, large volumes of highly alkaline HLLW had accumulated in tanks, mainly at Hanford and Savannah River Site. The highly acidic waste solutions mainly originating from the Bismuth Phosphate Process, the REDOX Process and the PUREX process, used to recover and purify Pu from irradiated fuel, had to be neutralized with caustic soda (NaOH), and sodium nitrite had to be added for corrosion control because they were stored in large underground carbon steel tanks. The separation of Cs from these solutions is very challenging since the cesium is present at low concentrations while other group I cations (mainly Na and K) are present in high concentrations as well as aluminate and oxalate salts. In addition, the handling of these wastes is complicated because it is corrosive due to the high hydroxide concentration and also oxidizing because of the high amounts of nitrate and nitrite. The aim was to develop waste pretreatment processes associated with a lower cost of implementation compared to the cost savings obtained by reducing the volume of HLLW that should be immobilized in borosilicate glass and disposed of in a geologic repository. In the early 2000s, preference was given to solvent extraction processes for further development.<sup>37</sup> However, more recently, there has been a renewed interest in the development of ion exchange methods.<sup>38–42</sup>

## Cesium precipitation and column separations

As cesium is an alkali metal, it is difficult to extract since it forms hardly any stable complexes due to its large size and low charge. One exception is the formation of mixed metal complexes with hexacyanoferrate compounds. Examples of hexacyanoferrate, also called ferrocyanide, compounds that have been studied for cesium separation include copper ferrocyanide,  $[\text{Cu}^{\text{I}}\text{Fe}^{\text{II}}(\text{CN})_6]^{2-}$ , hexacyanocobalt(II)-ferrate(II),  $[\text{CoFe}(\text{CN})_6]^{2-}$ , or Prussian blue (or Berlin blue),  $[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6]^-$ .<sup>43–45</sup> To balance the net negative charge of the complex anion, the centres of the face-centred cubic lattice are usually occupied by alkali metal ions, other metal ions or hydrogen ions, or mixtures thereof.<sup>44</sup> These cations that are not part of the complex anion are bound by relatively weaker forces and thus can be exchanged by cesium cations, although cesium sorption is often occurring without a true ion exchange.<sup>46</sup> Usually these metal ferrocyanides are available as very fine powders.<sup>44,46</sup> Phase separation has to be performed by filtration, however, due to the small size of the particles, this filtration is complicated. In addition, the permeability of these powders is so low that they cannot be applied in flow through columns. In order to improve the applicability of the hexacyanoferrates, granular forms have been prepared<sup>43,46</sup> or they have been immobilized on solid supports such as resins<sup>44</sup> or magnetic nanoparticles.<sup>45</sup> These adsorbents should work for removal of Cs from alkaline, neutral and slightly acidic solutions, but in highly acidic wastes the Cs adsorption is affected by the oxidation of the ferrocyanide to ferricyanide by nitric acid (nitrite).<sup>44,46</sup> Cobalt ferrocyanide and, to a lesser extent, nickel ferrocyanide precipitation were done at Hanford in the late 1950s and 1960s to recover cesium for the industry.<sup>34,47</sup> Therefore, the focus was on purity of the cesium product rather than on decontamination of the HLW solutions. The process was primarily used on alkaline tank waste. Nitrite scavenging with urea can be applied in order to use ferrocyanides in PUREX raffinates that cannot be neutralized because the acid needs to be recovered by evaporation.<sup>48</sup> Ferricyanides such as zinc ferricyanide  $[\text{ZnFe}^{\text{III}}(\text{CN})_6]^-$  can be applied for Cs removal from partially neutralized PUREX concentrates that contain large amounts of Fe, Ni and Cr due to corrosion of the evaporator.<sup>48</sup> These corrosion products interfere heavily with ferrocyanide precipitations, but not with zinc ferricyanide. However, they are less efficient because only one cation is available for exchange, a large excess of reagent should be added, and thus the volume of precipitate will be much

larger.<sup>46,48</sup> Elution (reverse ion exchange) of ferrocyanides is often unsuccessful.<sup>44,46</sup> The commercially available granular all-inorganic cobalt hexacyanoferrate(II) ion exchange material CsTreat<sup>49-52</sup> was developed in Finland and extensively studied. CsTreat is far more selective for cesium than zeolites, crystalline silicotitanate (CST) and the phenol-formaldehyde and resorcinol-formaldehyde ion exchange resins that have enhanced cesium selectivity compared to ordinary organic ion exchange resins. The high cesium selectivity is favorable for the processing capacity. Very high decontamination factors can usually be obtained. CsTreat has been used on an industrial scale in nuclear power plants to decontaminate a variety of waste solutions such as evaporator concentrates containing high amounts of salts, dilute floor drain waters and Medium Active reprocessing solutions high in sodium nitrate. It has also been employed to decontaminate reverse osmosis (used to remove the salt from the sea water that was used for emergency cooling) concentrates of the circulating cooling water of the damaged cores of the Fukushima Daiichi nuclear power plants.<sup>52,53</sup> The radiation resistance is very good. The CsTreat material can be used in a pH range from 1 to 13. It is recommended to adjust the pH of very acidic waste solutions by addition of sodium hydroxide. The presence of common alkali and alkaline earth metals in the solution does not affect the performance of the resin. High concentrations of ammonium and potassium do interfere with cesium sorption, however, the concentrations of these cations in nuclear waste solutions are usually acceptable. After saturation of the CsTreat columns, the stainless steel columns containing the ion exchanger (typically about 8-12 litres) can be disposed of in a special concrete container with holes.

In the 1960s, a process for the precipitation of cesium with phosphotungstic acid from Hanford current acid PUREX waste was developed.<sup>34,47</sup> Current acid waste is the acidic waste from the PUREX process that had been partially denitrated with sugar.<sup>54</sup> Cesium reacts with phosphotungstate to produce an insoluble precipitate in solution containing 0.5-2.0 M of HNO<sub>3</sub>.<sup>55</sup> Emphasis was on the purity of the cesium product and not on the decontamination of the waste solutions because the primary goal was to recover Cs for industrial use.<sup>34</sup> The phosphotungstic acid precipitation process was associated with excessive cesium losses.<sup>54</sup> In addition, phosphotungstic acid is expensive and cannot be recycled. Therefore, research to find a better process was started, however, because priorities were put on the processing of the very large volumes of stored alkaline waste, the phosphotungstic acid precipitation process was applied on actual PUREX waste from 1968-1972 at the B plant since it did not seriously interfere with the processing of the alkaline wastes by ion exchange.<sup>47,54</sup>

Centrifugation was used to remove the precipitate from the supernate.<sup>34</sup> After being washed with nitric acid to remove other fission products, the cake was dissolved in sodium hydroxide. The resulting caustic solution was subsequently processed by ion exchange to concentrate and purify the Cs.<sup>47,55</sup>

In the late 1970s and early 1980s, a process was developed to remove Cs from alkaline Savannah River Side tank waste by in-tank precipitation with sodium tetraphenylborate, Na[(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>B].<sup>56-59</sup> Cs, Na and Rb could be selectively precipitated from alkaline waste, and even from the salt cake that resulted from the volume reduction (by evaporation) of the alkaline waste. Very high decontamination factors (10<sup>4</sup>-10<sup>6</sup>) could be achieved by means of a single batch contact. The process was economical compared to alternative processes such as ion exchange, however the processing time was long (200 days processing and up to 2 years storage time per tank). The sodium tetraphenylborate precipitate can be easily filtered. The precipitate was treated by copper catalyzed formic acid hydrolysis.<sup>60</sup> The benzene resulting from the hydrolysis process could be removed by evaporation followed by incineration.<sup>58,59</sup> The aqueous solution that was left after the formic acid hydrolysis contains mainly Cs, K and B hydroxides and was vitrified. The decontaminated tank waste supernatant and salt solution could be immobilized in grout to be disposed as Low Level Waste. The solubility of the sodium tetraphenylborate in the supernatant was a concern for the leachability of the of the low level waste.<sup>61</sup> The process was demonstrated on large-scale in an actual HLW tank, Tank 48, in 1983.<sup>58</sup> Significant amounts of flammable benzene were formed due to decomposition of the sodium tetraphenylborate present in the alkaline solution, which was unexpected. In addition, foaming, which can have adverse effects on the phase separation and cause interruption of the flow through transfer lines, was observed. Initially, the decomposition of the tetraphenylborate was attributed to radiolysis. Studies were conducted to understand the decomposition of the tetraphenylborate and to minimize foaming.<sup>58,62</sup> Transition metals such as Cu and Pd catalyzed the decomposition, and temperature and oxygen influenced the decomposition rate, however, the exact decomposition mechanism remained unclear. In 1995, a large-scale production operation was conducted to assess benzene vapor phase mixing, temperature and oxygen concentration and to test filtration procedures. This tests were performed in Tank 48, which still contained the solutions (and decomposition products) used in the 1983 demonstration. During slurry pumping tests, high benzene vapour concentrations were observed repeatedly in the tank headspace.<sup>58</sup> Extensive analysis

of the contents of Tank 48 were carried out. The high rates of benzene releases could not be explained. Therefore, further studies on the tetraphenylborate decomposition and benzene generation were conducted. The role of noble metal, Pd, and catalysis in the presence of reaction intermediates such as diphenyl mercury became much clearer, and additional factors influencing the decomposition of tetraphenylborate were identified, however, a detailed understanding of the Pd catalytic cycle was still lacking. The high rates of benzene formation that occurred during the operations in Tank 48 could not be duplicated in any of the tests performed on real tanks waste or simulated tank waste solutions, although the decomposition rates were smaller during the tests with simulated wastes than with real waste solutions. Therefore, it seemed unlikely that a single mechanism for the decomposition of tetraphenylborate could explain the benzene excursion from 1995 and it was unclear if those other unidentified decomposition scenarios could also occur in a future processing operation. The variability of tank waste composition raised additional concerns. Because of safety concerns, the in-tank tetraphenylborate precipitation process was suspended in 1998. It was believed that by engineering, design of a small dedicated tank, and further testing to improve the mechanistic understanding of the decomposition, the development of a small tank tetraphenylborate precipitation process with significantly reduced processing times would be possible. In order to reduce the decomposition, it was important to keep the concentration of sodium tetraphenylborate in solution as low as possible.<sup>57</sup> A major concern was that due to decomposition, the concentration of the tetraphenylborate in solution would lower gradually during the processing. Thus, the precipitated Cs tetraphenylborate would partially re-dissolve, and sufficient decontamination would not be assured anymore.<sup>58</sup> Furthermore, regulatory issues (benzene release limits) were identified.

Ammonium 12-molybdophosphate (AMP),  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 4\text{H}_2\text{O}$ , has attracted the interest of chemists for nearly two hundred years since it was first prepared by J.J. Berzelius in 1826.<sup>63</sup> 12-Molybdophosphate,  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  was the first synthesized heteropolyoxometalate, a nanosized metal-oxygen cluster anion, that can be isolated as a solid with an appropriate counter cation like  $\text{NH}_4^+$  or an alkali metal.<sup>64</sup> In acidic solutions, AMP is a highly selective ion exchanger for monovalent cations such as  $\text{Cs}^+$ . However, because of its very fine microcrystalline form, column operation is almost impossible. A further disadvantage is that under many conditions, the exchange is irreversible and selectivity loss is observed at higher pH values. At pH values close to neutral, divalent and trivalent cations are also taken up. At higher pH values, a complete destruction of the heteropolyanion complex is observed. AMP has been investigated at the Hanford Site for the removal of Cs from acid dissolved sludge from a HLW tank.<sup>35</sup> First the transuranium elements were removed from the acid-dissolved sludge by means of TRUEX solvent extraction process, followed by a separation of Sr by solvent extraction with a crown ether extractant. About 10 g/L AMP was added to the resulting solution with a nitric acid concentration of 2 M. After three days, the solution was filtered and it was observed that about 98% of the Cs had been removed by a single batch contact. A serious drawback is that the Cs-loaded AMP cannot be sent directly to a vitrification plant since there is a relatively low limit for phosphorus in the HLW vitrification feed. One possibility is to mix it with alkaline high-level waste, where dissolution of the AMP due to the sodium hydroxide will take place. Subsequently the Cs should be removed from the alkaline waste solution by means of an organic ion exchange resin. Furthermore, because of the fine powder morphology of the AMP ion exchanger, it is difficult to employ it on an industrial scale. In order to make column operations possible, attempts have been made to immobilize AMP in a matrix. As long ago as 1959, a mixture of AMP and asbestos was employed as a column bed.<sup>65</sup> However, poor Cs uptake capacity was observed. Recently, organic binding polymers have been applied for the granulation of AMP. AMP-PAN, an inorganic-organic composite absorber with polyacrylonitrile (PAN) binding polymer has been developed at the Czech Technical University in Prague.<sup>66–68</sup> The Idaho National Engineering and Environmental Laboratory (INEEL) has investigated this material for the treatment of their acidic high-level wastes resulting from nuclear fuel reprocessing.<sup>69,70</sup> From these wastes the Cs would be removed first by using a series of AMP-PAN beds, before Sr and actinides will be removed via solvent extraction. AMP-PAN has the advantage over other inorganic ion exchangers that feed adjustment of acidic reprocessing waste is not necessary. AMP-PAN resin is commercially available from Triskem.

In Japan, AMP has been immobilized in the porous matrix of an alginate gel polymer for the separation of Cs from highly acidic radioactive waste solutions.<sup>71</sup> A fast uptake of Cs event in the presence of high concentrations of sodium nitrate has been observed.

Several inorganic ion exchangers, particularly aluminosilicates and crystalline silicotitanate (CST), have been used for Cs removal from large volumes of nuclear waste solutions. In general, these materials are usually not

regenerated but the loaded ion exchangers are finally treated by encapsulation in concrete or vitrification.<sup>72</sup> Furthermore, the radiation stability of these materials is usually very good.

Both natural and synthetic zeolites, *i.e.* microporous aluminosilicates, have been applied for cesium adsorption. In general, aluminosilicates have only a moderate selectivity for Cs. Decalso, a synthetic permutite, which is an amorphous aluminosilicate gel, was used at the Hanford tank farm in the 1960s for the isolation and concentration of Cs from aged PUREX supernatant.<sup>47,73</sup> The goal of the cesium separation from those basic high molarity sodium nitrate solutions was the production of <sup>137</sup>Cs heat and radiation sources and not the decontamination of the HLLW solutions. Loaded columns were washed with water and sent to Oak Ridge National Laboratory for cesium elution and returned to Hanford for reloading with cesium. After evaluation of several materials, Decalso was selected despite its lower selectivity for Cs over Na because of its fast sorption and elution rate, its mechanical and chemical stability in basic and neutral solutions (but it decomposes at pH < 2.7) and, importantly, the cesium was recoverable in a small volume of eluent (5 M NH<sub>4</sub>NO<sub>3</sub> at 85 °C). After 12 load/shipment/elute cycles the Decalso columns still had 90% of its original Cs capacity and still showed the same selectivity as in the first runs which was an illustration of its good radiation, temperature, chemical and mechanical stability. While processing, column plugging due to Al<sup>1</sup> precipitation was often encountered.<sup>37</sup> This was attributed to local pH changes. Addition of NaOH and a slight dilution of the feed with water were needed to prevent Al precipitation.

