# D2EHPA based strontium removal from strongly alkaline nuclear waste

N.M. Kocherginsky[a]*, Y.K. Zhang[a], J.W. Stucki[b]

[a]Department of Chemical and Environmental Engineering, National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260
Tel. +65 874-5083; Fax +65 779-1936; emails: chenk@nus.edu.sg, chezyk@nus.edu.sg
[b]University of Illinois at Urbana-Champaign, USA, e-mail: jstucki@uiuc.edu

## Abstract

A method for Sr removal from strong alkaline solutions in the presence of 1M NaOH and 3M $NaNO_3$ has been developed. The method is based on Di-2-ethyl hexyl phosphoric acid (D2EHPA) acting as a carrier in liquid membrane or as an extractant in simultaneous extraction-reextraction. After removal, Sr can be precipitated as $SrSO_4$ if $H_2SO_4$ is used as the stripping phase, thus giving the possibility to concentrate radioactive Sr in a small volume of solid phase within one technological step. Using this method in a bulk liquid membrane process without EDTA, a rate of Sr removal near $10^{-6}$ mol-m$^{-2}$-s$^{-1}$ could be achieved, which is typical for liquid membranes. The hindrance effect of EDTA on the Sr removal has been demonstrated and a simple method to reduce this effect by addition of $Ca^{2+}$ is suggested. In the case of the extraction-reextraction process with the membrane based demulsification, 98% of Sr was removed at a rate of $4.5 \times 10^{-9}$ mol-s$^{-1}$-L$^{-1}$. The process is simple and should allow removal of all radioactive Sr from radioactive waste at the Hanford site, USA, in one to two years, depending on the plant scale.

*Keywords*: Alkaline nuclear waster; Sr removal; D2EHPA; Bulk liquid membrane; Extraction-reextraction process; Hindrance effect of EDTA

## 1. Intorduction

Hanford site is a famous place in the USA for its reactors and processing plants that once produced plutonium for nuclear weapons [1]. There are 149 single-shell tanks and 28 double-shell tanks in Hanford site, in which 177 million gallons of high-level waste is stored. In some tanks the waste was made alkaline by addition of sodium hydroxide to precipitate metal species and to prevent corrosion of the tanks. Some other chemical reagents, such

*Corresponding author.

as sodium titanate, ferrocyanide, etc., have also been added into some tanks to precipitate $^{90}Sr$, which is the main radioactive component of the waste. As a result of these additions the nuclear waste in Hanford is marked with two main characteristics, pH above 14 and high sodium concentration, usually around 4M. Besides that, some storage tanks in Hanford site also contain organic compounds, such as EDTA, glycolic acid, and oxalic acid, thus making the removal of $^{90}Sr$ even more difficult.

It may take more than $50 billion to clean up the waste over the next 30 years [1]. Another estimate is $230 Billion over 75 years [2]. During the past half century, various techniques have been investigated as possible methods of Sr removal from acidic and neutral media, such as precipitation [3], ion exchange [4], selective uptake [5], complexation-aided filtration [6], solvent extraction [7,8], liquid membranes [9,10], etc. A precipitation scheme has been used to recover $^{90}Sr$ from diluted $HNO_3$ high-level waste at Hanford. D2EHPA extraction process has also been used for over ten years to recover and purify about 40 megaCurie of $^{90}Sr$ from acidified PUREX process sludge [3]. Although these two techniques have performed quite well for the removal of strontium from acidic waste, it seemed impossible to use D2EHPA for extraction from alkaline solutions. Usually it was assumed that being an acid, D2EHPA has high solubility in alkali and a third phase (gel) could be formed during extraction. In this paper, we will show the possibility of Sr removal from strong alkaline solutions similar to those in Hanford using D2EHPA. Experiments were conducted with both bulk liquid membranes and an extraction-reextraction process [11–13]. A new method to reduce the hindrance effect of organic components such as EDTA by addition of Ca ions is proposed.

