

Process for removal of strontium ions from strong alkaline solutions

Background of invention

This invention relates to a process for removal of strontium from nuclear wastes and more particularly a process for removal of strontium from alkaline waste solutions containing strontium and also high concentrations of cations of alkali and alkaline earth metals.

Many years of weapon-grade plutonium production and its chemical separation resulted in generation of several hundred thousand metric tons of waste. For the high-level waste generated by the chemical reprocessing plants, waste management involved adding sodium hydroxide and calcium carbonate to make the acidic waste alkaline ($\text{pH} > 13$), and then storing the waste in large underground tanks until a long-term disposal solution will be found. In the USA (Hanford Site) 149 tanks with capacity of 210,000 to 3,800,000 liters (total nearly 212 million liters) were built to store the high-level waste. Later 28 new double-shell tanks were designed that include an outer steel shell to contain any leaks that occur through the inner steel shell. The double-shell tank design provides for leak detection and recovery. It is planned to remove this big volume of radioactive waste from the tanks with its later vitrifying (melting and forming a glass), which would cost US\$16-24 billion. Removal of Sr from such waste into smaller volume or its transformation into solid phase is warranted because of safety and economic considerations. The problem of Sr removal from radioactive waste is important also for other countries with developed nuclear technology.

By now all main processes developed for recovery of large amounts of Sr were supposed to be used with acidic media. These processes included mainly precipitation, for example with lead sulphate and ion exchange for example with antimonious acid as sorbing agent and can not be used with alkaline solutions.

There are some papers describing extraction of Sr with extractants.

Selection of an appropriate extractant should be based on a number of important criteria. Among these criteria, the extractant must:

1. extract the metal at the required pH;
2. be selective for the required metal;

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REPLACED SHEETS		SG
☒	Description : paged	16
☒	Claim(s) : paged	18
☒	Drawing(s) : paged	4
☒	Abstract : paged	19

3. have acceptable rates of extraction and stripping;
4. be soluble in an organic phase and have a very low solubility in aqueous solution;
5. have high metal-loading capacity;
6. be easily stripped of the loaded metal;
7. be non-flammable, non-volatile, chemically and radiation-stable, and non-toxic;
8. be relatively inexpensive.

Strontium extraction from acidic solutions can be achieved by using different specific extractants, for example dibenzo-18-crown-6 or di-t-butylcyclohexano-18-crown-6. Usually synthesis of these compounds is a complex process, and they are not available in the amounts necessary to purify very big volumes of waste liquids. Besides, inorganic salts of Sr have high hydrophilic properties and exhibit a low distribution ratio. Therefore they have to be preliminary converted into for example metal picrates by adding the excess of picric acid prior extraction.

Besides there are no studies which demonstrated the applicability of these extractants in strong alkaline solutions. Even at low solubility of their complexes with Sr in aqueous solutions due to very big volumes of these solutions the losses of the extractant would make the process economically not feasible.

Dwórzak and Nazer described preliminary experiment, where 0.01 M Sr was removed from weak nitric acid (pH 6.4) to nitric acid solution with pH 1.5 with the help of polypropylene microporous fibers impregnated with 0.1M di-(2-ethylhexyl) phosphoric acid (D2EHPA).

Although this method could be useful for neutral and acidic solutions, its application in alkaline solutions is impossible due to the long term chemical nonstability of polymer at very high pH and in contact with radioactivity, and also due to the removal (leaching) of acidic extractant through membrane pores into the solution with high pH. After transfer of the extractant, initially present in the membrane in a limited amount, into a big volume of waste solution, the membrane becomes non effective. Application of hollow fiber modules for Sr extraction would also mean that radioactive waste is pumped from the tanks into the membrane module, which is hazardous.

Emulsion liquid membrane with D2EHPA as an extractant, nonionic polyamine as the surfactant and an aliphatic hydrocarbon solvent as the diluent also could be used to



extract Sr from solutions with pH 3.8-4.5. This system would also be unstable at high pH. Recovery of Sr from inner volume of emulsion is another technological step which is hazardous due to the radioactivity of the solutions.