From 1967 until 1984, cesium was recovered from alkaline PUREX HLLW, purified and encapsulated for utilization as gamma sources at the Hanford B Plant facility.<sup>37,74</sup> Recovery was performed until 1979, purification continued until 1984. During the first period, the synthetic crystalline zeolite, Linde AW-500 (synthetic pelletized chabazite with a binder; originally manufactured by the Linde Division of Union Carbide Corporation, now manufactured by UOP Honeywell) was used. A threefold increase in Cs loading on Linde AW-500 columns compared to Decalso columns could be achieved.<sup>75</sup> Cesium sorption was marginally influenced by the pH, furthermore, the decrease of the Cs sorption as a function of the Na concentration is not so strong as with Decalso.<sup>76</sup> Because a large amount of sodium was also sorbed on the column bed, the column had to be washed with water and sodium had to be scrubbed with 0.2 M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>/0.1 M NH<sub>4</sub>OH before Cs could be eluted with 1.75-3.0 M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>/0.8-2.0 M NH<sub>4</sub>OH.<sup>37,74</sup> After about 18 months of operation, the material was abandoned because of problems with the chemical stability of the exchanger in the caustic solutions and column clogging due to Al precipitation. In addition, the cesium losses were quite large. It was presumed that gluconate present in the feed solution was at least partially responsible for the Al precipitation problems. The gluconate in the feed solution originated from washing metallic impurities from the cesium phosphotungstate cake that was precipitated from PUREX current acid waste. The cesium phosphotungstate was dissolved in caustic solution and blended with PUREX alkaline supernate before it was fed to the Linde AW-500 column. The Linde AW-500 ion exchange medium was replaced by Norton Zeolon-900, a self-bonded synthetic mordenite.<sup>37,74</sup> The cesium sorption was higher on Norton Zeolon 900 than on Linde AW-500. The influence of pH and Na and K concentration on the sorption of Cs was similar to the Line AW-500.<sup>76</sup> Norton Zeolon-900 was operated for only one month (July 1970) to process REDOX supernate which was more alkaline than PUREX alkaline supernate and contained relatively high amounts of Al and Na and relatively low amounts of Cs.<sup>37,74</sup> Serious problems with degradation of the material were encountered. Later investigations revealed that a 6 M NaOH solution was inadvertently introduced into the column instead of a 2 M NaOH solution that is used for regeneration. In addition, gluconate may have caused leaching of aluminium from the zeolite matrix. The gluconate was present in one batch of PUREX current acidic waste/phosphotungstate that was processed next to 8 batches of REDOX supernate. During the next 10 years, an organic resin (Duolite ARC-359, which is described later) was used for cesium recovery at the Hanford B plant. The natural zeolite clinoptilolite is used for large-scale cesium isolation in the Site Ion Exchange Effluent Plant (SIXEP) of BNFL at the Sellafield fuel reprocessing plant.<sup>72,77</sup> The SIXEP plant was installed in 1984 in order to reduce the radioactivity levels in effluent discharges from the fuel storage ponds in Sellafield into the Irish Sea. A pH adjustment of the feed to a pH of 8 ± 1 was performed by addition of CO<sub>2</sub> because silica leaching was observed at a pH of 11 and above. Zeolites have also been investigated for processing of acidic PUREX waste solutions.<sup>54,78–80</sup> Because zeolites are not very acid resistant, a denitration with formaldehyde, sugar or formic acid must be performed prior to the ion exchange.

<sup>1</sup> aluminum clad uranium fuel was reprocessed

Ionsiv IE-95 (currently Ionsiv R9150-G from Honeywell UOP LLC.), made commercially available by UOP Inc., was essentially the same as the Linde AW-500 zeolite.<sup>81,82</sup> It is made from mined chabazite and erionite which have been refined by firing, sized, pelletized and manufactured into a bead form using a clay binder. Ionsiv IE-96 (currently Ionsiv R9160-G) is sodium aluminosilicate similar to Ionsiv IE-95 but in a different cationic form. At the West Valley Demonstration Project, Ionsiv IE-96 was used from 1988 to 1995 to remove Cs from neutralized PUREX and THOREX supernates.<sup>37,82</sup> The Cs removal efficiency was 99.99%. It should be remarked that the waste at West Valley was alkaline, but the pH was much lower (about 10-11) than alkaline waste at other places (11-14 at Hanford, ORNL or Savannah River). The loaded material was not eluted, but ground, mixed with PUREX sludge and vitrified. Ionsiv IE-96 was also used at Three Miles Island from 1973-1983 and at Fukushima Daiichi from 2011 onwards to remove Cs from cooling water from the damaged reactor cores.

In general zeolites offer excellent thermal, mechanical and radiation stability, lack of swelling and a stable column packing.<sup>37,82</sup> Zeolites have a much larger loading capacity for Cs than organic resins such as Duolite CS-100. First zeolite-type ion exchangers were reasonably elutable. Later products were more difficult to elute and more suitable for once-through use. Spent zeolites can be conditioned for long-term disposal by means of vitrification. The use of zeolites is limited to moderate pH ranges since they decompose in highly acidic (pH < 4) and highly alkaline (pH > 13) solutions. Another disadvantage of aluminosilicates is that they are associated with a significant heat of hydration during wetting. Column cementation can occur due to fines generated during transportation or charging of the columns.

In the cases where Cs has to be removed from highly acidic or caustic solutions, various synthetic inorganic materials have been developed such as titanium and zirconium phosphates,<sup>83-85</sup> hexacyanoferrate(II)-molybdate,<sup>83</sup> antimony pentoxide,<sup>86</sup> zirconium oxide,<sup>84</sup> or hydrous mixed metal oxides.<sup>87</sup> However, those materials have not been implemented on industrial scale.

Amorphous hydrous titanium oxide (HTO) materials were developed in the 1960s and 1970s at Sandia National Laboratory in the framework of the development of electroactive ceramic materials for defense applications.<sup>88-90</sup> In 1975 Sandia National Laboratories started to investigate the use of these materials for conversion of HLLW into a stable ceramic waste form.<sup>91-93</sup> After sorption of (cationic) radionuclides from neutralized HLLW, the titanate ion exchange material can be consolidated by calcination into a stable ceramic waste form. A monolithic ceramic can be produced by hot pressing. The HTO material was tested in a hot cell at ORNL with the PUREX raffinate of a small amount of spent commercial light-water reactor fuel in support of the Barnwell reprocessing facility.<sup>88,92</sup> The HTO sorbed most cationic radionuclides such as Sr and Pu, however, the highly soluble Cs was not sorbed. Also application of HTO on neutralized PUREX waste from the plutonium production has been tested. Dissolved salt cake simulants and dissolved salt cake from Hanford were tested at Sandia and Hanford.<sup>93</sup> In addition, also Savannah River Site performed tests on their wastes.<sup>88</sup> At about 1980 it was decided to conclude the R&D at Sandia for nuclear waste applications because the US DOE preferred vitrification over ceramics as the baseline wasteform, however, R&D for application of HTO as catalysts for coal liquefaction was continued. In addition, at Savannah River Site, HTO was used for in-tank precipitation of Sr and Pu. In the framework of the catalyst R&D, a new class of ion exchangers, crystalline silicotitanates (CSTs) were developed in collaboration with Texas A&M University. Initial tests at Sandia showed that the CSTs had a high affinity for Cs at neutral pH. Further R&D on Cs sorption and systematical improvement of the CST composition was performed jointly by Sandia National Laboratories and Texas A&M University in the early 1990s.<sup>94,95</sup> The Cs ion exchange performance was dramatically improved, especially at high pH. Additional funding from the DOE office of Environmental Management was obtained and a cooperation agreement with UOP Inc. (Des Plaines, Illinois) was signed to scale up the production of the CST powder and to make it commercially available. Tests with simulated Hanford wastes performed at Pacific Northwest Laboratories confirmed the excellent performance of the new ion exchanger.<sup>96</sup> Partial neutralization of the solutions (by carbon dioxide addition) to pH 10.8 resulted in an even more efficient Cs removal. Also Sr is sorbed extremely well and Pu is sorbed well. In addition, the chemical stability was investigated and was very good. UOP also converted CST powder into a granular material that allowed column operation. The granular material became commercially available in 1995 under the tradename Ionsiv IE-911 (now IONSIV R9120-B). It is a microporous bound form (amorphous Zr(OH)<sub>4</sub> binder) of hydrous crystalline silicotitanate.<sup>89,97-99</sup> Ionsiv IE-911 has an extremely high selectivity for Cs and is therefore perfectly suited to remove Cs from highly alkaline solutions that contain a low concentration of Cs in the presence of a high concentration of competing cations, particularly Na and K.<sup>82</sup> CST retains its Cs selectivity over a very broad range of pH and can thus be used for highly acidic waste solutions as well.<sup>18,82,100-102</sup> The selectivity for Cs was enhanced

by incorporation of Nb in the crystalline structure.<sup>101,103,104</sup> The Nb-substituted forms of CST possess circular openings in the silicotitanate framework that represent an ideal-sized tunnel for Cs.<sup>37,105</sup> At neutral to high pH, CST will also have a high affinity for Sr.<sup>18,82</sup> In addition, the ion exchange capacity is very high. This is attributed to the open and rigid tunnel structure of CST and the fact that the exchange process is a two-step process mediated by conformational changes in the silicotitanate framework.<sup>82,105</sup> Unfortunately, the ion exchange kinetics is pore diffusion (mass transfer) limited and relatively slow.<sup>106</sup> Therefore, the size of the beads has an important influence on the kinetics. For full-scale operation, however, only large beads should be used at decreased flow rates because of the improved hydrodynamic behavior and the reduced attrition.<sup>37</sup> Attrition causes fines production which leads to plugging of the column after extended use. Because they are responsible for the remediation of the legacy waste from nuclear weapons production at the US DOE sites, the Office of Science and Technology and the Office of Waste Management, both assistant offices of the DOE Office of Environmental Management in the USA have funded a process demonstration of Cs removal from real waste on an industrial scale.<sup>89,97,98</sup> Prior to this demonstration, an extensive comparison of different resins for Cs removal was performed on bench scale (in a hot cell) in continuous flow, with real waste solutions (from Oak Ridge and Hanford). Based on the results of the bench-scale experiments, Ionsiv IE-911 was selected for an industrial-scale demonstration at Oak Ridge National Laboratory with a modular system consisting of several transportable units. Between September 1996 and June 1997, about 120 m<sup>3</sup> of low-level liquid waste (LLLW) supernatant from the Melton Valley storage tanks at ORNL were processed with minimal operational problems. The high capacity of the resin allowed single-pass operation.

In contrast, regenerable ion exchangers such as CS-100 require multiple elution/regeneration cycles to remove an equivalent amount of Cs. The demonstration showed that Cs could be efficiently removed from the supernate and concentrated on a small volume of Ionsiv IE-911. Loaded Ionsiv IE-911 cannot be eluted and must be disposed of as radioactive waste, either after vitrification or as a final waste form. Because of this successful application, a 2 m<sup>3</sup> column with Ionsiv IE-911 was used from December 1997 through April 2000 in the Waste Triad Project, an integrated tank waste management for the ORNL LLLW stored in the Melton Valley storage tanks.<sup>107</sup> About 7700 Ci of <sup>137</sup>Cs were successfully removed from more than 400 m<sup>3</sup> of LLLW. Besides the ion exchange unit, the modular system also comprised evaporation and liquid-solid separation units. In general, the performance of the system met the expectations. In addition, the produced secondary waste (liquid waste concentrate obtained by evaporation as well as the loaded Ionsiv IE-911) met the acceptance requirements for final disposal. A portion of the loaded Ionsiv IE-911 was successfully dewatered and packaged and met the waste acceptance criteria for the Nevada Test Site. Another portion of the loaded Ionsiv IE-911 was used at Savannah River for demonstration of vitrification. The high <sup>137</sup>Cs loading was associated with a very high thermal load on the column.<sup>37</sup> Issues with column plugging (cementation) were observed during tests at ORNL and SRS.<sup>89,108-110</sup> That was attributed to the precipitation of niobium and silicon oxides in the Ionsiv IR-911 columns. In addition to the column plugging, precipitates on the surface of the ion exchanger also seriously decreased the Cs exchange capacity over time. A thorough analysis of the used CST materials by Sandia identified some leachable Si and Nb impurities that were responsible for the precipitation.<sup>104</sup> In a collaborative effort with Sandia, SRS, ORNL and PNNL, UOP adapted the manufacturing process which resulted in much lower chance of column plugging and loss of capacity.<sup>104,111,112</sup> Column plugging has not been observed anymore in recent testing.<sup>37</sup> Ionsiv IR-911 has been used in the polishing column of the SARRY system since 2011 in at the Fukushima Daiichi NPP.<sup>37</sup> The CST is used after most of the Cs has already been removed from the cooling water of the damaged reactors by four Ionsiv IE-96 columns. The Ionsiv IE-96 was selected for the first four columns because it has a lower Cs capacity which allows to safely shield and cool the columns during operation. The polishing column is used to further decontaminate the water in order to obtain the required decontamination in a single pass through the SARRY system. The US DOE has selected Ionsiv IE-911 for processing tank waste supernate at the Tank Side Cesium Removal System and at the larger Low-Activity Waste Pretreatment System, both belonging to the future Hanford Tank Waste Treatment and Immobilization Plant (WTP) and at the Tank Closure Cesium removal system at the SRS.<sup>37,41</sup> Numerous additional studies were performed, however, some issues need to be addressed more thoroughly before industrial application. Ionsiv IE-911 is physically very robust to heating. The morphology of the material does not change up to 200 °C. The Cs capacity, however, decreases significantly with increasing temperatures. Normally, columns are cooled by the process solutions. Due to the high capacity of the CST for Cs, it is expected that this will result in increased self-heating of the column during operation. The heat generation during a full-scale process run has to be taken into account in the design of the plant since it impacts the Cs capacity. Cooling of the feed solution could be considered, however, this is associated with the

risk of precipitation of salts from the supersaturated waste solutions. Column design could be adapted to improve heat exchange *e.g.* by incorporating an inner annulus. Numerous studies with simulated waste solutions have proven the chemical and physical stability of Ionsiv IE-911. In addition, gamma exposure studies and subsequent performance testing of the material allow assessment of radiolytic stability. The influence of radiolysis by the beta radiation of  $^{137}\text{Cs}$  on the capacity loss of the CST material has not been rigorously tested yet. Also the production of hydrogen gas due to the radiolysis of water is of concern and should be investigated further. Furthermore, studies on the combined effects of exposure to chemical, physical and radiolytic effects are needed. Affinity for other (toxic) metals such as Cd, Pb, Sr, Ca, Pu, U and Am was investigated with simulated SRS tank waste and with real Hanford tank waste.<sup>113-117</sup> The final waste form of the spent Ionsiv IE-911 will likely become TRU waste because the concentration of Pu and other actinides in the spent material will most probably be too high, both with Hanford tank wastes and SRS wastes.<sup>37</sup> The handling of the spent columns will require extensive shielding and/or remote handling, cooling and management of the hydrogen gas produced by radiolysis. Hydrogen gas production can be minimized by dewatering *i.e.* by passing dry air through the column. Although direct vitrification of the spent ion exchanger has been demonstrated, it will most probably be stored first in interim storage facilities at SRS and Hanford for an unspecified time period.<sup>37,82</sup> Therefore, the removal of the ion exchanger from the columns after a long storage time should also be investigated. Hot isostatic pressing of the loaded ion exchanger into a monolithic ceramic waste form has also been demonstrated and seems to have potential as an acceptable waste form.<sup>99</sup>