## 2. Experimental part

Di-2-ethylhexyl phosphoric acid (D2EHPA, ACROS, the purity 98%), xylene, *n*-heptane, tributylphosphate (TBP) and amyl alcohol were used without further purification.

Peristaltic pumps with Viton (Cole-Parmer) tubing were used. Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin Elmer, USA) was used for Sr measurements at 460.73 nm in the presence of high sodium concentration [12]. The concentration of Sr in the organic phase was calculated based on mass balance.

### 2.1. Bulk liquid membrane

The experiment was carried out in a special coaxial cylinder chamber (Fig. 1). The wall of the inner cylinder separated aqueous donor and acceptor solutions. Liquid organic phase with carrier was added on the top of both aqueous solutions. The only possible way for ion transport from one aqueous phase to the other was through the liquid organic phase, which thus played the role of a bulk membrane phase. An important feature is that the membrane area in contact with the inner solution (7 cm$^2$) differs from that in contact with the outer solution (21 cm$^2$). The transparent walls of the chamber permitted visual observation of the formation of any new phase. Sr fluxes were calculated based on the surface area of the acceptor phase.
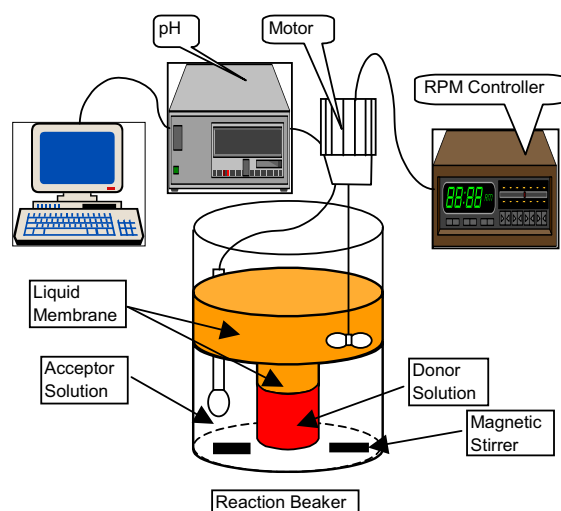


Fig. 1. Bulk liquid membrane experimental setup for Sr removal.

## 2.2. Extraction-reextraction

In order to study the possibility of removal of Sr from the Hanford storage tanks, an extraction-reextraction process with recycling of the organic phase was developed (Fig. 2). The upper layer in the two bottles (1 and 5) was the organic phase, for example 0.15 M D2EHPA in *n*-heptane. 5% amyl alcohol was used to avoid third phase formation. The lower part in the donor solution was 3 M $NaNO_3$ + 1 M NaOH solution with $10^{-4}$ M Sr ions. The lower part in the stripping bottle is 2 M $HNO_3$ solution. To prevent the donor solution from coming into the stripping solution directly due to circulation of the organic phase, an oil/water separator was used (Fig. 2). All of the experiments were conducted at ~25°C. The volumes of donor solution, organic phase and stripping solution were 150 ml, 260 ml, and 150 ml, respectively. The volume of organic phase is the sum of those in bottles, tubes, membrane module, and separation funnel. At predetermined time intervals, 0.1 ml of both aqueous solutions after 10 times dilution were analysed with ICP.

## 3. Results and discussion

### 3.1. Bulk liquid membrane

Liquid membrane is potentially a very effective way for removal and recovery of metals form wastewater [14]. A typical transport of Sr through a bulk liquid membrane is shown in Fig. 3. The donor solution in this case contained 30 ml of NaOH solution (pH 13.5), saturated with $Sr(OH)_2$
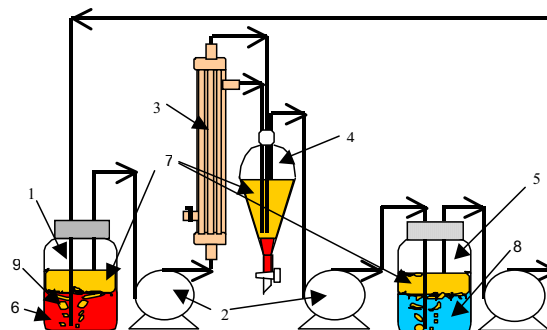