Neither of these studies addressed how high concentrations of alkaline metals and calcium and also some other metals in the alkaline media would effect the process. As will be discussed later, it has been found that these metals and high pH play a key role in determining the efficiency of Sr removal. Usually it is assumed that acidic extractants have a high water solubility at high pH and cannot be used in these conditions. Preliminary neutralisation of the waste solutions with acids would increase the waste volume, which is not particularly safe nor economical due to necessity of new storage tanks.

Accordingly, a need in the art exists for a simple method of Sr removal from strong alkaline solutions that does not require acidification of the media, is economically feasible, and works in the presence of high concentrations of cations of alkaline metals, calcium and some other metals.

Summary of the Invention

In view of the above need, it is an object of this invention to provide a process for strontium removal from strong alkaline aqueous solutions containing high concentrations of alkali metal and calcium cations.

Another object of this invention is to provide a process as in the above object that does not require acidification of the aqueous solution and does not require usage of organic polymeric membranes and emulsions which may not be stable in the strong alkaline solutions.

Further, it is an object of the invention to provide a process which could be easily implemented for the treatment of big volumes of aqueous solutions and would allow to collect Sr in a much smaller volume.

It is another object of the invention to provide, from a technological point of view, a simple process, which would minimize the danger of personal contact with radioactive materials.



While investigating the behaviour of D2EHPA in strong alkaline solutions we discovered that its solubility in these solutions is not very high and in the presence of water-insoluble liquid organic phase it is possible to saturate the strong alkaline solution with D2EHPA and still have its high concentration in organic phase.

Briefly, the present invention is a process for extracting strontium from strong alkaline solution, comprising steps of:

contacting the aqueous strong alkaline solution containing at least one alkali metal hydroxide and strontium cation with high enough volume of organic solvent consisting of D2EHPA in a diluent, the diluent being a water-immisible organic liquid in which D2EHPA is soluble, and subsequently contacting of the above solvent with aqueous solution of sulphuric acid, thus stripping strontium into the above acidic solution till its saturation and formation of solid precipitate of strontium sulphate.

The contact of the organic solvent with the waste solution can be achieved by its cyclic supplying into the bottom part of the tank in a dispersed form and then collecting it from a top of the tank with subsequent supply of the strontium containing solvent to the bottom of another volume with sulphuric acid and its collecting after stripping and pumping back into the waste solution.

In another implementation the organic solvent is located on a top of a tank with double walls, having inner walls lower than outer. Stirred organic solvent is in contact with both waste solution and stripping sulphuric acid solution and its upper surface is above the inner walls. Sulphuric acid can be located not necessarily between double walls but also in an extra cylinder partly inserted into the liquid waste.

Brief description of the drawings

Fig.1 shows the mechanism of D2EHPA-facilitated transport of strontium ions from strong alkaline to acidic solution.

Fig. 2 shows schematic of a bulk liquid membrane apparatus.

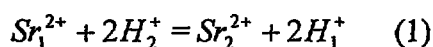
Fig. 3 shows kinetics of changes of strontium concentration in the acidic solution with a xylene bulk liquid membrane.



Fig. 4 shows kinetics of strontium concentration changes in the donor strong alkaline aqueous solution and acceptor solution of sulfuric acid.

Detailed description

Our experiments demonstrated that in a system, where strong alkaline solution with Sr^{2+} is in contact with liquid organic solvent, having D2EHPA, and simultaneously this organic solvent is in contact with acidic aqueous solution, Sr^{2+} is extracted into the organic solvent and then it is reextracted (stripping) into acidic solution. Simultaneously H^+ ions are transferred into opposite direction. Total ion-exchange process is described by Eq. 1,



and is facilitated by D2EHPA in the organic solvent. The mechanism, thus, is a coupled transport of 2H^+ in one direction simultaneously with Sr^{2+} transport in the other direction (Fig. 1), and its equilibrium is described by Eq. 2,