Organic ion exchange resins have also found wide application in the removal of Cs from radioactive waste solutions. In general, these resins lack selectivity and can be used only with diluted solutions. Duolite ARC-359, a granular macroporous (gel type) phenol-formaldehyde polymer ion exchange resin with methylene sulfonic acid cation exchange groups, manufactured by Diamond Shamrock Corporation, was used from 1970-1979 at the Hanford B plant for the recovery of Cs from stored REDOX wastes which have higher alkalinity than the PUREX wastes.<sup>37,54,74</sup> These wastes would attack and dissolve zeolites (aluminosilicates).<sup>55,74</sup> Also at Savannah River Plant, an ion exchange process for the removal of Cs from alkaline HLLW has been developed.<sup>118</sup> Duolite ARC-359 is a refined version of the Duolite C-3 that has been used in early research. It has a good selectivity for Cs at high pH, even in solutions with high amounts of Na. This is attributed to the fact that the resin has two types of exchangeable protons: strongly acidic protons on the sulfonic acid group and very weakly acidic phenolic protons that become only involved in Cs sorption at high pH. At a  $\text{pH} \leq 10$ , the total Cs capacity was lower than the ones of Linde AW-500 and Norton Zeolon-900, however, at pH values above 12, the capacities were comparable.<sup>37</sup> In addition, the kinetics for binding Cs to the resin are faster than for binding Na.<sup>74</sup> Therefore, the capacity for Cs during column operation with the stored REDOX wastes was much higher than for the zeolites Linde AW-500 and Norton Zeolon-900 because equilibrium was not reached for Na. If necessary, adjustment of the feed pH to 12 was performed. After loading, the column was washed with 0.2 M  $(\text{NH}_4)_2\text{CO}_3$  and Cs was eluted with 3 M  $(\text{NH}_4)_2\text{CO}_3$  and 2 M  $\text{NH}_4\text{OH}$ . The mechanical stability and irradiation stability were very good. Cs recovery was near 100% and the decontamination from Na was 10 times better than with Linde AW-500. The resin was not stable in nitric acid and the resin bed needed to be repacked periodically by means of up-flow water washes.<sup>37</sup> Column conditioning/regeneration with NaOH is very important to avoid precipitation of Al.<sup>118</sup> The commercial availability of Duolite ARC-359 has been discontinued after the ion exchange division of Diamond Shamrock was sold to Rohm and Haas Company in 1984.<sup>36</sup> At Savannah River Laboratory, the use of Duolite ARC-359 has been considered for the decontamination of alkaline HLLW supernate,<sup>118</sup> however, it was suggested in 1980 to replace Duolite ARC-359 by Duolite CS-100.<sup>119,120</sup> Duolite CS-100 is a granular phenol-formaldehyde polymer ion exchange resin from Rohm and Haas Company, Philadelphia, Pennsylvania, USA, (formerly Diamond Shamrock Corporation). The resin contains weakly acidic carboxylate groups instead of the strongly acidic sulfonate groups in Duolite ARC-359. The sorption characteristics of Duolite Cs-100 are very similar to those of Duolite ARC-359. Divalent cations are also strongly sorbed by the carboxylic and phenolic ion exchange groups.<sup>121</sup> Cs is mainly sorbed by the phenolic groups. The Cs capacity is significantly improved at pH of about 12. Column regeneration and conditioning should be performed with 2 M NaOH. A small amount of Sr will be sorbed by Duolite Cs-100 as well if Sr is present in the alkaline waste solutions.<sup>119</sup> Due to the weakly acidic groups Cs can be eluted with 2 M formic acid instead of 3 M  $(\text{NH}_4)_2\text{CO}_3$  and 2 M  $\text{NH}_4\text{OH}$ . Sr will also be eluted with formic acid. The latter eluent is troublesome with regards to the conditioning of the Cs waste. Prior to calcination and vitrification, the ammonium carbonate has to be thermally decomposed and recovered. The Cs present in the resulting solution of Cs and Na carbonate must be concentrated on a non-elutable zeolite column with high Cs capacity before it can be blended with other waste at the vitrification plant. Sodium formate

can be easily recycled or destroyed prior or during calcination and vitrification of Cs. Formic acid does not damage the resin in contrary to nitric or hydrochloric acid elution, which was used at ORNL when they employed Duolite CS-100 for decontamination of low level waste waters.<sup>121-127</sup> The Low-Level Waste Treatment plant at ORNL started operation in 1976, and the resin was used from 1976-1981, however, research was already started in the early 1960s. Another advantage of formic acid elution is that the largest amount of the Na sorbed on the column can be eluted with formic acid and collected separately before the Cs is eluted, which gives a Cs product containing less Na which is favourable for waste conditioning.<sup>119</sup> It was expected that due to the elimination of a number of process steps compared to the use of Duolite ARC-359, the required hot cell space and costs for the processing of alkaline HLLW could significantly be reduced. It is not clear whether this process based on Duolite Cs-100 has been implemented on an industrial scale at SRS. During operation of the Low-Level Waste Treatment plant at ORNL, a large volume of secondary liquid waste was created.<sup>37</sup> In order to avoid early exhaustion of the resin by Mg and Ca uptake, a water softener had to be used on the feed. Furthermore, the initial pH ranging from 7 to 8 had to be adjusted to 11.8 in order to optimize the uptake of Cs and Sr. In the 1990s, it was used in numerous Cs removal studies with simulated Hanford wastes and it was considered to be the baseline Cs ion exchange resin at Hanford for the conceptual design of the new Waste Treatment Plant (WTP) design.<sup>35-37</sup> As mentioned earlier, if present, TRU elements and Sr should be removed from the waste prior to eliminating Cs. The performance of other resins was compared to Duolite Cs-100. The resin was no longer pursued for use in the WTP when other products proved to be superior.

Resorcinol-formaldehyde (RF) ion exchange resin, has been developed at Savannah River Site and is now manufactured by Boulder Scientific Company (Boulder, Colorado).<sup>128,129</sup> RF resin is based on the earlier work of Walker, Wallace and Ebra.<sup>130-132</sup> They developed porous Cs and Sr specific ion exchange resins. Several phenol-formaldehyde copolymers with iminodiacetic acid functional groups were prepared and tested for Cs and Sr sorption. Best results were obtained with a porous granular resorcinol-formaldehyde polymer containing iminodiacetic acid. The porosity was induced by using a calcium carbonate template that was removed by acid dissolution after the polymerization reaction was completed. The iminodiacetate groups were responsible for the ion exchange with Sr while Cs selectivity was induced by the phenolic groups. Based on these results, RF resin was developed. RF resin is a condensation polymer of the potassium salt of resorcinol with formaldehyde.<sup>129</sup> The condensed RF resin is ground to the desired mesh size.<sup>37</sup> After grinding, the particles have a variety of sizes and shapes with angular edges. RF resin has about 6-20 times the Cs capacity of the Duolite™ CS-100 resin in the pH range 3-14 and temperatures between 10 and 40 °C.<sup>37,38,129,133,134</sup> The high Cs selectivity is attributed to the two weakly acidic phenol groups on the resorcinol that become functional at high pH. The optimum pH is about 12.5. Sodium concentration (up to 7M) has almost no influence on Cs sorption at equilibrium, unlike potassium concentration. In addition, the kinetics of Cs sorption is affected in highly concentrated (viscous) salt solutions. Sr sorption is limited and suffers from competition from Na. Temperature changes do not affect the separation. Cs can be eluted with diluted nitric acid or formic acid solutions. The resin has been thoroughly tested with simulated wastes at SRS, Hanford and ORNL in collaboration with Pacific Northwest National Laboratories (PNNL).<sup>129,133-138</sup> Serious swelling (up to 50%) and shrinking, sometimes causing channeling of the resin, were observed.<sup>134</sup> Serious hydraulic performance issues were observed during hydraulic testing with simulated waste.<sup>139</sup> Due to severe swelling and shrinking during loading, elution and regeneration cycles, the granular resin was exposed to high stress and particle breakage was observed. This gave rise to a stepwise decrease in resin bed permeability after each process cycle. The RF resin was also sensitive to oxidation by dissolved oxygen, which caused capacity loss after each process cycle.<sup>37</sup> In addition, oxidation during storage was observed. Due to these disadvantages, the Duolite™ CS-100 resin was preferred as the baseline ion exchanger for the conceptual design of the WTP at Hanford in the period of 1994-1996, and the RF resin was only considered as the best alternative despite its much better Cs capacity. The use of Duolite CS-100 was considered as a conservative, technologically feasible option for Cs decontamination.<sup>36</sup>

SuperLig® 644 (also referred to as SL-644), manufactured by IBC Advanced Technologies, (American Fork, Utah, USA) is an elutable resin that contains covalently bound macrocyclic ligands (crown ethers) with a very high affinity for cesium in alkaline solution in the presence of sodium and potassium.<sup>140-144</sup> The exact composition and functionality of the resin are proprietary.<sup>37</sup> The morphology of the granular SL-644 resin is similar to that of RF resin. The optimum pH was 14. The cesium capacity decreases rapidly with decreasing pH below pH 14. In 1996 it was decided to replace Duolite™ CS-100 by SL-644 as the new baseline ion exchanger for the design of the WTP at Hanford due to its superior Cs selectivity, particularly in presence of high amounts of alkaline metals because the alkaline Hanford tank waste supernatant contains high concentrations of NaNO<sub>3</sub> and NaOH.<sup>37</sup>

Elution of Cs with 0.5 M of nitric acid is more efficient from Superlig 644 than from RF resin. However, the resin has some important drawbacks.<sup>37,139–143,145–148</sup> Similar to RF resin, the different loading and washing solutions cause severe swelling and shrinkage of the resin. However, the compressibility of SuperLig 644 was much higher than that of RF resin. As a result, porosity and permeability are seriously affected in large columns. Also, particle breakage due to the stress induced by repeated swelling and shrinking contributes to a decreasing permeability. The presence of atmospheric oxygen in the waste solution can cause dramatic resin degradation, particularly at higher temperatures. The rate of degradation is accelerated (catalytic effects) in the presence of transition metals such as iron and copper that are always present in the waste solutions. Transition metals such as Cr, Zr, Ag, Fe, Cd, Pb, As, Se, Pd, <sup>99</sup>Tc, U, Pu and Am are also sorbed onto the resin. A major part of them is eluted together with Cs, however, small amounts of transition metals, TRU elements and Cs will be found in the spent resin. After several elution cycles, the resin should be disposed of as Low-Level Waste in a surface repository. Further research is needed to determine whether or not regulatory thresholds for leachable heavy metals and TRU elements for Low-Level Waste (land disposal) can be respected. IBC Advanced Technologies was the sole-source provider of SL-644.<sup>37</sup> Therefore, the use of this resin for the Hanford WTP would be associated with a high risk of supply chain disruption. Because of these concerns, it was decided in 2003 to abandon the SL-644 resin at the WTP and to start looking for an alternative ion exchanger. Both elutable and non-elutable ion exchangers were considered.<sup>106,149</sup>

For minimal impact on the flowsheet, an elutable organic resin was preferred, however, CST materials were still considered as a backup.<sup>106</sup> A patent from Sinvent A/S (Trondheim, Norway)<sup>150</sup> was found in which a process was claimed for the production of mono-sized spherical resorcinol-formaldehyde resin by means of slightly cross-linked polystyrene seed particles.

Spherical resorcinol-formaldehyde resin (sRF) was, together with CST, considered to be a promising candidate ion exchanger to replace SuperLig 644 for the Hanford WTP. US DOE started discussions with Sinvent A/S and a collaborative effort with Microbeads AS (Skedsmokorset, Norway) in order to improve the Cs capacity and performance of the sRF resin.<sup>151,152</sup> After upscaling the production of the optimized sRF by Microbeads AS, an agreement was made with Boulder Scientific (Boulder, Colorado, USA) to transfer the necessary knowledge so they could also successfully demonstrate the production of a large batch of sRF and thus dependence on a sole supplier could be overcome. The Cs capacity is strongly dependent on the pH of the solution.<sup>37</sup> The Cs capacity increases dramatically with increasing hydroxide concentration up to 0.05 M [OH<sup>-</sup>]. Between 0.05 and 3.7 M [OH<sup>-</sup>], there is a minimal effect on the Cs capacity. Cs is eluted as soon as the pH drops below 7. Cs can be eluted in a relatively small volume using 0.45 or 0.5 M nitric acid. Hydraulic tests revealed that the hydraulic performance and permeability of sRF resin are much better than the ones of the granular RF resin and the SuperLig 644 resin.<sup>139,147</sup> Extensive testing of the sRF resin with simulants on small, pilot as well as large scales has been performed, along with small column tests with actual Hanford tank waste.<sup>153–155</sup> sRF resin also exhibits some affinity for Sr, Ca, Cd, Fe, and Pb that are almost fully recovered in the eluate.<sup>153</sup> Determination of the nuclides and elements relevant for the LLW land disposal requirements in the spent resin revealed that Cr was the only metal that could be of concern. Actinide elements were well below the TRU waste limit. On the other hand, after tests with Savannah River waste that contains higher levels of <sup>238</sup>Pu than the Hanford waste, the amounts of <sup>238</sup>Pu left on the spent resin would qualify it as TRU waste.<sup>156</sup> Moreover, the levels of Hg after processing SRS waste might need further attention. SRF columns should be operated at a temperature between 15 and 35 °C.<sup>37</sup> At higher temperatures, the Cs capacity decreases dramatically. Furthermore, sRF resin is not physically stable at higher temperatures. Column plugging was observed after extended (> 336 h) exposure to temperatures higher than 45 °C. Radiolysis and the combined effects of radiolytic and physico-chemical degradation have not been extensively studied, however, from differences between tests with simulants and actual wastes, it can be expected that there is a significant synergistic effect between chemical and radiolytic degradation. In order to avoid exothermic reactions between nitric acid and the organic material, the nitric acid concentration in the eluent should be carefully controlled. In addition, the heat caused by <sup>137</sup>Cs decay on a fully loaded column should be taken into account in safety studies. For instance, an interruption of the eluent flow at the start of the elution could cause concentration of the nitric acid due to evaporation. Dissolved oxygen will cause degradation of the sRF resin, although the effects (capacity loss and physical changes) are not as severe as with the SuperLig-644 resin. Long-term storage of the resin is possible under water that has been purged with nitrogen and maintained under nitrogen pressure. sRF was the baseline resin for the WTP in Hanford between 2004 and 2018.