Fig. 2. Simultaneous extraction-reextraction process. 1, feeding tank; 2, peristaltic pump; 3, oil-water separator; 4, separation funnel; 5, stripping tank; 6, donor solution; 7, organic phases; 8, acceptor solution; 9, organic emulsion.
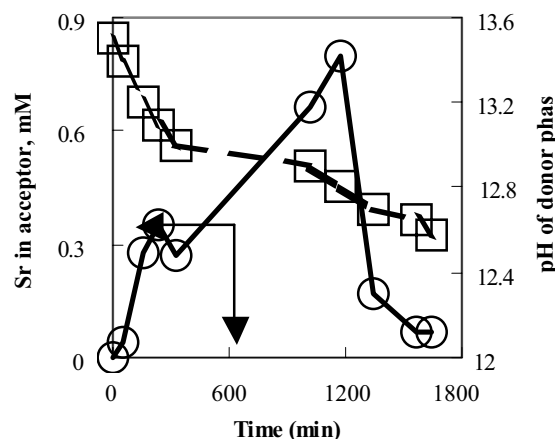


Fig. 3. A typical kinetics o f Sr transport through bulk liquid membrane. Conditions as in Table 1, Experiment 1.

Table 1

Conditions and the flux in bulk liquid membrane experiments

| Exp. No. | Inner chamber | Membrane | Outer chamber | Stirring rate, Rpm | Flux, $mol.cm^{-2}s^{-1}.10^{10}$ |
|---|---|---|---|---|---|
| 1 | 0.005M $SrCl_2$, pH13.5, 30ml | 12% D2EHPA in xylene, 20 ml | HCl, pH 1.6, 105 ml | 300 | 0.6 |
| 2 | The same | 9% D2EHPA in mineral oil | The same | 300 | 3.2 |
| 3 | HCl, pH 1.5 | 20% D2EHPA in mineral oil, 56 ml | $SrCl_2$, pH13.6 | 500 | 0.94 |
| 4 | $H_2SO_4$, pH 0.18 | 9% D2EHPA in mineral oil and octanol, 100 ml | $Sr(NO_3)_2$, pH 14 | 300 | 1.4 |

+ SrCl$_2$. The Sr concentration in the acceptor solution increased during the first 20 h to 0.8 mM, but then decreased to less than 0.1 mM. The decrease of Sr concentration in the acceptor solution was due to the liquid crystal phase ("third-phase") formation in the membrane because of the high metal-ion loading in the organic phase. To overcome this problem a third component, known as a diluent or modifier, could be added [12]. The corresponding pH value in the acceptor increased to 2.2. The kinetics of pH change in the donor solution initially was determined by fast 2H$^+$/Sr$^{2+}$ ion exchange at the interface and secondly by slower transmembrane transport (Fig. 3).

One of the most important characteristics of membrane is the effective rate of Sr transport, which was calculated based on the expression:

$$F = \frac{\Delta\left[Sr^{2+}\right]}{\Delta T}\frac{V}{S}$$

where $F$ is the rate of Sr transport (mol-cm$^{-2}$-s$^{-1}$), $\Delta[Sr^{2+}]$ is the change of Sr$^{2+}$ concentration in the acceptor solution, $V$ is its volume, $S$ is the surface area in contact with the acceptor, and $\Delta T$ is the time required for the observed changes. Using the initial stage of kinetics in the acceptor phase we obtain the value of $F$ near $0.6 \times 10^{-10}$ mol-cm$^{-2}$-s$^{-1}$.

In a similar second experiment, where aliphatic mineral oil was used instead of aromatic xylene, the rate of transport was $\cong 3.2 \times 10^{-10}$ mol-cm$^{-2}$-s$^{-1}$, while [Sr$^{2+}$] measured directly in the organic phase was about 10 times less than in the aqueous solutions. Aromatic diluents often result in slower kinetics both of the extraction and stripping steps with higher solubility of the metal complex in the membrane [15].