$$K_{eq} = \frac{[\text{H}^+]_1^2 [\text{Sr}^{2+}]_2}{[\text{H}^+]_2^2 [\text{Sr}^{2+}]_1} = I \quad (2)$$

where subscripts 1 and 2 represent the stripping and feed solutions, respectively. The thermodynamics of the process thus shows that at equilibrium an active transport of Sr^{2+} occurs against its concentration gradient due to the difference in pH of solutions 1 and 2, and the ratio of Sr concentrations is determined by the second power of the H^+ concentration ratio. This means that if the pH gradient is high enough during the process, and it easily could be 14, all radioactive Sr can be transferred and concentrated in a small volume of an acidic stripping solution. Moreover, if sulphuric acid is present in a stripping solution, with time concentration of Sr in the acidic solution is high enough and the ion product $[\text{Sr}^{2+}][\text{SO}_4^{2-}]$ becomes equal to the solubility product. After that Sr ions precipitate out as strontium sulphate. This possibility of collecting all Sr into a small volume is a major advantage of this process.



D2EHPA is soluble in different organic diluents, such as N-decanol, benzene, heptane, etc. These substances as well as their mixtures or other aromatic hydrocarbons, aliphatic hydrocarbons, alcohol solvents or their mixtures, or other such as but not limited to kerosenes, dodecane, octanone, or any combination of these in any proportion, could be used as a diluent. The organic solvent can additionally contain added organic compounds which act as modifiers or synergists. These include but not limited to octanol, decanol, other alcohols, crown ethers, detergents, containing phosphor organic compounds, etc.

Although the process of the present invention was developed especially for the recovery of radioactive Sr-90, addition of some modifiers or synergists allows simultaneously remove some other radioactive components. For example technetium can be removed from strong alkaline waste solutions in the presence of some crown ethers. The modifier is typically present in a solvent at a concentration ranging from 0.01 M to about 2M, and its typical volume content is from 0.1 to 50%. The presence of the modifiers or their mixture could be important because of the ability of D2EHPA to form very viscous gel-like structures in the presence of strong alkaline aqueous solutions. Its distribution coefficient is solvent-dependent and for n-octane/H₂O it is $2 \cdot 10^3$.

The loss of D2EHPA from organic into aqueous solution is pH dependent and it strongly increases at high pH. Still, as it will be described later in the examples, it is possible to saturate the alkaline solution with acceptable, from a practical point of view, amount of the substance. In the process of present invention efficiency of the Sr removal is obtained by using saturating amounts of D2EHPA in the waste solutions. If the solution is not saturated, D2EHPA is removed from organic phase and the rate of the process falls to negligibly small value. This possibility to remove Sr from big volumes of strong alkaline solutions in the presence of competing ions Ca and Mg by addition of EDTA and simultaneous saturation of the waste with D2EHPA in the presence of organic solvents which are also in contact with stripping acidic solutions, especially sulphuric acid, was not previously described in the prior art.



Examples.

The following examples are given to illustrate the process of the invention and are not to be taken as limiting the scope of the invention which is defined in the appended claims.

The following methods were employed in the procedures described in the succeeding Examples. We used commercial form of D2EHPA without any further purification, xylene (J. T. Baker Chemicals Co), strontium nitrate (Mallinckrodt), mineral oil (paraffin oil, heavy), and other reactants (Fisher) were used without special purification.

The main experiment was carried out in the special coaxial cylinder chamber with the diameters of inner and outer glass cylinders of 3 and 6 cm, respectively (FIG. 2). The height of the inner cylinder was 5.5 cm and of the outer was 9.5 cm. In the standard experimental arrangement, the aqueous donor and acceptor solutions were separated by the wall of the inner cylinder, and then liquid organic phase, with or without carrier, was added to the top of the aqueous solutions in such a way that the transport of ions from one aqueous phase to the other was possible only through the liquid organic phase, which thus played the role of a bulk membrane phase. An important feature to note 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). Mechanical stirring of the organic phase was achieved by a speed-controlled motor (Cole-Palmer). Both aqueous phases were stirred by magnetic stirring bars, one in the inner and two in the outer semichamber. The transparent walls of the chamber permitted visual observation of the formation of any precipitates or turbid phases.