The regenerable organic ion exchangers used for the processing of large volumes of liquid radioactive waste are associated with the disadvantage that extensive processing equipment is needed to handle the ion exchanger, the eluant, washing and regeneration liquids, and the highly concentrated radioactive solution obtained after elution of the Cs.<sup>88</sup> Residual Cs on the eluted column will leak into the feed of the next process cycle, which can compromise decontamination.<sup>37</sup> This can be mitigated by adding a clean polishing column to the column array. Depending on the pH and salt concentration of the liquids, organic resins can undergo significant swelling and shrinking which can compromise hydraulic performance. A large volume of associated liquid waste streams is produced. Volume reduction by evaporation could be applied, however, off-gas handling is needed. In addition, after performance degradation due to radiolysis and chemical attack, a large volume of spent ion exchanger resin has to be disposed.

The Diphonix-Cs resin, a chelating ion exchange resin containing diphosphonic acid chelating groups and phenolic groups chemically attached to the polymeric matrix, has been designed for the simultaneous adsorption of actinides, cesium and strontium from alkaline media due to the combined action of the diphosphonic acid and the phenolic groups.<sup>157,158</sup> In contrast to Sr resin and several other resins that have been commercialized by Eichrom Industries Inc. (Darien, Illinois, USA) and Triskem, and have been widely used for preconcentration and separation in analytical sample preparation, e.g. for applications of Sr resin, the Diphonix-Cs resin, although developed by the same researchers, did not break through in radiochemical separation science.<sup>159–161</sup> The Diphonix-Cs resin has been rarely reported in the literature and is not commercially available. This might be related to the difficult stripping. Extraction chromatography materials employing extractants known from liquid-liquid extraction processes have been reported in the literature as well, but have not been very successful. Cobalt Dicarbolide dissolved in nitrobenzene has been immobilized on Kel-F beads, a polytrifluoroethylene polymer, for the concentration and separation of Cs from a mixture of long-lived fission products, however, elution of Cs was only possible by eluting the organic phase from the inert support with acetone.<sup>162</sup> Also extraction chromatography materials employing crown ethers dissolved in a chlorinated diluent have been developed, however, Cs retention was often poor or highly dependent on experimental conditions.<sup>163,164</sup> The calixcrown ether compound BC6B, which was developed for liquid-liquid extraction of Cs from highly acidic solutions, has been impregnated on an inert support after dissolution in 1,2-dichloroethane.<sup>165</sup> In contrary to the equivalent liquid-liquid extraction process where maximum Cs extraction is observed at 4 M nitric acid, Cs sorption is more or less constant in a nitric acid concentration ranging from 0.01 to 1 M and falls precipitously when the concentration of nitric acid is raised above 1 M. The efficiency of the resin was lower than other resins using the same inert support. In addition, the Cs capacity is not so high and could not be increased because of the limited solubility of BC6B in 1,2-dichloroethane and the maximum solvent loading of the resin. Preliminary evaluations have been carried out with the more soluble calixcrown ether BobCalix, however, the Cs capacity did not increase proportionally to the concentration of BobCalix which is an indication that not all the extractant is accessible for the Cs<sup>+</sup> ions. The calixcrown ether based resins were also not commercialized by Eichrom/Triskem.

## Strontium precipitation and column separations

Some ion exchangers developed for Cs removal also sorb Sr or have been modified to enhance Sr sorption. Natural zeolites such as clinoptilolite have been used at the SIXEP plant in Sellafield to remove Cs and Sr from storage pond water.<sup>72,166</sup> Zeolites cannot be used at high pH. Therefore, pH adjustment was necessary. The synthetic zeolite Ionsiv TIE-96 is essentially Ionsiv IE-96 that has been treated with a titanium solution. It is made for Sr and Pu removal from alkaline solutions. Cs is also sorbed, but not as well as on Ionsiv IE-96. Ionsiv TIE-96 has been used at the West Valley Demonstration project for the processing of neutralized PUREX and THOREX wastes.<sup>37</sup> It was used in addition to Ionsiv IE-96, which was the primary zeolite. The high-alumina zeolite Ionsiv A-51 (made by UOP, now Honeywell), a synthetic type A zeolite, has a good selectivity and capacity for Sr. Mixtures of Ionsiv IE96 and Ionsiv A-51 have been used in the Submerged demineralizer System at Three Mile Island from 1979 to 1983 to decontaminate approximately 3000 m<sup>3</sup> high activity level water.<sup>37,167,168</sup> Ionsiv A-51 was mixed with Ionsiv IE-96 because Sr was not sufficiently sorbed on Ionsiv IE-96. Since zeolites only exhibit a fairly low selectivity for Sr, they can only be used to decontaminate dilute solutions. Furthermore, they cannot be used with highly alkaline or acidic solutions without prior pH adjustment. From alkaline media, Sr will also be sorbed by crystalline silicotitanate (CST) or Ionsiv IE-911, however from nitric acid solutions only Cs will be removed.<sup>27,82</sup>

Lead sulfate co-precipitation has been applied for the recovery of Sr from PUREX wastes at Hanford.<sup>169-171</sup> Precipitation with lead sulfate can, in contrary to most other precipitation methods for Sr, be applied to acidic waste solutions.<sup>172</sup> Similar to the early Cs removal methods from PUREX waste at the Hanford B plant, the goal was not the decontamination of the waste solutions, but the recovery of <sup>90</sup>Sr. Therefore, it was accepted that the decontamination of the waste solutions was very low. The sulfate precipitate had to be converted into carbonate and the lead had to be removed by metathesis reaction with carbonate-hydroxide mixtures.

In order to purify the Sr from co-precipitated lanthanides, dissolution in nitric acid followed by oxalate precipitation was carried out. The crude Sr product then needed further purification by cation exchange on a DOWEX-50 column. Besides the low decontamination that can be achieved, this method also introduces high amounts of S and very toxic Pu into the waste streams. Titanium hydroxide and calcium phosphate precipitation methods have been studied in the UK for the precipitation of Sr from low and medium alkaline radioactive waste waters such as contaminated spent fuel storage pond water or PUREX solvent wash solutions.<sup>173</sup> In order to achieve good decontamination without addition of a large excess of reagent, ultrafiltration (use of a membrane) was needed. Techniques such as gravity settling and centrifugation that were frequently used in radiochemical processes were less successful. The inorganic ion exchanger polyantimonic acid (PAA) has a high affinity for Sr in solutions containing 1-2 M nitric acid.<sup>83,120,174</sup> Unfortunately, the Sr capacity is not so high and the exchange kinetics are rather slow. In addition, to elute the Sr, drastic conditions are needed or the matrix should be volatilized by dry HCl at high temperatures, leaving solid SrCl<sub>2</sub>.

Sodium titanate and hydrous titanium oxide (HTO) sorb Sr from neutral and alkaline solutions even in the presence of high amounts of sodium salts.<sup>47,120,175,176</sup> It can be applied as a precipitant<sup>56,61,91,92</sup> as well as in an ion exchange column.<sup>175,176</sup> Unfortunately, sodium titanate has a low selectivity for Sr. Other polyvalent ions such as U, Pu, Am, Mo, Zr, Y, lanthanides, and Ba are also sorbed well on this material from neutralized liquid waste solutions. After loading, the material can be hot pressed into a compact glass-like ceramic final waste form.<sup>91-93,176</sup> Therefore, sodium titanate is rather suited for decontamination and solidification of liquid wastes than for partitioning of Sr. Treatment with monosodium titanate (MST) has been chosen for Sr and TRU element removal from Savannah River alkaline tank wastes.<sup>47</sup> In the 1980s it was selected for Sr and Pu removal in conjunction with Cs removal by means of tetraphenylborate precipitation from HLW as part of the In-Tank Precipitation (ITP) process.<sup>177</sup> The original sol-gel synthesis method developed by Sandia<sup>92</sup> was modified at Savannah River National Laboratory to optimize the performance, and the knowledge was transferred to commercial vendors.<sup>177,178</sup> Extensive testing was performed in the 1980s and 1990s and the MST proved to be acceptable for the ITP. Due to operational and safety concerns related to the use of tetraphenylborate, the ITP facility was operational only for a brief time before it was shut down permanently in 1998. In the beginning of the current century, MST was selected for use in the Integrated Salt Disposition Process (ISDP).<sup>177,179</sup> The ISDP consist of 2 parts: the Actinide Removal Part (ARP) and the modular Caustic Side Solvent Extraction Unit. In the ARP, the salt solutions from the Tank Farm are batch contacted with MST in the MST strike tank. After mixing for 24 hours, the MST solid on which Sr and actinides are sorbed including entrained sludge is removed from the resulting slurry by ultrafiltration on a cross-flow filter (sintered metal). After washing with water to reduce the Na content, the solids are transferred for vitrification. The ISDP started hot operations in 2008.<sup>179</sup> It was a kind of pilot for the Salt Waste Processing Facility (SWPF) that has been hot commissioned very recently. The ISDP was also used for interim treatment of waste. Because of the high radionuclides content of the waste that was projected to be processed in the SWPF facility and the limited solubility of Ti in HLW borosilicate glass, the loading capacity of the MST had to be improved.<sup>180</sup> In addition, because the overall throughput of waste in the entire SWPF is limited by the throughput of the batch adsorption process, improvement in the adsorption kinetics was also desirable. A new peroxotitanate material, referred to as modified MST or mMST has been developed.<sup>180-182</sup> mMST can be prepared by post-synthesis treatment of commercially produced MST with peroxide. mMST exhibits higher capacities and better kinetics for the adsorption of Sr and actinides from alkaline waste solutions. The researchers from the University of Helsinki that have developed CsTreat have also developed SrTreat, which is a granular inorganic ion exchanger based on sodium titanate.<sup>183,184</sup> The material is commercially available from Fortum (Helsinki, Finland) and is particularly suited for the decontamination of alkaline waste solutions containing high concentrations of sodium nitrate. The pH has a tremendous effect on Sr sorption. From neutral solutions, Sr is not sorbed well, however, with increasing pH, Sr sorption improves. CsTreat works most efficiently at pH values of 10 and above. K and Li have practically no influence on the uptake of Sr. Ca concentration has a strong influence on Sr uptake. Even low concentrations decrease Sr uptake strongly. If the pH of the waste solutions is 10 or above, the solutions will absorb CO<sub>2</sub> from the atmosphere and thus the solubility of Ca is extremely low.

NH<sub>4</sub> and Mg also decrease Sr uptake, however at concentrations typically present in waste solutions, the interference is low. The material exhibits an excellent radiation stability. CsTreat is a weakly acidic ion exchanger.

Therefore, it might be possible to elute Sr from loaded CsTreat by using acids. However, because all inorganic ion exchangers are slightly soluble, especially in highly acidic and alkaline solutions, regeneration and reuse is not foreseen. SrTreat, in combination with CsTreat, has been applied on an industrial scale in Murmansk to decontaminate large volumes of low and medium active wastes originating from the refuelling of nuclear driven icebreakers. At JAERI (Japan), a combination of CsTreat and SrTreat columns were installed in 1997 to remove Cs and Sr from reprocessing waste effluents. Prior to the removal of Cs and Sr, actinides were already removed and the solutions were neutralized to the alkaline region. Due to the neutralization, Sr was already partially precipitated. SrTreat was also used at Fukushima to decontaminate reverse osmosis concentrates of the circulating cooling water of the damaged cores of the Fukushima Daiichi nuclear power plants.<sup>53</sup>

Also organic resins have been developed for Sr separations. Amberlite IRC-718 was an organic crosslinked macroreticular chelating cation exchange resin with a particular selectivity for heavy metal cations.<sup>61,119</sup> It contains iminodiacetate groups. It was tested for removing Sr from West Valley alkaline waste. Sr was more effectively sorbed from solutions at pH 10 than at pH 13. Unfortunately, relative small changes in pH dramatically affect the removal of Sr from the waste solution. The loaded resin can be eluted effectively with formic acid and regenerated with sodium hydroxide. Even in the presence of carbonate and sulfate anions, the selectivity of the resin for Sr over competing ions remains high.

Sr resin (formerly Sr-spec) is an SPE resin that is already commercially available from Eichrom Industries Inc., Darien, Illinois, USA for the analytical scale extraction of Sr. Sr resin was developed by Horwitz *et al.*<sup>185</sup> The extractant system on Sr resin is 1 M 4,4'(5')-di-*t*-butylcyclohexano 18-crown-6 (DtBC18C6), a crown ether, dissolved in 1-octanol. The extractant is identical to the one used in the SREX solvent extraction process. A 40% (w/w) loading of this organic solution is impregnated onto an inert chromatographic support: Amberchrom CG-71. The uptake of strontium by Sr resin increases with increasing nitric acid concentration. At 8 M nitric acid, Sr is sorbed very well. At concentrations of nitric acid below 0.05 M, Sr is basically eluted. The alkaline and other alkaline earth metals show much lower affinity for the Sr resin than Sr over the whole concentration range of nitric acid (from 0.01 to 10 M). Ca has a low uptake and thus it is easy to separate Sr from Ca. Barium retention is somewhat high, but its uptake reaches a maximum at about 3 M HNO<sub>3</sub> and falls off at higher concentrations, so it is recommended that Sr should be loaded onto the resin from a 8 M nitric acid solution. Although lab-scale testing with actual Hanford neutralized cladding removal waste was performed,<sup>186</sup> the majority of the reported applications of Sr-spec are for analytical sample preparation.<sup>187-191</sup> Pu(IV) and Np(IV) are also sorbed on Sr-spec, however, the retention of tetravalent actinides and Zr on the Sr resin can be prevented by adding oxalic acid as a competitive complexing agent. Alternatively, the sorbed actinides can be selectively eluted by rinsing the column with a solution of oxalic acid and nitric acid.

## Conclusions

In this deliverable, an overview of the existing literature is given regarding the partitioning of cesium and strontium isotopes in the nuclear field. Solvent extraction on one hand, and column separations on the other hand are discussed. It can be concluded that the partitioning of Cs and Sr originating from a PUREX raffinate is quite challenging using ion exchange columns. These solutions are very acidic ( $\text{pH} < 1$ ) and way more radioactive as compared to the historic tank waste solutions. The literature also shows that the majority of the methods is not suitable for very acidic feed solutions, particularly the inorganic materials that are more stable against radiolysis. CST could be applied in acidic solutions, however, due to the high capacity and relatively young spent fuel solutions, the expected heat load and radiation of the columns will make the operation and handling complicated. The handling of the spent ion exchanger material and the conditioning into an accepted waste form will also be challenging. Organic resins, from the other hand, are not very stable against radiolysis and physicochemical degradation and often issues with the hydraulic performance are encountered. Therefore, they will need to be replaced frequently and thus a large volume of spent ion exchange resin will be produced besides a large volume of liquid waste due to the operation in load/elute/conditioning cycles. The conditioning of the spent organic ion exchanger materials into an accepted waste form will be challenging.