When the acceptor solution was placed in the inside cylinder, the surface area for reextraction became about one-third of that in the outside cylinder (7 vs. 21 cm$^2$). The rate of transport also decreased (experiment 3), demonstrating the role of the interfacial area organic/stripping solution.

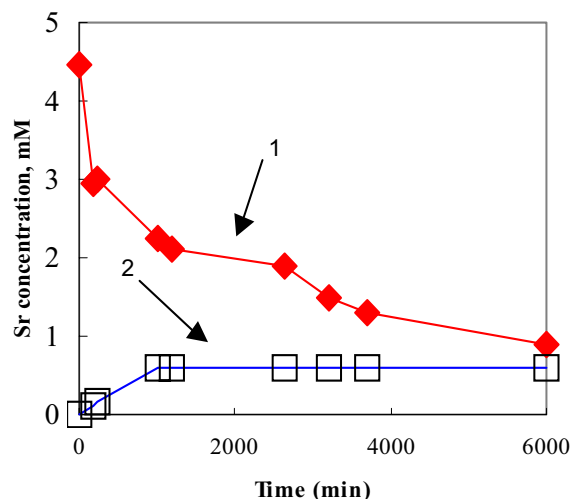Sulphuric acid was used in the acceptor in experiment 4 (Fig. 4). Octanol was added to avoid



Fig. 4. The variation of Sr concentration in donor and acceptor solutions in bulk liquid membrane process. Conditions as in Table 1. Experiment 4. 1, Sr in donor solution; 2, Sr in acceptor solution.

third phase formation. The concentration of Sr in the acceptor solution increased initially, but then it stabilized at a constant value, $6 \times 10^{-4}$ M, which is determined by solubility of SrSO$_4$. Final pH of acceptor in this case was –0.1, and the transport rate was at least 30% greater than before. 80% of the Sr was removed from the donor solution after 100 h.

### 3.2. Extraction-reextraction process

In order to demonstrate the possibility for Sr removal from the storage tanks as those in Hanford, a simple extraction-reextractioin process (Fig. 2) was studied. The ratio of Sr concentrations in organic and donor solutions varied as a function of time, ranging from 0 to 0.3 and because of the reextraction in the acceptor it was always less than the equilibrium distribution coefficient of Sr, equal to 0.3 in these conditions [11].

Kinetics of Sr removal (Fig. 5) was first order and after two-hours its concentration in the stripping phase became higher than in the donor phase. Active transport was possible due to the
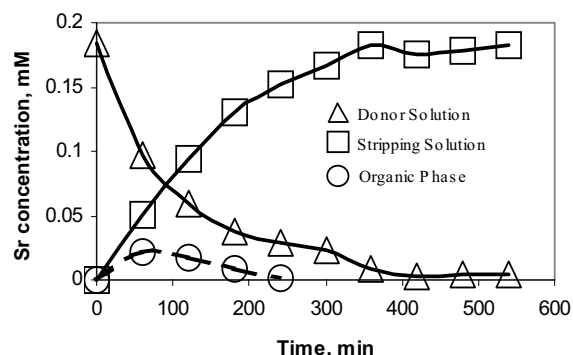
Fig. 5. Variation of Sr concentration in extraction-reextraction process. Organic phase: 0.15 M D2EHPA + 5% V/V amylalcohol in n-heptane; initail donor solution: $3\,M\,NaNO_3 + 1\,M\,NaOH + 2\times10^{-4}\,M\,SrCl_2$; initial stripping solution: $2\,M\,HNO_3$.
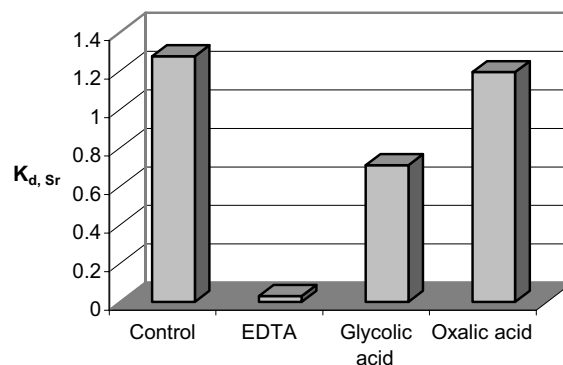