The concentration of Sr was determined by atomic absorption spectrophotometry (Perkin-Elmer, 460.7 nm, acetylene nitrous oxide flame). In some experiments, qualitative estimates of Sr content were determined from the colour of the Sr-indicator Eriochrome Black T, or with a Ca-selective electrode (Microelectrodes, Inc.). Atomic absorption was measured during the experiments using 5 ml aliquots from the chamber solution (in the first group of experiments, equal volumes of blank solution were added to the chamber after the aliquot was removed in order to maintain constant volume in the chamber), and later 1 ml aliquots followed by their dilution with the same pH as the Sr standard solution. In the end of the experiments atomic absorption (AA) was measured directly by aspirating (0.8ml/s) different solutions from the chamber into spectrophotometer. The pH of solutions was



controlled continuously by combined pH-selective electrodes (Microelectrodes, Inc), connected to an Accumet 50 pH meter and a computer (IBM PC).

Example 1.

The donor solution in this case contained 30 ml of NaOH solution (pH 13.5) saturated with $\text{Sr}(\text{OH})_2 + \text{SrCl}_2$. The acceptor solution contained 105 ml of HCl (pH 1.6). The membrane layer consisted of 18 ml of xylene mixed with 2.5 ml of D2EHPA. The problem of lack of stability of the organic liquid in the pores of a polymer support is absent in the case of a bulk liquid membrane, and we were able to demonstrate transmembrane transport of Sr through a bulk liquid membrane. The typical kinetics of Sr transport from alkaline to acidic solution are shown in FIG. 3. The Sr concentration in the acceptor solution increased during the first 20 hr to 0.8 mM and then decreased to less than 0.1 mM, and the pH increased slightly to 2.2. The kinetics of pH change in the donor solution revealed two stages, the first fast process finished after less than 400 min, during which time the pH decreased by 0.5. The buffer capacity of the initial donor solution was approximately $2 \cdot 10^{-1}$ M and the pH change of 0.5 during the first stage gives a change in $[\text{H}^+]$ concentration of 10^{-1} M. These changes approximately correspond to the effective concentration of Sr and to the ion-exchange stoichiometry of 2:1 for the D2EHPA, and can be determined by the release of H^+ during the extraction step at the donor-membrane interface and then by the coupled transport through the membrane. This means that, simultaneously, a significant amount of Sr was at least extracted from the donor solution into the organic (membrane) phase, and may have been transported through the latter. This conclusion is supported by the direct measurement of Sr, using atomic absorption spectroscopy, in donor and membrane solutions after the experiment. In the membrane, $[\text{Sr}^{2+}]$ was 0.4 mM, which was comparable to 0.8 mM found in the donor solution and greater than 0.1 mM in the acceptor solution.

The decrease of Sr concentration in the acceptor solution (see FIG. 3) deserves special discussion. An explanation is that a liquid crystal phase was formed in the membrane during the experiment. This phenomenon of so called third-phase separation is well-known in extraction chemistry and is determined by solubility limitations of the metal complexes in the organic membrane phase. Usually the organic phase splits into two phases, yielding a phase rich in the metal complex at the aqueous interface and a diluent-rich phase on the organic side



of the interface. To overcome this problem, a third component, known as a diluent modifier, may be added to restore the liquid properties of the organic phase. The most common modifiers are tributyl phosphate, isodecanol, or nonyl phenol. To make this liquid crystal phase more evident, the Sr-sensitive indicator Eriochrome Black T was added, which gave an intensive red-blue colour in the liquid crystal phase, where Sr was concentrated with time. Direct atomic absorption measurements in this phase proved the idea of Sr localization in the third phase. The structure of this phase is determined by the surface-active properties of D2EHPA. Usually it depends on the surfactant concentration, pH, and temperature, and should disappear at very high or very low salinity or pH. Changes in ion concentration and pH (mainly in alkaline solution) during the experiment apparently induced the formation of the third phase, and resulted in the reextraction of Sr and its binding into the liquid crystal phase.