The most promising route towards Cs and Sr separation from the highly active, acidic PUREX raffinate is the solvent extraction route. In contrary to column separations, solvent extraction offers the advantage that Sr and Cs can be easily separated simultaneously. To be compliant with all safety and environmental measures, an optimized FPEX II solvent extraction system would be interesting to study more in depth.

## Bibliography

- (1) NEA OECD. State-of-the-Art Report on the Progress of Nuclear Fuel Cycle Chemistry. *NEA No. 7267* **2018**.
- (2) Rais, J.; Kyrš, M.; Pivonkova, M. The Distribution of Alkali Metal, Ammonium, and Tetraethylammonium Dipicrylamminates between Water and Nitrobenzene Phases. *J. Inorg. Nucl. Chem.* **1968**, *30*, 611–619.
- (3) Rais, J.; Selucký, P.; Kyrš, M. Extraction of Alkali Metals into Nitrobenzene in the Presence of Univalent Polyhedral Borate Anions. *J. Inorg. Nucl. Chem.* **1976**, *38* (7), 1376–1378. [https://doi.org/10.1016/0022-1902\(76\)80156-X](https://doi.org/10.1016/0022-1902(76)80156-X).
- (4) Hawthorne, M. F. Recent Developments in the Chemistry of Polyhedral Complexes Derived from Metals and Carboranes. *Pure Appl. Chem.* **1972**, *29* (4), 547–568. <https://doi.org/10.1351/pac197229040547>.
- (5) Kyrš, M.; Selucký, P. A Rapid Separation of Sr from Ca by Solvent Extraction with Dicarbolides in the Presence of EDTA and Polyethylene Glycols. *J. Radioanal. Nucl. Chem. Artic.* **1993**, *174* (1), 153–165. <https://doi.org/10.1007/BF02040343>.
- (6) Raut, D. R.; Mohapatra, P. K. Simultaneous Extraction of Cs and Sr from Synthetic High Level Waste Solutions Using a Solvent Containing Chlorinated Dicarbolide and PEG-400 in PTMS. *J. Radioanal. Nucl. Chem.* **2014**, *299* (1), 75–80. <https://doi.org/10.1007/s10967-013-2731-4>.
- (7) Galkin, B. Y.; Esimantovskii, V. M.; Lazarev, L. N.; Lyubtsev, R. I.; Romanovskii, V. N.; Shishkin, D. N.; Kadletsova, L.; Kyrsh, M.; Rais, I.; Selutskii, P. Extraction of Cesium, Strontium, Rare Earths and Transplutonium Elements from Highly Radioactive Wastes by Extractant Based on Cobalt Dicarbolide. In *Proceedings of ISEC-88; Moscow, 1988*; pp 215–217.
- (8) Chopin, G. R.; Khankhasayev, M. K.; Plendl, H. S. *Chemical Separations in Nuclear Waste Management*; Chopin, G. R., Khankhasayev, M. K., Plendl, H. S., Eds.; Batelle Press: Columbus, OH, 2002.
- (9) Herbst, R. S.; Law, J. D.; Todd, T. A.; Romanovskii, V. N.; Babain, V. A.; Esimantovskii, V. M.; Zaitsev, B. N.; Smirnov, I. V. Separation Science and Technology Development and Testing of a Cobalt Dicarbolide Based Solvent Extraction Process for the Separation of Cesium and Strontium from Acidic Tank Waste. *Sep. Sci. Technol.* **2002**, *37* (8), 1807–1831. <https://doi.org/10.1081/SS-120003045>.
- (10) Law, J. D.; Herbst, R. S.; Peterman, D. R.; Tillotson, R. D.; Todd, T. A. Development of a Cobalt Dicarbolide/Polyethylene Glycol Solvent Extraction Process for Separation of Cesium and Strontium to Support Advanced Aqueous Reprocessing. *Nucl. Technol.* **2004**, *147* (2), 284–290. <https://doi.org/10.13182/nt04-a3532>.
- (11) Romanovskiy, V. N.; Smirnov, I. V.; Babain, V. A.; Todd, T. A.; Herbst, S.; Law, J. D.; Brewer, K. N. The Universal Solvent Extraction (UNEX) Process. I. Development of the UNEX Process Solvent for the Separation of Cesium, Strontium and the Actinides from Acidic Radioactive Waste. *Solvent Extr. Ion Exch.* **2001**, *19* (1), 1–21. <https://doi.org/10.1081/SEI-100001370>.
- (12) Law, J.; Herbst, R.; Todd, T.; Romanovskiy, V.; Esimantovskiy, V.; Smirnov, I.; Babain, V.; N. Zaitsev, B.; V. Logunov, M. *Demonstration of the UNEX Process for the Simultaneous Separation of Cesium, Strontium, and the Actinides from Actual INEEL Tank Waste*; Bechtel BWXT IDAHO, LLC, 1999. <https://doi.org/10.2172/774229>.
- (13) Herbst, R. S.; Law, J. D.; Todd, T. A.; Romanovskiy, V. N.; Smirnov, I. V.; Babain, V. A.; Esimantovskiy, V. N.; Zaitsev, B. N. Development of the Universal Extraction (UNEX) Process for the Simultaneous Recovery of Cs, Sr, and Actinides from Acidic Radioactive Wastes. *Sep. Sci. Technol.* **2003**, *38* (12–13), 2685–2708. <https://doi.org/10.1081/SS-120022567>.
- (14) Dozol, J. F.; Dozol, M.; Macias, R. M. Extraction of Strontium and Cesium by Dicarbolides, Crown Ethers and Functionalized Calixarenes. *J. Incl. Phenom. Macrocycl. Chem.* **2000**, *38*, 1–22. <https://doi.org/10.1002/chin.200105265>.
- (15) Horwitz, H.; Dietz, D.; Fisher, F. Extraction of Strontium from Nitric Acid Solutions Using Dicyclohexano-18-Crown-6 and Its Derivatives. *Solvent Extr. Ion Exch.* **1990**, *8* (4–5), 557–572. <https://doi.org/10.1080/07366299008918017>.
- (16) Horwitz, E. P.; Dietz, M. L.; Fisher, D. E. SREX: A New Process for the Extraction and Recovery of Strontium from Acidic Nuclear Waste Streams. *Solvent Extr. Ion Exch.* **1991**, *9* (1), 1–25. <https://doi.org/10.1080/07366299108918039>.
- (17) Filippov, E. A.; Yakshin, V. V.; Abashkin, V. M.; Fomenkov, V. G.; Serebryakov, I. S. Extraction of Alkaline Earth Metals with Crown Ether, Dicyclohexyl-18-Crown-6 from Nitric Acid Solutions. *Radiokhimiya* **1982**, *24* (2), 214–216.
- (18) Todd, T. A.; Batcheller, T. A.; Law, J. D.; Herbst, R. S. *Cesium and Strontium Separation Technologies Literature Review*; 2004. <https://doi.org/10.2172/910643>.
- (19) Wood, D. J.; Law, J. D. Evaluation of the SREX Solvent Extraction Process for the Removal of <sup>90</sup>Sr and Hazardous Metals from Acidic Nuclear Waste Solutions Containing High Concentrations of Interfering Alkali Metal Ions. *Sep. Sci. Technol.* **1997**, *32* (1–4), 241–253. <https://doi.org/10.1080/01496399708003197>.
- (20) Wei, Z.; Gao, Y.; Zhou, Y.; Jiao, C.; Zhang, M.; Hou, H.; Liu, W. The Extraction of Sr<sup>2+</sup> with Dicyclohexano-18-Crown-6 in Conventional Organic Solvent and Ionic Liquid Diluents. *J. Serbian Chem. Soc.* **2020**, *87* (07), 909–922. <https://doi.org/10.2298/JSC190417111W>.
- (21) Ao, Y.; Yuan, W.; Yu, T.; Peng, J.; Li, J.; Zhai, M.; Zhao, L. Radiolysis of Crown Ether-Ionic Liquid Systems: Identification of Radiolytic Products and Their Effect on the Removal of Sr<sup>2+</sup> from Nitric Acid. *Phys. Chem. Chem. Phys.* **2015**, *17*, 3457–3462. <https://doi.org/10.1039/c4cp04294h>.
- (22) Xu, Y.; Gao, Y.; Zhou, Y.; Fan, C.; Hou, H.; Zhang, M. Extraction Behavior of Strontium from Nitric Acid Medium with N,N'-Dimethyl-N,N'-Dioctyldiglycolamide. *Solvent Extr. Ion Exch.* **2017**, *35* (7), 507–518.

<https://doi.org/10.1080/07366299.2017.1373997>.

- (23) Onizaki, M.; Morita, K.; Hirayama, N. Synergistic Ion-Pair Extraction of Strontium Ion with Tri-n-Octylphosphine Oxide and Dicyclohexano-18-Crown-6. *Anal. Sci.* **2016**, *32* (12), 1367–1370. <https://doi.org/10.2116/analsci.32.1367>.
- (24) Takahashi, T.; Ito, T.; Kim, S.-Y. Extraction Behavior of Sr (II) from High-Level Liquid Waste Using Ionic Liquid Extraction System with DtBuCH18C6. *Energy Procedia* **2017**, *131*, 170–177. <https://doi.org/10.1016/j.egypro.2017.09.462>.
- (25) Saha, D.; Vithya, J.; Kumar, R.; Subramani, C. R. V.; Rao, P. R. V. Studies on the Separation of Sr-89(II) from Irradiated Yttria Target Using 4, 4'(5') Di-Tert-Butyl-Cyclohexano-18-Crown-6 (DtBuCH18C6) by Solvent Extraction Technique. *Radiochim. Acta* **2016**, *104* (3), 195–204. <https://doi.org/10.1515/ract-2015-2399>.
- (26) Delmau, L. H.; Bonnesen, P. V.; Engle, N. L.; Haverlock, T. J.; Sloop, F. V.; Moyer, B. A. Combined Extraction of Cesium and Strontium from Alkaline Nitrate Solutions. *Solvent Extr. Ion Exch.* **2006**, *24* (2), 197–217. <https://doi.org/10.1080/07366290500511290>.
- (27) Todd, T.; Batcheller, T. A.; Law, J. D.; Herbst, R. S. *Cesium and Strontium Separation Technologies Literature Review*; Idaho National Engineering and Environmental Laboratory: Idaho, 2004.
- (28) Wang, J.; Zhuang, S. Cesium Separation from Radioactive Waste by Extraction and Adsorption Based on Crown Ethers and Calixarenes. *Nucl. Eng. Technol.* **2020**, *52* (2), 328–336. <https://doi.org/10.1016/j.net.2019.08.001>.
- (29) Zhang, A.; Hu, Q. Removal of Cesium by Countercurrent Solvent Extraction with a Calix[4]Crown Derivative. *Sep. Sci. Technol.* **2017**, *52* (10), 1670–1679. <https://doi.org/10.1080/01496395.2017.1297456>.
- (30) Riddle, C. L.; Baker, J. D.; Law, J. D.; McGrath, C. A.; Meikrantz, D. H.; Mincher, B. J.; Peterman, D. R.; Todd, T. A. Fission Product Extraction (FPEX): Development of a Novel Solvent for the Simultaneous Separation of Strontium and Cesium from Acidic Solutions. *Solvent Extr. Ion Exch.* **2005**, *23* (3), 449–461. <https://doi.org/10.1081/SEI-200058035>.
- (31) Law, J. D.; Garn, T. G.; Herbst, R. S.; Meikrantz, D. H.; Peterman, D. R.; Riddle, C. L.; Todd, T. A.; Tripp, J. L. *Development of Cesium and Strontium Separation and Immobilization Technologies in Support of an Advanced Nuclear Fuel Cycle*; 2006.
- (32) Sharma, J. N.; Kumar, A.; Kumar, V.; Pahan, S.; Janardanan, C.; Tessi, V.; Wattal, P. K. Process Development for Separation of Cesium from Acidic Nuclear Waste Solution Using 1,3-Dioctylloxycalix[4]Arene-Crown-6 + Isodecyl Alcohol/n-Dodecane Solvent. *Sep. Purif. Technol.* **2014**, *135*, 176–182. <https://doi.org/10.1016/j.seppur.2014.08.016>.
- (33) Partridge, J. D. DEVELOPMENT OF THE FPEX II SOLVENT SYSTEM FOR SIMULTANEOUS EXTRACTION OF CESIUM AND STRONTIUM, 2010.
- (34) Orth, R. J.; Brooks, K. P.; Kurath, D. E. *Review and Assessment of Technologies for the Separation of Cesium from Acidic Media*; United States, 1994.
- (35) Lumetta, G. J.; Wagner, M. J.; Carlson, C. D. Actinide, Strontium, and Cesium Removal from Hanford Radioactive Tank Sludge. *Solvent Extr. Ion Exch.* **1996**, *14* (1), 35–60.
- (36) Brooks, K. P.; Kim, A. Y.; Kurath, D. E. *Assessment of Commercially Available Ion Exchange Materials for Cesium Removal from Highly Alkaline Wastes*; Pacific Northwest National Laboratory: Richland, Washington, 1996.
- (37) Fiskum, S. K.; Pease, L. F.; Peterson, R. A. Review of Ion Exchange Technologies for Cesium Removal from Caustic Tank Waste. *Solvent Extr. Ion Exch.* **2020**, *38* (6), 573–611. <https://doi.org/10.1080/07366299.2020.1780688>.
- (38) Brown, G. *Literature Review of Spherical Resorcinol-Formaldehyde for Cesium Ion Exchange*; Office of Scientific and Technical Information (OSTI), 2014. <https://doi.org/10.2172/1160199>.
- (39) King, W. D.; Taylor-Pashow, K. M.; Hang, T.; Fondeur, F. F. *Characterization and CST Batch Contact Equilibrium Testing of Aged TCCR Tank 10H Batch 1A and 2 Process Supernate Samples*; Savannah River National Laboratory, 2019.
- (40) Fiskum, S.; Rovira, A.; Colburn, H.; Carney, A.; Peterson, R. *Cesium Ion Exchange Testing Using a Three-Column System with Crystalline Silicotitanate and Hanford Tank Waste 241-AP-107*; Office of Scientific and Technical Information (OSTI), 2019. <https://doi.org/10.2172/1645027>.
- (41) Pease Iii, L. F.; Fiskum, S. K.; Colburn, H. A.; Schonewill, P. P. *Cesium Ion Exchange with Crystalline Silicotitanate Literature Review*; Office of Scientific and Technical Information (OSTI), 2019. <https://doi.org/10.2172/1491494>.
- (42) Colburn, H. A.; Peterson, R. A. A History of Hanford Tank Waste, Implications for Waste Treatment, and Disposal. *Environ. Prog. Sustain. Energy* **2021**, *40* (1), e13567. <https://doi.org/https://doi.org/10.1002/ep.13567>.
- (43) Prout, W. E.; Russell, E. R.; Groh, H. J. Ion Exchange Absorption of Cesium by Potassium Hexacyanocobalt (II) Ferrate (II). *J. Inorg. Nucl. Chem.* **1965**, *27* (2), 473–479. [https://doi.org/https://doi.org/10.1016/0022-1902\(65\)80367-0](https://doi.org/https://doi.org/10.1016/0022-1902(65)80367-0).
- (44) Clarke, T. D.; Wai, C. M. Selective Removal of Cesium from Acid Solutions with Immobilized Copper Ferrocyanide. *Anal Chem* **1998**, *70* (17), 3708–3711. <https://doi.org/10.1021/ac971138b>.
- (45) Jang, S.-C.; Hong, S.-B.; Yang, H.-M.; Lee, K.-W.; Moon, J.-K.; Seo, B.-K.; Huh, Y. S.; Roh, C. Removal of Radioactive Cesium Using Prussian Blue Magnetic Nanoparticles. *Nanomater. (Basel, Switzerland)* **2014**, *4* (4), 894–901. <https://doi.org/10.3390/nano4040894>.
- (46) Haas, P. A. A REVIEW OF INFORMATION ON FERROCYANIDE SOLIDS FOR REMOVAL OF CESIUM FROM SOLUTIONS. *Sep. Sci. Technol.* **1993**, *28*, 2479–2506.
- (47) Wilmarth, W.; Lumetta, G.; Johnson, M.; Poirier, M.; Thompson, M.; Suggs, P.; Machara, N. Review: Waste-Pretreatment Technologies for Remediation of Legacy Defense Nuclear Wastes. *Solvent Extr. Ion Exch. - SOLVENT EXTR ION EXCH* **2011**, *29*, 1–48. <https://doi.org/10.1080/07366299.2011.539134>.
- (48) Tuyl, H. H. van; Moore, R. L. RECOVERY OF FISSION PRODUCT CESIUM FROM ACIDIC WASTES. *Ind. Eng. Chem.* **1959**, *51*, 741–744.