Fig. 6. The effects of organic compounds on the distribution coefficient of Sr. Organic phase: 5% D2EHPA + 10% TBP + 5% octanol in kerosene; aqueous phase: 0.2 mM $SrCl_2 + 0.7\,M\,NaNO_3 + 1\,M\,NaOH$; organic compounds in aqueous phase: [EDTA] = 0.02 M; [Glycolic acid] = 0.25 M; [Oxalic acid] = 0.01 M.

driving force, which was the $H^+$ concentration difference between two aqueous phases. At equilibrium, based on thermodynamics, a pH difference of 14 could result in $10^{28}$ increase of Sr concentration. After 7 h of operation more than 98% of Sr was removed to the stripping solution.

### 3.3. The hindrance effect of EDTA and its minimization with Ca salts

Fig. 6 shows the effect of EDTA, glycolic and oxalic acids on the distribution coefficient of strontium. The concentrations of these organic compounds were similar to those in nuclear waste in Hanford (M. Johnson, 1998, personal communication). A significant decrease in the distribution coefficient of strontium was found when EDTA was added to the aqueous solution. The stability constant for the EDTA-Sr complex is $4.27\times10^8$ [16], and it means that nearly 100% strontium exists as the EDTA complex.

The stability constant of $Ca^{2+}$-EDTA complex is even higher ($3.7\times10^{10}$) and the effective distribution coefficient of strontium can be increased significantly by addition of $Ca^{2+}$ because of ion exchange reactions [12]. Therefore, addition of Ca ions in the proper concentrations when Ca interacts with EDTA, but not competes

yet with Sr for D2EHPA, releases strontium from the Sr-EDTA complex and increases its distribution coefficient and the rate of its removal. Since only a small amount of Ca is required, it is also an economical way to treat nuclear waste compared with methods suggested for degradation of EDTA and its complexes [17].

### 3.4. Discussion

Membrane processes, based on a low-molecular weight extractant-carrier (D2EHPA), can be used for Sr recovery from strong alkaline solutions similar to radioactive waste in Hanford, USA. Active transport of Sr against its concentration gradient, driven by a large pH difference allows the transfer of virtually all Sr into a small volume of acid, as well as precipitation, for example, by $H_2SO_4$. The rate-limiting step of the process is the striping of Sr from the liquid organic phase into the acid.

We can roughly estimate the time necessary for the treatment of one storage tank (4.5 million litres of wastewater with Sr-90 concentration of $\sim10^{-5}$ M) as follows. Assume that the average diameter of the organic particles is 5 mm. If 4.5 thousand L of organic phase (only 0.1% V/V) is

dispersed in the wastewater, it corresponds to a surface area $5.4 \times 10^7$ cm$^2$. Now assume that the Sr removal rate is $10^{-12}$ mol/cm$^2$s (actually this far below optimal conditions). Based on these conservative assumptions, the time required to treat the tank would be less than one month.

The solubility of D2EHPA in aqueous phase at high pH and high concentration of Na$^+$ is less than 10 ppm [18], which is mainly due to the salting out effect of high sodium concentration. For the 4.5 million litres tank, the loss of D2EHPA should be less than 50 L, which is certainly affordable for this very common, widely used and radioactivity resistant substance.

The extraction-reextraction technology with recirculation of dispersed organic phase is simple, safe, inexpensive and energy saving; and it is similar to the method already used for the treatment of acidic radioactive waste. It is possible to use this method simultaneously and in parallel with other methods of waste treatment, including precipitation. This would certainly help to solve the most expensive problem in the whole civil history.

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