One of the most important characteristics of a membrane is the average or effective rate of transport through it, which can be calculated by the expression

$$F = \frac{\Delta[Sr^{2+}]V}{\Delta TS} \quad (3)$$

where F is the rate of transport in $\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, $\Delta[Sr^{2+}]$ is the change in Sr^{2+} concentration in the acceptor solution, V is the volume of the acceptor solution, ΔT is the time required for the observed changes, and S is the surface area of the membrane. Using the initial stage of kinetics (before the concentration goes down), and assuming S to be that of the membrane in contact with the acceptor, the value of F becomes $0.6\cdot 10^{-10} \text{ mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$.

Example 2.

In a similar experiment (Table 1, experiment 2), in which aliphatic mineral oil was used as the liquid membrane instead of aromatic xylene, the rate of transport was $3.2\cdot 10^{-10} \text{ mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, while the $[Sr^{2+}]$ measured directly in the organic phase was about 10 times less than in the aqueous solutions. The use of aromatic diluents results in slower kinetics both of the extraction and stripping steps, but the solubility of the metal complex is higher in the aromatic diluents.



Example 3

Increasing the stirring rate in the organic phase from 300 to 1000 rpm increased by 8-fold the transport rate (Table 1, experiment 3). Too high stirring rate can cause the direct break through or transfer of Sr solution across the organic phase. In subsequent examples the stirring rate was, therefore, decreased to 500 rpm or less.

Example 4

When the acceptor solution was placed in the inside cylinder, where the membrane surface area is about one-third that of the outside cylinder (7 vs. 21 cm²), the rate of transport decreased to only $0.94 \cdot 10^{-10}$ mol-cm⁻²-s⁻¹, which is one-third of the rate observed with the acceptor solution in the outer cylinder (Table 1, experiment 2). Obviously, the transport rate corresponds to the interfacial surface area of the membrane in contact with the stripping solution (Table 1, experiment 4). This result means that the rate-limiting step is the reextraction from the membrane phase, the rate of which is proportional to the membrane area.

The initial pH of the acceptor solution in this experiment was 1.5. The donor solution sometimes was cloudy or milky white due to the presence of a Sr precipitate and in some cases it became transparent with time, obviously because enough Sr was taken into the membrane phase to decrease donor-solution Sr concentration below the solubility product value. This is further evidence that the solubilization and extraction processes are not rate limiting.

Example 5.

Sulphuric acid was used instead of HCl in the acceptor solution, and the results of one of these attempts are shown in FIG. 4. Simultaneously, the H⁺ activity was increased to pH_{acc} = -0.1. The apparent rate of transport was 30% greater, using the Sr concentration after 1000 min in the calculations. Clearly, at least 80% of the Sr was removed from the donor solution after only 100 hr. The concentration of Sr in the acceptor solution increased initially, then stabilized at a constant value which is similar to the solubility of SrSO₄, i.e., $6 \cdot 10^{-4}$ M. The process took less than 1000 min and produced a white precipitate. Initial pH values in the donor and acceptor solutions were 14 and -0.1, respectively, and were almost constant



over the 5-day duration of the experiment. For example 0pH in the acceptor solution was 0.3, thus demonstrating that the intensity of stirring was not too high and no transfer of either aqueous solutions occurred. Combination of extraction with D2EHPA and then precipitation with sulphuric acid allowed an active transport of Sr and also its selective separation

Example 6.