- (49) Lehto, J.; Harjula, R. Separation of Cesium from Nuclear Waste Solutions with Hexacyanoferrate(II)s and Ammonium Phosphomolybdate. *Solvent Extr. Ion Exch.* **1987**, *5*, 343. <https://doi.org/https://doi.org/10.1080/07366298708918571>.
- (50) Lehto, J.; Haukka, S.; Harjula, R.; Blomberg, M. Mechanism of Cesium Ion Exchange on Potassium Cobalt Hexacyanoferrates(II). *J. Chem. Soc. Dalton Trans* **1990**, *3*, 1007.
- (51) Lehto, J.; Paajanen, A.; Harjula, R. Selectivity of Potassium Cobalt Hexacyanoferrate(II) to Alkali and Alkaline Earth Metal Ions. *J. Radioanal. Nucl. Chem. Lett.* **1992**, *164*, 39.
- (52) Harjula, R.; Lehto, J.; Paajanen, A.; Brodtkin, L.; Tusa, E. Removal of Radioactive Cesium from Nuclear Waste Solutions with the Transition Metal Hexacyanoferrate Ion Exchanger CsTreat. *Nucl. Sci. Eng.* **2001**, *137* (2), 206–214. <https://doi.org/10.13182/NSE01-A2186>.
- (53) Tusa, E. Efficiency of Fortum's CsTreat and SrTreat in Cesium and Strontium Removal in Fukushima Daiichi NPP. In *Proceedings of the European Nuclear Conference - ENC 2014*; European Commission (EC), 2014; p 1238.
- (54) Murphy, P. P.; Buckingham, J. S. *Preliminary Laboratory Investigation for the Removal of Radioactive Cesium from Purex Aqueous Waste Solutions*; United States, 1979. <https://doi.org/10.2172/5916388>.
- (55) Schulz, W. W.; Bray, L. A. Solvent Extraction Recovery of Byproduct 137Cs and 90Sr from HNO<sub>3</sub> Solutions—A Technology Review and Assessment. *Sep. Sci. Technol.* **1987**, *22* (2–3), 191–214. <https://doi.org/10.1080/01496398708068948>.
- (56) Lee, L. M.; Kilpatrick, L. L. *A Precipitation Process for Supernatant Decontamination*; 1992.
- (57) McCabe, D. J. *Cesium, Potassium, and Sodium Tetraphenylborate Solubility In Salt Solution*; Westinghouse Savannah River Company: Aiken, South Carolina, 1996.
- (58) *Alternatives for High-Level Waste Salt Processing at the Savannah River Site*; Council, N. R., Ed.; The National Academies Press: Washington, DC, 2000. <https://doi.org/doi:10.17226/9959>.
- (59) Lambert, D. P.; Peters, T. T.; Fink, S. S. PROCESSING ALTERNATIVES FOR DESTRUCTION OF TETRAPHENYLBORATE. In *International Conference on Incineration and Thermal Treatment Technologies Conference*; Phoenix, AZ, 2007.
- (60) Ferrara, D. M.; Bibler, N. E.; Ha, B. C. *Decomposition of Tetraphenylborate Precipitates Used to Isolate Cs-137 from Savannah River Site High-Level Waste*; Westinghouse Savannah River Company: Aiken, South Carolina, 1993.
- (61) Bray, L. A.; Holton, L. K.; Myers, T. R.; Richardson, G. M.; Wise, B. M. *Experimental Data Developed to Support the Selection of a Treatment Process for West Valley Alkaline Supernatant*; United States, 1984.
- (62) Barnes, M. J. *Decomposition of Sodium Tetraphenylborate*; Westinghouse Savannah River Company: Aiken, South Carolina, 1990.
- (63) Berzelius, J. J. Beitrag Zur Näheren Kenntniss Des Molybdäns. *Poggendorffs Ann. Phys. Chem* **1826**, *6*, 369–380.
- (64) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer: Berlin, 1983.
- (65) van Smit, J. R.; Robb, W.; Jacobs, J. J. Cation Exchange on Ammonium Molybdophosphate—I: The Alkali Metals. *J. Inorganical Nucl. Chem.* **1959**, *12*, 104.
- (66) Sebesta, F.; John, J.; Motl, A.; Stamberg, K.; Watson, J. Development of PAN-Based Absorbers for Treating Waste Problems at U.S. DOE Facilities; Slate, S., Feizollahi, F., Creer, J., Eds.; ACME, 1995; Vol. 1, pp 361–365.
- (67) Sebesta, F.; John, J.; Motl, A. Removal of Cesium and Strontium from Highly Saline Acidic or Alkaline HLW Using PAN-Based Composite Absorbers; Baker, R., Slate, S., Benda, G., Eds.; ACME International; pp 241–244.
- (68) John, J.; Sebesta, F.; Motl, A. Absorbers with Polyacrylonitrile Binding Matrix for Separation of Radionuclides from Liquid Radioactive Wastes. In *Chemical Separation Technologies and Related Methods of Nuclear Waste Management: Applications, Problems, and Research Needs. Proceedings of the NARO Advanced Study Institute, Dubna, Russia, May 18-28, 1998*; Choppin, G., Khankhasayev, M. K., Eds.; Kluwer academic publishers, 1999; pp 155–168.
- (69) Brewer, K. N.; Todd, T. A.; Wood, D. J.; Tullock, P. A.; Sebesta, F.; John, J.; Motl, A. AMP-PAN Column Tests for the Removal of 137Cs from Actual and Simulated INEEL High-Activity Wastes. *Czechoslov. J. Phys.* **1999**, *49* (1), 959–964. <https://doi.org/10.1007/s10582-999-1024-1>.
- (70) Tranter, T. J.; Herbst, R. S.; Todd, T.; Olson, A. L.; Eldredge, B. Evaluation of Ammonium Molybdophosphate-Polyacrylonitrile (AMP-PAN) as a Cesium Selective Sorbent for the Removal of 137Cs from Acidic Nuclear Waste Solutions. *Adv. Environ. Res.* **2002**, *6*, 107–121. [https://doi.org/10.1016/S1093-0191\(00\)00073-3](https://doi.org/10.1016/S1093-0191(00)00073-3).
- (71) Mimura, H.; Saito, M.; Akiba, K.; Onodera, Y. Selective Uptake of Cesium by Ammonium Molybdophosphate (AMP)-Calcium Alginate Composites. *J. Nucl. Sci. Technol.* **2001**, *38* (10), 872–878.
- (72) Howden, M.; Pilot, J. The Choice of Ion Exchanger for British Nuclear Fuels Ltd's Site Ion Exchange Effluent Plant. In *Ion Exchange Technology*; Naden, D., Streat, M., Eds.; Ellis Horwood: London, 1984; pp 66–73.
- (73) Lewis, R. E.; Butler, T. A.; Lamb, E. An Aluminosilicate Ion Exchanger for Recovery and Transport of 137Cs from Fission-Product Wastes. *Nucl. Sci. Eng.* **1966**, *24* (2), 118–122. <https://doi.org/10.13182/NSE66-A18296>.
- (74) Barton, W.; Gale, L.; Johnson, M. Sixteen Years of Cesium Recovery Processing at Hanford's B Plant. In *American Nuclear Society International, Spectrum 86*; Niagara Falls, 1986.
- (75) Platt, A. M. *Quarterly Progress Report: Research and Development Activities Fixation of Radioactive Residues, October - December, 1964*; Hanford Atomic Products Operation; U. S. Atomic Energy Commission: Richland, Wash., 1965.
- (76) Harjula, R.; Lehto, J. Effect of Sodium and Potassium Ions on Cesium Absorption from Nuclear Power Plant Waste Solutions on Synthetic Zeolites. *Nucl. Chem. Waste Manag.* **1986**, *6* (2), 133–137. [https://doi.org/https://doi.org/10.1016/0191-815X\(86\)90051-3](https://doi.org/https://doi.org/10.1016/0191-815X(86)90051-3).

- (77) Koivula, R. Inorganic Ion Exchangers for Decontamination of Radioactive Wastes Generated by the Nuclear Power Plants. Academic Dissertation., University of Helsinki, Faculty of Science, Department of Chemistry, Laboratory of Radiochemistry, 2003.
- (78) Nelson, J. L.; Alkire, G. J.; Mercer, B. W. Inorganic Ion Exchange Separation of Cesium from Purex-Type High-Level Radioactive Wastes. *Ind. Eng. Chem. Process Des. Dev.* **1964**, *3* (2), 143–148. <https://doi.org/10.1021/i260010a009>.
- (79) Buckingham, J. S. *Laboratory Evaluation of an Ion Exchange Process for Removing Cesium from Purex Acid Waste Solutions*; United States, 1979.
- (80) Donnet, L.; Morita, Y.; Yamagishi, I.; Kubota, M. *DEVELOPMENT OF PARTITIONING METHOD: ADSORPTION OF CESIUM WITH MORDENITE IN ACIDIC MEDIA*; Japan Atomic Energy Research Institute: Tokai-mura, Naka-gun, Ibaraki-ken, Japan, 1998.
- (81) Hamm, B. A. *Tank Farm Zeolite. Historical Review and Current Inventory Assessment*; 2005.
- (82) Kot, W. K.; Brandys, M.; Pegg, I. L.; Penafiel, M. *Final Report: Vitrification of Inorganic Ion-Exchange Media*; Vitreous State Laboratory The Catholic University of America: Washington, 2016.
- (83) Baetslé, L.; Huys, D.; Speeckaert, P. *Separation of 137Cs and 90Sr from Highly Radioactive Fission Product Solutions*; Centre d'Etudes de l'Energie Nucléaire: Mol (Belgium), 1973.
- (84) FAUBEL, W.; ALI, S. A. Separation of Cesium from Acid ILW-Purex Solutions by Sorption on Inorganic Ion Exchangers. *Radiochim. Acta* **1986**, *40* (1), 49–56. <https://doi.org/doi:10.1524/ract.1986.40.1.49>.
- (85) Bortun, A. I.; Bortun, L. N.; Stepin, A. A.; Pekhamkina, N. P. 137Cs Sorption on Granular Inorganic Ion-Exchangers Based on Titanium and Zirconium Hydroxophosphates. *J. Radioanal. Nucl. Chem.* **1993**, *174* (2), 279–289. <https://doi.org/10.1007/BF02037915>.
- (86) Narbutt, J.; Bilewicz, A.; Bartos, B. Composite Ion Exchangers: Prospective Nuclear Applications. *J. Radioanal. Nucl. Chem.* **1994**, *183* (1), 27–32. <https://doi.org/https://doi.org/10.1007/bf02043113>.
- (87) Möller, T.; Clearfield, A.; Harjula, R. The Effect of Cell Dimensions of Hydrous Mixed Metal Oxides with a Pyrochlore Structure on the Ion-Exchange Properties. *Chem. Mater.* **2001**, *13* (12), 4767–4772. <https://doi.org/10.1021/cm011151j>.
- (88) Dosch, R. G.; Klavetter, E. A.; Stephens, H. P.; Brown, N. E.; Anthony, R. G. *Crystalline Silicotitanates—New Ion Exchanger for Selective Removal of Cesium and Strontium From Radwastes*; Sandia National Laboratories: Albuquerque, New Mexico and Livermore, California, 1996.
- (89) Walker, J. F.; Taylor, P. A.; Lee, D. D. CESIUM REMOVAL FROM HIGH-PH, HIGH-SALT WASTEWATER USING CRYSTALLINE SILICOTITANATE SORBENT. *Sep. Sci. Technol.* **1999**, *34* (6–7), 1167–1181. <https://doi.org/10.1080/01496399908951087>.
- (90) Miller, J.; Brown, N.; Krumhansl, J.; Trudell, D.; Anthony, R.; Philip, C. Development and Properties of Cesium Selective Crystalline Silicotitanate (CST) Ion Exchangers for Radioactive Waste Applications; 1998; pp 269–286. [https://doi.org/10.1007/978-1-4899-1543-6\\_21](https://doi.org/10.1007/978-1-4899-1543-6_21).
- (91) Dosch, R. G. *Ceramics from Ion Exchangers: An Approach to Nuclear Waste Solidification*; United States, 1975.
- (92) Lynch, R. W.; Dosch, R. G.; Kenna, B. T.; Johnstone, J. K.; Nowak, E. J. *Sandia Solidification Process: A Broad Range Aqueous Waste Solidification Method*; United States, 1976.
- (93) Dosch, R. G. *Application of Titanates, Niobates, and Tantalates to Neutralized Defense Waste Decontamination: Materials Properties, Physical Forms, and Regeneration Techniques. Final Report*; United States, 1981. <https://doi.org/10.2172/6886911>.
- (94) Poojary, D. M.; Cahill, R. A.; Clearfield, A. Synthesis, Crystal Structures, and Ion-Exchange Properties of a Novel Porous Titanosilicate. *Chem. Mater.* **1994**, *6* (12), 2364–2368. <https://doi.org/10.1021/cm00048a024>.
- (95) Bortun, A. I.; Bortun, L. N.; Clearfield, A. Ion Exchange Properties of a Cesium Ion Selective Titanosilicate. *Solvent Extr. Ion Exch.* **1996**, *14* (2), 341–354. <https://doi.org/10.1080/07366299608918343>.
- (96) Bray, L. A.; Carson, K. J.; Elovich, R. J. *Initial Evaluation of Sandia National Laboratory-Prepared Crystalline Silico-Titanates for Cesium Recovery*; United States, 1993.
- (97) Walker, J. F.; Taylor, P. A.; Cummins, R. L.; Evans, B. S.; Heath, S. D.; Hewitt, J. D.; Hunt, R. D.; Jennings, H. L.; Kilby, J. A.; Lee, D. D.; et al. *Cesium Removal Demonstration Utilizing Crystalline Silicotitanate Sorbent for Processing Melton Valley Storage Tank Supernate*; Oak Ridge, Tennessee, 1998.
- (98) Energy, U. S. D. of. *Innovative Technology, Summary Report: Cesium Removal Using Crystalline Silicotitanate*; 1999.
- (99) Chen, T.-Y.; Maddrell, E. R.; Hyatt, N. C.; Gandy, A. S.; Stennett, M. C.; Hriljac, J. A. Transformation of Cs-IONSIV® into a Ceramic Wasteform by Hot Isostatic Pressing. *J. Nucl. Mater.* **2018**, *498*, 33–43. <https://doi.org/https://doi.org/10.1016/j.jnucmat.2017.10.011>.
- (100) Todd, T. A.; Brewer, K. N.; Wood, D. J.; Tullock, P. A.; Mann, N. R.; Olson, L. G. EVALUATION AND TESTING OF INORGANIC ION EXCHANGE SORBENTS FOR THE REMOVAL OF CESIUM-137 FROM ACTUAL IDAHO NUCLEAR TECHNOLOGY AND ENGINEERING CENTER ACIDIC TANK WASTE. *Sep. Sci. Technol.* **2001**, *36* (5–6), 999–1016. <https://doi.org/10.1081/SS-100103633>.
- (101) Todd, T. A.; Romanovskiy, V. N. A Comparison of Crystalline Silicotitanate and Ammonium Molybdophosphate-Polyacrylonitrile Composite Sorbent for the Separation of Cesium from Acidic Waste. *Radiochemistry* **2005**, *47* (4), 398–402. <https://doi.org/10.1007/s11137-005-0109-3>.
- (102) Mann, N. R.; Todd, T. A. Removal of Cesium From Acidic Radioactive Tank Waste Using IONSIV IE-911 (CST). *Sep. Sci.*