In this example the tank-waste model solution was used, simulating all components of waste water from the Hanford Site except for Ca salts. The mixture of these components even without Sr gave a precipitate, which was filtered before the addition of $\text{Sr}(\text{NO}_3)_2$. Strontium gives a co-precipitate in the sludge, especially in the presence of $\text{Ca}(\text{OH})_2$. In the presence of Sr salt, the solution was filtered a second time. Sulphuric acid was in the acceptor solution in order to increase the total rate of transport. The organic phase contained the modifiers octanol and xylene right from the start of the experiment. Even in the presence of Mg, Na, Al, K, and Cs, Sr transport through the membrane was significant ($0.48 \cdot 10^{-10} \text{ mol-cm}^{-2}\text{-s}^{-1}$), although the flux was lower than in previous experiments. The decrease of the transport rate in this case was determined by the competitive binding of other metals with the carrier. Atomic absorption analysis of the donor solution in the very beginning gave an instrument reading of less than 0.1 absorbance, which decreased after 5 hr to about 0. The estimated (by atomic absorption) concentration of Sr in the donor solution was an order of magnitude less than in all previous experiments ($5 \cdot 10^{-3}$ and $5 \cdot 10^{-4} \text{ M}$), but still the rate decreased only by half, indicating a saturation of the transport rate as a function of Sr concentration. In separate experiments it was demonstrated that $[\text{Sr}]_{50\%} = 2.5 \cdot 10^{-4} \text{ M}$.

Example 7.

In the seventh experiment a model tank-waste solution was used with Ca concentrations corresponding to those in radioactive waste storage tanks at the Hanford Site. Simultaneously EDTA was added in the same concentration. The chemical composition of this solution is given in Table 2, together with the stability constants of complexes of EDTA with several divalent metals and Al.

From the data given in Table 2, clearly the presence of EDTA will transform almost all of the Ca and other heavy metals into chelate complexes, especially in light of the fact that



the concentrations of Ca and EDTA are equal. The values of K_{stab} for Mg and Sr with EDTA are similar, but much lower than for the other metals that are present (Table 2). Further, the concentration of Mg is at least two orders of magnitude greater than Sr, indicating that Mg will occupy the remainder of the EDTA sites and Sr will be in its free unchelated form, from which it can be carried through the liquid membrane as in previous experiments. Simultaneously Ca, other metals, and part of the Mg should be chelated and thus unavailable to compete with Sr for D2EHPA sites during-facilitated transport. So the concentration of EDTA added has to be high enough to chelate Ca and heavy metals, but still not too high to transform all Sr into chelate form, which would decrease its rate of extraction with D2EHPA.

Concentration of Sr in the model tank-waste solution after filtration estimated by atomic absorption was only approximately $2\cdot 4\cdot 10^{-5}$ M but still after 1300 min of transport, atomic absorption intensities from the donor and acceptor solutions revealed that a substantial part of Sr was extracted into the organic phase and appeared in the acceptor solution. The intensity ratios of donor: organic membrane: acceptor solution were 1:0.5:1:1. Even though the precision of these measurements was low ($CV \approx 20\%$ due to the small Sr concentration, large pH, and large Na concentration) clearly the concentration in the acceptor solution was at least similar to that in the donor solution. After accounting for the volume differences among the donor, liquid organic solution, and acceptor phases, approximately 60% of the total Sr originally in the donor solution was transferred into the acceptor phase.

Transport rate was $2\cdot 10^{-12}$ mol-cm⁻²-s⁻¹ or $2\cdot 10^{-8}$ mol-m⁻²-s⁻¹, which is one order of magnitude smaller than in the previous experiments. This may be explained by the fact that the Sr concentration in the donor solution was less than in experiments 1-6 and it was an order of magnitude less than the semisaturation of D2EHPA. In the beginning of the experiment a third (gel) phase was formed at the surface of contact of organic and alkaline solutions, but it disappeared with time and, by the end of the experiment, both the membrane and acceptor solutions were transparent. The donor solution was turbid and white after 1300 minutes due to the formation of D2EHPA salt precipitate. With time it also became transparent, and the volume of precipitate was less than 2 cm³, so the loss of D2EHPA was less than 10 %.

The third phase is probably determined by the formation of Na and Sr salts of D2EHPA and their aggregation in reversed micelles. This phase has a high viscosity and can perform an essential resistance to Sr transfer into organic phase, but it can be destroyed with



time due to stirring and/or the presence of common modifiers, like tributyl phosphate, octanol, isodecanol or nonyl phenol.

Taking into account very big volume of the waste, even at low solubility in water essential amounts of D2EHPA can be removed from organic solution. The rate of Sr removal in this case is negligible. We demonstrated that solubility of D2EHPA in water is pH dependent. In acidic solutions ($\text{pH} < 1$) it is less than 10^{-4} M. Distribution coefficient of D2EHPA in the system xylene/acidic solution is higher than 5500. In contact with alkaline solutions ($\text{pH} > 13$) D2EHPA dissociates and its solubility in the anion form is much higher and can be nearly $2 \cdot 10^{-2}$ M, or 0.5% v/v.

The rates of Sr transport in optimal conditions are comparable to the typical rates of transport through liquid supported membranes, which are of the order of 10^{-10} mol-cm⁻²-s⁻¹. This rate translates into the complete removal of Sr from 36 L of 10^{-4} M Sr waste water per hr per m² of membrane surface area.

Potential applications of the method at Hanford Site can be illustrated by another estimate. If we assume that Sr concentration in waste solution is 10^{-4} M, and the solution volume is $2 \cdot 10^8$ L, total amount of Sr is $2 \cdot 10^4$ mol. Assuming that every tank and stripping solution is in contact with a organic solvent having surface of contact 100 m², for 100 tanks we have total surface of contact 10⁴ m². At the transport rate equal to $2 \cdot 10^{-8}$ mol-m⁻²-s⁻¹ time, necessary to remove Sr at this transfer rate is 10⁸s or approximately 3.2 years. Amount of D2EHPA necessary to saturate this volume of waste is $4 \cdot 10^6$ mol or approximately 1000 tones, which is practically feasible, taking into account that D2EHPA has already found broad applications in a hydrometallurgical industry and is made by several companies.

Contact of the organic solution of D2EHPA with the waste solution and stripping acidic solution can arranged in different ways. For example in the case of double wall tanks the stripping solution can be located in the space between the two walls with the organic solution above both aqueous solutions, separated by the wall. In this case the only way for the Sr to be transferred into the stripping solution is to be extracted into the organic solvent and then to be reextracted into the stripping phase. All liquid phases have to be stirred.

In another modification of the process the lighter organic solution of D2EHPA is supplied through the pipe with a nozzle as a dispersed phase into the waste solution at the bottom of the tank. The organic phase as small drops or microemulsions enriched by Sr is



delivered to the top of the tank due to its lower density, where it is collected and then supplied through another pipe with a nozzle into the stripping solution at a bottom of the its corresponding vessel. The organic solution comes up to the surface, simultaneously it is stripped of Sr and then the solution is supplied back at the bottom of the tank with the waste. In this case the process of Sr removal has a cyclic character, though it can be varied in many ways. Due to the high surface area of the dispersed phase the rate of Sr removal and stripping is much higher than in the case of the bulk organic liquid. Such variations are not to be regarded as a departure from the spirit and scope of invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the claims attached to and forming a part of this specification.

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Table 1. Summary of conditions used in the various bulk liquid membrane experiments, using the concentric cylinder reaction chamber described in Fig. 2.

No.	Inner chamber	Membrane	Outer Chamber	Stirring Rate, rpm	Flux, $\text{mol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}\cdot 10^{10}$
1	0.005 M SrCl_2 , pH 13.5 30 ml	xylene 12% D2EHPA, 20 ml	HCl, pH 1.6-2.1, 105 ml	300	0.6
2	the same	mineral oil, 9% D2EHPA	the same	300	3.2
3	the same	the same	the same	1000	25
4	HCl, pH 1.5	mineral oil 20% D2EHPA 56 ml	SrCl_2 , pH 13.6	500	0.94
5	H_2SO_4 , pH -0.18	mineral oil, 50% D2EHPA +octanol 100ml	$\text{Sr}(\text{NO}_3)_2$, 80 ml	300	1.4
6	Tank-Waste Simulant w/o Ca or EDTA, $5\cdot 10^{-4}$ M SrCl_2	50% D2EHPA, 20% mineral oil, 20% xylene, 10% octanol	H_2SO_4 , 80 ml	300	0.48
7	Tank-Waste Simulant with Ca and EDTA $2\cdot 10^{-5}$ M SrCl_2	33% D2EHPA, 25% mineral oil 25% xylene, 17% octanol, 75 ml total	1 N H_2SO_4 90 ml	400	0.02