- Technol.* **2004**, 39 (10), 2351–2371. <https://doi.org/DOI:101081/SS-120039321>.
- (103) Tripathi, A.; Medvedev, D.; Nyman, M.; Clearfield, A. Selectivity for Cs and Sr in Nb-Substituted Titanosilicate with Sitinakite Topology. *J. Solid State Chem. - J SOLID STATE CHEM* **2003**, 175, 72–83. [https://doi.org/10.1016/S0022-4596\(03\)00145-2](https://doi.org/10.1016/S0022-4596(03)00145-2).
- (104) NYMAN, M. A. Y. D.; NENOFF, T. M.; HEADLEY, T. J. *Characterization of UOP IONSIV IE-911*; United States, 2001. <https://doi.org/10.2172/791880>.
- (105) Celestian, A. J.; Kubicki, J. D.; Hanson, J.; Clearfield, A.; Parise, J. B. The Mechanism Responsible for Extraordinary Cs Ion Selectivity in Crystalline Silicotitanate. *J. Am. Chem. Soc.* **2008**, 130 (35), 11689–11694. <https://doi.org/10.1021/ja801134a>.
- (106) Hamm, L. L.; Hang, T.; McCabe, D. J.; King, W. D. *Preliminary Ion Exchange Modeling for Removal of Cesium from Hanford Waste Using Hydrous Crystalline Silicotitanate Material*; Westinghouse Savannah River Company: Aiken, 2002.
- (107) Walker, D. D.; Kent, T. E. *Wastewater Triad Project: Final Summary Report*; Oak Ridge National Laboratory: Oak Ridge, 2001.
- (108) Taylor, P. A.; Mattus, C. Thermal and Chemical Stability of Crystalline Silicotitanate Sorbent. **1999**. <https://doi.org/10.2172/750983>.
- (109) Walker, D. D.; Adamson, D. J.; Allen, T. D.; Blessing, R. W.; Boyce, W. T.; Croy, B. H.; Drewberry, R. A.; Diprete, D. P.; Fink, S. D.; Hang, T.; et al. *Cesium Removal from Savannah River Site Radioactive Waste Using Crystalline Silicotitanate (Ionsiv IE911)*; Westinghouse Savannah River Company: Aiken, South Carolina, 1999.
- (110) Welch, T. D.; Anderson, K. K.; Bostick, D. A.; Dillow, T. A.; Getting, M. W.; Hunt, R. D.; Lenarduzzi, R.; Mattus, A. J.; Taylor, P. A.; Wilmarth, W. R. *Hydraulic Performance and Gas Behavior of a Tall Crystalline Silicotitanate Ion-Exchange Column*; Oak Ridge National Laboratory: Oak Ridge, TN, 2000.
- (111) Nyman, M.; Krumhansl, J. L.; Jove-Colon, C.; Zhang, P.; Nenoff, T. M.; Headley, T. J.; Su, Y.; Li, L. Chemical Interactions of UOP IONSIV® IE-911 (CST) with SRS Waste Simulants. *MRS Online Proc. Libr.* **2002**, 713 (1), 124. <https://doi.org/10.1557/PROC-713-JJ12.4>.
- (112) Taylor, P. A.; Mattus, C. Thermal And Chemical Stability Of Baseline And Improved Crystalline Silicotitanate. *Sep. Sci. Technol. - SEPAR SCI TECHNOL* **2003**, 38, 3031–3048. <https://doi.org/10.1081/SS-120022585>.
- (113) Wilmarth, W.; Dukes, V. H.; Mills, J. T. *Reactivity of Crystalline Silicotitanate (CST) and Hazardous Metal/Actinide Loading During Low Curie Salt Use*; Westinghouse Savannah River Company: Aiken, South Carolina, 2004.
- (114) Adu-Wusu, K.; Pennebaker, F. LITERATURE REVIEW ON MAXIMUM LOADING OF RADIONUCLIDES ON CRYSTALLINE SILICOTITANATE. **2010**. <https://doi.org/10.2172/1041519>.
- (115) Rovira, A. M.; Fiskum, S. K.; Colburn, H. A.; Allred, J. R.; Smoot, M. R.; Peterson, R. A.; Colisi, K. M. Cesium Ion Exchange Testing Using Crystalline Silicotitanate with Hanford Tank Waste 241-AP-107. *Sep. Sci. Technol.* **2019**, 54 (12), 1942–1951. <https://doi.org/10.1080/01496395.2019.1577895>.
- (116) Campbell, E.; Westesen, A.; Colon, F.; Boglaienko, D.; Levitskaia, T.; Peterson, R. Elemental Characterization of Crystalline Silicotitanate Following Hanford Tank Waste Processing. *Sep. Sci. Technol.* **2020**, 56, 1–9. <https://doi.org/10.1080/01496395.2020.1777429>.
- (117) Campbell, E. L.; Fiskum, S. K.; Trang-Le, T. T.; Peterson, R. A. Ion Exchange of Selected Group II Metals and Lead by Crystalline Silicotitanate and Competition for Cs Exchange Sites. *Solvent Extr. Ion Exch.* **2021**, 39 (1), 90–103. <https://doi.org/10.1080/07366299.2020.1830481>.
- (118) Baumgarten, P. K.; Wallace, R. M.; Whitehurst, D. A.; Steed, J. M. DEVELOPMENT OF AN ION-EXCHANGE PROCESS FOR REMOVING FROM HIGH-LEVEL RADIOACTIVE LIQUID WASTES. In *Proceedings of the Symposium on the Scientific Basis for Nuclear Waste Management*; Plenum Press, New York: Boston, Massachusetts, 1979; Vol. 2, p 875.
- (119) Wallace, R. M.; Ferguson, R. B. DEVELOPMENT OF AN IMPROVED ION-EXCHANGE PROCESS FOR REMOVING CESIUM AND STRONTIUM FROM HIGH-LEVEL RADIOACTIVE LIQUID WASTES. In *The third International Symposium on the Scientific Basis for Nuclear Waste Management*; Plenum Press: Boston, Massachusetts, 1980; Vol. 3, p 75.
- (120) Kolarik, Z. *Separation of Actinides and Long-Lived Fission Products from High-Level Radioactive Wastes (a Review)*; Kernforschungszentrum Karlsruhe GmbH (Germany). Inst. fuer Heisse Chemie, 1991.
- (121) Chilton, J. M. *An Evaluation of the Low-Level Waste Treatment Plant at Oak Ridge National Laboratory, and Suggested Changes in the Design and Operation*; Oak Ridge National Laboratory: Oak Ridge, Tennessee, 1980.
- (122) Roberts, J. T.; Holcomb, R. R. A PHENOLIC RESIN ION EXCHANGE PROCESS FOR DECONTAMINATING LOW-RADIOACTIVITY- LEVEL PROCESS WATER WASTES; United States, 1961. <https://doi.org/Other Information: Orig. Receipt Date: 31-DEC-61>.
- (123) Holcomb, R. R.; Roberts, J. T. LOW LEVEL WASTE TREATMENT BY ION-EXCHANGE, II. USE OF A WEAK ACID, CARBOXYLIC-&HENOLIC ION-EXCHANGE RESIN; Oak Ridge National Laboratory.; Oak Ridge, Tenn.;, 1961.
- (124) Holcomb, R. R. LOW-RADIOACTIVITY-LEVEL WASTE TREATMENT. PART I. LABORATORY DEVELOPMENT OF A SCAVENGING-PRECIPIATION ION-EXCHANGE PROCESS FOR DECONTAMINATION OF PROCESS WATER WASTES; United States, 1963. <https://doi.org/10.2172/4686390>.
- (125) Brooksbank, R. E.; Browder, F. N.; Holcomb, R. R.; Whitson, W. R. *Low-Radioactivity-Level Waste Treatment, Part II; Pilot Plant Demonstration of the Removal of Activity from Low-Level Process Wastes by a Scavenging-Precipitation Ion-Exchange Process*; Oak Ridge National Laboratory: Oak Ridge, Tennessee, 1963.

- (126) Harrington, F. E.; Holmes, J. M. *Design Study - New ORNL Process Waste Treatment Plant*; Oak Ridge National Laboratory: Oak Ridge, Tennessee, 1972.
- (127) Chilton, J. M.; Lasher, L. C. Decontamination of Low-Level Liquid Waste at Oak Ridge National Laboratory Using a Scavenging-Precipitation, Ion Exchange Process. In *Waste Management '82 Conference*; Tucson, Arizona, 1982.
- (128) Bibler, J. P.; Wallace, R. M.; Laboratory, S. R. *Preparation and Properties of a Cesium-Specific Resorcinol-Formaldehyde Ion Exchange Resin*; Aiken, 1987.
- (129) Bibler, J. P.; Wallace, R. M.; Bray, L. A. Testing a New Cesium-Specific Ion Exchange Resin for Decontamination of Alkaline High-Activity Waste; 1990; Vol. 2, pp 747–751.
- (130) Ebra, M. A.; Wallace, R. M. Phenolic Cation Exchange Resin Material for Recovery of Cesium and Strontium, 1983.
- (131) Kaczvinsky, J.; Fritz, J.; Walker, D.; Ebra, M. Synthesis and Development of Porous Chelating Polymers for the Decontamination of Nuclear Waste. *J. Radioanal. Nucl. Chem.* **1985**, *91* (2), 349–360. <https://doi.org/10.1007/bf02061038>.
- (132) Kaczvinsky, J. R.; Fritz, J. S.; Walker, D. D.; Ebra, M. A. The Effects of Reaction Conditions on Porous Chelating Polymers Designed for the Decontamination of Nuclear Waste. *J. Radioanal. Nucl. Chem.* **1987**, *116* (1), 63–75. <https://doi.org/10.1007/BF02037211>.
- (133) Campbell, D. O.; Lee, D. D.; Dillow, T. A.; Laboratory, O. R. N. *Low-Level Liquid Waste Decontamination by Ion Exchange*; 1990.
- (134) Kurath, D. E.; Bray, L. A.; Brooks, K. P.; Brown, G. N.; Bryan, S. A.; Carlson, C. D.; Carson, K. J.; DesChane, J. R.; Elovich, R. J.; Kim, A. Y. *Experimental Data and Analysis to Support the Design of an Ion-Exchange Process for the Treatment of Hanford Tank Waste Supernatant Liquids*; United States, 1994.
- (135) Wallace, R. M.; Bibler, J. P.; Laboratory, S. R. *An Improved Method for Decontamination Soluble High-Level Waste Using Ion Exchange*; Aiken, 1988.
- (136) Bibler, J. P.; Company, W. S. R. *A Comparison of Duolite[TM] CS-100 and SRS Resorcinol-Formaldehyde Ion Exchange Resins with Three High-Level Waste Simulants Before and After  $\gamma$ -Irradiation*; 1991.
- (137) Bray, L. A.; Carson, K. J.; Elovich, R. J.; Kurath, D. E.; Laboratories, P. N. *Equilibrium Data for Cesium Ion Exchange of Hanford CC and NCAW Tank Waste*; 1992.
- (138) Campbell, D. O.; Lee, D. D.; Dillow, T. A. *Low-Level Liquid Waste Decontamination by Ion Exchange*; p 389.
- (139) Brooks, K. P.; Augspurger, B. S.; Blanchard, D. L.; Cuta, J. M.; Fiskum, S. K.; Thorson, M. R. Hydraulic Testing of Ion Exchange Resins for Cesium Removal from Hanford Tank Waste. *Sep. Sci. Technol.* **2006**, *41* (11), 2391–2408. <https://doi.org/10.1080/01496390600742724>.
- (140) Hassan, N. M.; McCabe, D. J.; King, W. D.; Hamm, L. L.; Johnson, M. E. SuperLig 644 Equilibrium Sorption Data for Cesium from Hanford Tank Waste Supernates. *J. Radioanal. Nucl. Chem.* **2002**, *253* (3), 361–367.
- (141) Hassan, N. M.; McCabe, D. J.; King, W. D.; Hamm, L. L.; Johnson, M. E. Ion Exchange Removal of Cesium from Hanford Tank Waste Supernates with SuperLig 644 Resin. *J. Radioanal. Nucl. Chem.* **2002**, *254* (1), 33–40.
- (142) Hassan, N. M.; Nash, C. A.; Saito, H. H.; Marra, J. C.; Company, W. S. R. *The Effect of Temperature on SuperLig 644 Cesium Removal from Simulated Hanford Tank Waste Supernate*; Aiken, South Carolina 29808, 2002.
- (143) Hassan, N. M.; Nash, C. A.; Saito, H. H.; Marra, J. C.; Company, W. S. R. *SuperLig 644 Resin Accelerated Aging Study*; Aiken, South Carolina 29802, 2002.
- (144) Fiskum, S. K.; Blanchard, D. L.; Arm, S. T.; Peterson, R. A. Cesium Removal from Simulated and Actual Hanford Tank Waste Using Ion Exchange. *Sep. Sci. Technol.* **2005**, *40* (1–3), 51–67. <https://doi.org/10.1081/SS-200041760>.
- (145) Steimke, J. L.; Norato, M. A.; Steeper, T. J.; McCabe, D. J. *Summary of Initial Testing of SuperLig 644 at the TFL Ion Exchange Facility*; Westinghouse Savannah River Company: Aiken, SC, 2001.
- (146) Kurath, D. E.; Wagner, J. J. *Analysis of Spent Ion Exchange Media: Superlig 639 and Superlig 644*; Pacific Northwest National Lab. (PNNL): Richland, WA (United States), 2000. <https://doi.org/10.2172/755816>.
- (147) Arm, S. T.; Blanchard, D. L.; Brooks, K. P.; Buchmiller, W. C.; Cook, B. J.; Cuta, J. M.; Fiskum, S. K.; Hontz, Z.; Isackson, C.; Schepmoes, A. A.; et al. *Laboratory Scale Hydraulic Testing of Spherical Resorcinol Formaldehyde Ion Exchange Resins*; Batelle - Pacific Northwest Division: Richland, Washington, 2006.
- (148) Fiskum, S. K.; Blanchard, D. L.; Steele, M. J.; Wagner, J. J. Analysis of Spent SuperLig® 644 Resin Used for Cesium Removal from Hanford Tank Wastes. *Solvent Extr. Ion Exch.* **2006**, *24* (1), 65–79. <https://doi.org/10.1080/07366290500388426>.
- (149) Hassan, N. M.; Adu-Wusu, K. Cesium Removal from Hanford Tank Waste Solution Using Resorcinol-Formaldehyde Resin. *Solvent Extr. Ion Exch.* **2005**, *23* (3), 375–389. <https://doi.org/10.1081/SEI-200056519>.
- (150) Berge, A.; Nilsen, T.-N.; Bjørgum, J.-O.; Ugelstad, J. Process for Preparing a Dispersion and for Preparing Polymer Particles, 1997.
- (151) Fiskum, S. K.; Augspurger, B. S.; Brooks, K. P.; Buchmiller, W. C.; Russell, R. L.; Schweiger, M. J.; Snow, L. A.; Steele, M. J.; Thomas, K. K.; Wallace, D. E.; et al. *Comparison Testing of Multiple Resorcinol-Formaldehyde Resins for the River Protection Project—Waste Plant*; Batelle-Pacific Northwest Division: Richland, WA, 2004.
- (152) Fiskum, S. K.; Arm, S. T.; Buchmiller, W. C.; Trang-Le, T.; Martinez, J. E.; Matyas, J.; Steele, M. J.; Thomas, K. K.; Blanchard Jr., D. L. *Comparison Testing of Multiple Spherical Resorcinol-Formaldehyde Resins for the River Protection Project—Waste Treatment Plant*; Batelle-Pacific Northwest Division: Richland, WA, 2006.
- (153) Fiskum, S. K.; Arm, S. T.; Steele, M. J.; Thorson, M. R. Spherical Resorcinol-Formaldehyde Performance Testing with