Table 2. Chemical composition of reference tank-waste solution, and stability constants ($\text{Log } K_{\text{stab}}$) of several divalent metals and Al with EDTA.

Chemicals	Concentration (mol/L)	$\text{Log } K_{\text{stab}}^{\S} (\text{M}^{-1})$
NaOH	2.61	
KOH	0.09	
SrCl_2	10^{-4} to 10^{-6}	8.73
CaSO_4	0.02	10.69
$\text{Mg}(\text{NO}_3)_2$	0.01	8.79
$\text{Al}(\text{NO}_3)_3$	0.04	16.3
NaNO_3	0.59	
NaNO_2	0.4	
Na_3PO_4	0.1	
CsCl	10^{-4}	

$^{\S} K_{\text{stab}}$ for Co, Cu, Fe, Mn Ni, Pb and Zn are in the range 10^{14} to 10^{25}M^{-1} .





Claims

We claim:

1. A process for removal of strontium ions from a strong alkaline aqueous solution, comprising the steps of :

contacting said aqueous alkaline solution with a solvent consisting of a di-(2-ethylhexyl) phosphoric acid in a diluent for a period of time sufficient to extract said strontium ions from said aqueous alkaline solution into said solvent and form di-(2-ethylhexyl) phosphoric acid complex with strontium ;

transfer of the di-(2-ethylhexyl) phosphoric acid complex with strontium and contacting with an acidic solution;

stripping said strontium ions from said solvent by contacting said solvent with said acidic solution.

2. The process of claim 1 wherein the pH of said aqueous alkaline solution is above 9.
3. The process of the claim 2 wherein the said diluent is an organic liquid which has a very low solubility in water and can dissolve di-(2-ethylhexyl) phosphoric acid.
4. The process of the claim 3 wherein the said diluent is an organic liquid lighter than water and selected from the group consisting of kerosene, aliphatic hydrocarbons, aromatic hydrocarbons, long chain alcohols, ketones, ethers, pyridines, organo-phosphorus derivatives and mixtures thereof.
5. The process of the claim 4 wherein the concentration of said di-(2-ethylhexyl) phosphoric acid in said diluent is from about 1.0×10^{-6} molar to 5 molar.
6. The process of the claim 5 wherein the said strong alkaline aqueous solution is saturated with said di-(2-ethylhexyl) phosphoric acid.
7. The process of the claim 4 wherein EDTA is added in the said strong alkaline aqueous solution in the concentration higher than the concentration of the said Ca but lower than the total concentration of two- and three-valent metals.
8. The process of the claim 4 wherein the said strong alkaline aqueous solution is saturated with said di-(2-ethylhexyl) phosphoric acid and wherein EDTA is added in the said strong alkaline aqueous solution in the concentration from about the concentration of the said Ca to the total concentration of two- and three-valent metals.





9. The process of the claim 4 wherein the said organic liquid further includes specific extractants or chelating agents, such as crown ethers.
10. The process of the claim 4 wherein the said organic liquid is transferred into the said strong alkaline solution as microdrops or microemulsions.
11. The process of the claim 4 wherein the said acidic solution has sulphuric acid with the concentration from about 0.001molar to 10 molar.
12. The process of the claim 10 wherein the said strong alkaline aqueous solution is saturated with said di-(2-ethylhexyl) phosphoric acid and wherein EDTA is added in the said strong alkaline aqueous solution in the concentration from about the concentration of the said Ca to the total concentration of two- and three-valent metals and wherein the said organic liquid is transferred into the said strong alkaline solution as microdrops or microemulsions.