- Hanford Tank Waste. *Solvent Extr. Ion Exch.* **2008**, 26 (4), 435–452. <https://doi.org/10.1080/07366290802182691>.
- (154) Fiskum, S. K.; Allred, J. R.; Colburn, H. A.; Rovira, A. M.; Smoot, M. R.; Peterson, R. A. *Multi-Cycle Cesium Ion Exchange Testing Using Spherical Resorcinol-Formaldehyde Resin with Diluted Hanford Tank Waste 241-AP-105*; United States, 2018. <https://doi.org/10.2172/1511057>.
- (155) Fiskum, S. K.; Peterson, R. A.; Colburn, H. A.; Smoot, M. R.; Landon, M. R.; Colosi, K. A.; Wilson, R. A. Small- to Large-Scale Comparisons of Cesium Ion Exchange Performance with Spherical Resorcinol Formaldehyde Resin. *Sep. Sci. Technol.* **2019**, 54 (12), 1922–1931. <https://doi.org/10.1080/01496395.2019.1570262>.
- (156) Nash, C.; Duignan, M. *CHARACTERIZATION OF CYCLED SPHERICAL RESORCINOL-FORMALDEHYDE ION EXCHANGE RESIN*; United States, 2010. <https://doi.org/10.2172/1024202>.
- (157) Chiarizia, R.; Horwitz, E. P.; Alexandros, S. D. Diphenyl-Cs: A Novel Combined Cesium and Strontium Selective Ion Exchange Resin. *Solvent Extr. Ion Exch.* **1998**, 16, 875–898.
- (158) Chiarizia, R.; Horwitz, E. P. Radiolytic Stability of Some Recently Developed Ion Exchange and Extraction Chromatographic Resins Containing Diphosphonic Acid Groups. *Solvent Extr. Ion Exch.* **2000**, 18 (1), 109–132.
- (159) Lin, Z. C.; Inn, K. G. W. An Accurate, Precise, and Rapid Method for Analysis of Low-Level Sr-90 in NIST Bone Ash Standard Reference Material in: Abstracts of Conference Presentations and Posters of the 44th Bioassay Analytical & Environmental Radiochemistry (BEAR) Conference, Alb; 1998.
- (160) Chu, T. C.; Wang, J. J.; Lin, Y. M. Radiostromium Analytical Method Using Crown-Ether Compound and Cerenkov Counting and Its Applications in Environmental Monitoring. *Appl. Radiat. Isot.* **1998**, 49, 1671–1675.
- (161) Heilgeist, M. Use of Extraction Chromatography, Ion Chromatography and Liquid Scintillation Spectrometry for Rapid Determination of Strontium-89 and Strontium-90 in Food in Cases of Increased Release of Radionuclides. *J. Radioanal. Nucl. Chem.* **2000**, 245 (2), 249–254.
- (162) Scasnar, V.; Koprda, V. Extraction Chromatographic Concentration of <sup>137</sup>Cs from a Mixture of Radionuclides. *Radiochem. Radioanal. Lett.* **1982**, 50 (6), 333–343.
- (163) Smulek, W.; Lada, W. Separation of Alkali Metals by Extraction Chromatography Using Polyethers. *Radiochem. Radioanal. Lett.* **1977**, 30 (3), 199–207.
- (164) Peimli, E. Extraction Chromatography of Cs and Na Using Crown Ethers Loaded on a Solid Support. *J. Radioanal. Nucl. Chem.* **1990**, 144 (1), 9–15.
- (165) Dietz, M. L.; Ensor, D. D.; Harmon, B.; Seekamp, S. Separation and Preconcentration of Cesium from Acidic Media by Extraction Chromatography. *Sep. Sci. Technol.* **2006**, 41 (10), 2183–2204. <https://doi.org/10.1080/01496390600744480>.
- (166) Horsley, D. M. C.; Howden, M. The Reduction of Radioactive Discharges from Sellafield. In *Effluent treatment and waste disposal conference*; Leeds, 1990.
- (167) Hofstetter, K. J.; Hitz, C. G. The Use of the Submerged Demineralizer System at Three Mile Island. *Sep. Sci. Technol.* **1983**, 18 (14–15), 1747–1764. <https://doi.org/10.1080/01496398308056125>.
- (168) Collins, E. D.; Campbell, D. O.; King, L. J.; Knauer, J. B.; Wallace, R. M. Evaluation of Zeolite Mixtures for Decontaminating High-Activity-Level Water at the Three Mile Island Unit 2 Nuclear Power Station. *Conference: IAEA Technical Committee meeting on inorganic ion exchangers and absorbents for chemical processing in the nuclear fuel cycle, Vienna, Austria, 12-15 Jun 1984; Other Information: Portions are illegible in microfiche products*. United States 1984, p Medium: ED; Size: Pages: 20.
- (169) Bray, L. A.; Van Tuyl, H. H. *LABORATORY DEVELOPMENT OF A CARRIER-PRECIPITATION PROCESS FOR THE RECOVERY OF STRONTIUM FROM PUREX WASTES*; United States, 1961. <https://doi.org/10.2172/4789683>.
- (170) Bray, L. A.; Lust, L. F.; Moore, R. L.; Roberts, F. P.; Smith, F. M.; Van Tuyl, H. H.; Wheelwright, E. J. *THE RECOVERY AND PURIFICATION OF MULTI-KILOCURIE QUANTITIES OF FISSION PRODUCT STRONTIUM BY CATION EXCHANGE*; Hanford Atomic Production Operations: Richland, WA, 1961. <https://doi.org/10.2172/4800556>.
- (171) Richardson, G. L. *RECOVERY OF STRONTIUM FROM STORED PUREX WASTE BY LEAD SULFATE CARRIER PRECIPITATION--PILOT PLANT STUDIES*; Pacific Northwest Laboratory: Richland, WA, 1965.
- (172) Orth, R. J.; Kurath, D. E. *Review and Assessment of Technologies for the Separation of Strontium from Alkaline and Acidic Media*; Pacific Northwest Laboratory, 1994.
- (173) Gutman, R. G.; Cumming, I. W.; Williams, G. H. *Active Liquid Treatment by a Combination of Precipitation and Membrane Processes*; United Kingdom, 1986.
- (174) Haomin, W.; Zhaoxiang, S. Recovery of Cesium and Strontium from Acidic HLW from Power Reactors with Inorganic Ion Exchangers. In *Waste management '92*; Arizona Board of Regents: Tucson, Arizona, 1992.
- (175) Lehto, J.; Miettinen, J. K. *Sodium Titanate A Highly Selective Inorganic Ion Exchanger for Strontium*; International Atomic Energy Agency (IAEA), 1985.
- (176) Ying, Y.; Meiqiong, L.; Xiannua, F. TREATMENT OF LIQUID WASTES CONTAINING ACTINIDES AND FISSION PRODUCTS USING SODIUM TITANATE AS AN ION EXCHANGER; IAEA: Vienna, 1984; pp 223-.
- (177) Hobbs, D. T.; Barnes, M. J.; Pulmano, R. L.; Marshall, K. M.; Edwards, T. B.; Bronikowski, M. G.; Fink, S. D. Strontium and Actinide Separations from High Level Nuclear Waste Solutions Using Monosodium Titanate 1. Simulant Testing. *Sep. Sci. Technol.* **2005**, 40 (15), 3093–3111. <https://doi.org/10.1080/01496390500385129>.
- (178) Peters, T. B.; Barnes, M. J.; Hobbs, D. T.; Walker, D. D.; Fondeur, F. F.; Norato, M. A.; Fink, S. D.; Pulmano, R. L. Strontium and Actinide Separations from High Level Nuclear Waste Solutions Using Monosodium Titanate 2. Actual Waste

- Testing. *Sep. Sci. Technol.* **2006**, *41* (11), 2409–2427. <https://doi.org/10.1080/01496390600742963>.
- (179) Peters, T. B.; Poirier, M. R.; Fink, S. D. Processing Macrobatch 2 at the Savannah River Site Integrated Salt Disposition Process (ISDP). *Sep. Sci. Technol.* **2010**, *45* (12–13), 1801–1806. <https://doi.org/10.1080/01496395.2010.494710>.
- (180) Hobbs, D.; Peters, T.; Taylor-Pashow, K.; Fink, S. Development of an Improved Titanate-Based Sorbent for Strontium and Actinide Separations under Strongly Alkaline Conditions. *Sep. Sci. Technol.* **2011**, *46*, 119–129. <https://doi.org/10.1080/01496395.2010.492772>.
- (181) Nyman, M.; Hobbs, D. A Family of Peroxo-Titanate Materials Tailored for Optimal Strontium and Actinide Sorption. *Chem. Mater.* **2006**, *18*. <https://doi.org/10.1021/cm061797h>.
- (182) Nyman, M. D.; Hobbs, D. T. Hydrogen Peroxide Modified Sodium Titanates with Improved Sorption Capabilities, 2009.
- (183) Lehto, J.; Brodtkin, L.; Harjula, R.; Tusa, E. SrTreat - A Highly Effective Ion Exchanger for the Removal of Radioactive Strontium from Nuclear Waste Solutions; Singapore, 1997; pp 245–248.
- (184) Lehto, J.; Brodtkin, L.; Harjula, R.; Tusa, E. Separation of Radioactive Strontium from Alkaline Nuclear Waste Solutions with the Highly Effective Ion Exchanger SrTreat. *Nucl. Technol.* **1999**, *127* (1), 81–87. <https://doi.org/10.13182/NT99-A2985>.
- (185) Horwitz, E. P.; Chiarizia, R.; Dietz, M. L. A Novel Strontium Selective Extraction Chromatographic Resin. *Solvent Extr. Ion Exch.* **1992**, *10*, 313–336.
- (186) Lumetta, G. J.; Wester, D. W.; Morrey, J. R.; Wagner, M. J. PRELIMINARY EVALUATION OF CHROMATOGRAPHIC TECHNIQUES FOR THE SEPARATION OF RADIONUCLIDES FROM HIGH-LEVEL RADIOACTIVE WASTE. *Solvent Extr. Ion Exch.* **1993**, *11* (4), 663–682. <https://doi.org/10.1080/07366299308918180>.
- (187) Rodríguez, M.; Suárez, J. A.; Espartero, A. G. Separation of Radioactive Strontium by Extraction Using Chromatographic Resin. *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.* **1996**, *369* (2), 348–352. [https://doi.org/https://doi.org/10.1016/S0168-9002\(96\)80007-6](https://doi.org/https://doi.org/10.1016/S0168-9002(96)80007-6).
- (188) Tavčar, P.; Smodiš, B.; Benedik, L. Radiological Characterization of Low-and Intermediate-Level Radioactive Wastes. *J. Radioanal. Nucl. Chem.* **2007**, *273* (3), 593–596. <https://doi.org/10.1007/s10967-007-0916-4>.
- (189) Lee, M. H.; Park, J.-H.; Song, K. Determination of Plutonium, Uranium and Americium/Curium Isotopes in Environmental Samples with Anion Exchange, UTEVA, Sr and DGA Resin. *Proc. Radiochem.* **2011**, *1* (1), 189–194. <https://doi.org/doi:10.1524/rcpr.2011.0034>.
- (190) Shao, Y.; Yang, G.; Tazoe, H.; Ma, L.; Yamada, M.; Xu, D. A Review of Measurement Methodologies and Their Applications to Environmental <sup>90</sup>Sr. *J. Environ. Radioact.* **2018**, *192*, 321–333. <https://doi.org/https://doi.org/10.1016/j.jenvrad.2018.07.013>.
- (191) Piraner, O.; Jones, R. L. The Effect of Sr Resin Cartridge Age on Stable Sr Recovery Methods Used in Sr-90 Analysis. *J. Radioanal. Nucl. Chem.* **2021**, *328*, 369–375. <https://doi.org/10.1007/s10967-021-07628-9>.