Strontium Extraction from the Geo-environment

Rajiv Ranjan Srivastava and Sadia Ilyas

Contents

Abstract Strontium, a highly reactive alkaline earth metal, is very stable in natural occurrence minerals; however, the mobility of its isotope ^{90}Sr produced from the nuclear fallout is one of the deadly fission products. Celestite, $SrSO_4$, is the most important primary source of it following the exploitation via either the black ash or direct leach process. For which, the illustration of the thermal and aqueous chemistry of strontium is very crucial. In the case of ^{90}Sr, its separation from the other radionuclide, most specifically over the ^{137}Cs from the high-level waste (HLW) of fission products, is vital, converting the HLW to low-level waste (LLW). Liquid-liquid (solvent) extraction technology has been widely accepted for the efficient separation and recovery of strontium from the fission products, as the radionuclide already remains in its soluble form therein the waste solution. Interaction strategy between the metal ion and dipole from the donor atom of crown ether is prominently being used, whereas the poorly hydrated anions of dicarbollide, a boron cluster with

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a π-bonded trivalent cobalt ion, form ion-pair neutral compounds in the extraction process. In this chapter, the extraction processes of strontium from both natural mineral and synthetic source of the waste fission solution are being discussed, which includes the process technology, adopted techniques behind the technology, crucial points, and key parameters.

Keywords Geo-environment · Mineral · Recovery · Solvent extraction · Strontium

1 Introduction

Strontium (Sr) is a highly reactive alkaline earth metal. The occurrence of natural strontium is stable, but the mobility of its synthetic isotope ^{90}Sr obtained from the nuclear fallout is one of the most harmful fission products [1, 2]. Therefore, the extraction of strontium can also be divided mainly into two parts: (1) minerals, commonly the celestite and strontianite (as shown in Fig. 1), and (2) spent fuels of nuclear fission containing ^{90}Sr [3, 4], which has been focused primarily in this chapter.

2 Extraction from the Primary Minerals

Celestite or say celestine ($SrSO_4$) is the main mineral source of strontium that commonly exists in highly gypsiferous soils. The preferential occurrence in decalcified parts of the groundmass suggests its resultant formation of calcite dissolution without getting affected by the conditions resulting in the dehydration and rehydration of gypsum minerals [3]. The carbonate mineral, strontianite ($SrCO_3$), is another principal mineral of strontium albeit limited and sometimes mixed with celestite. Strontium predominantly as its carbonate salt is largely produced from Sr concentrates by following either black ash or direct leach process.

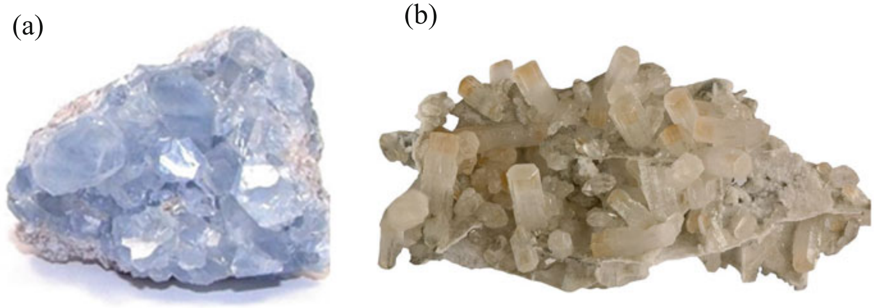


Fig. 1 A pictorial representation of the two major natural minerals of strontium

2.1 Extraction by a Black Ash Process

In the first process, the water-soluble species of strontium sulfide is formed via calcinating the celestite with coal fines in a rotary kiln at a higher temperature ~1100°C to expel out oxygen by forming the CO_2. Thus obtained soluble sulfide of strontium is subjected to dissolve in water and filtered, where the residue contains most of the metal impurities as their insoluble sulfides. The presence of silicon and iron compounds has found to be problematic in this process as they can form water-insoluble silicates and ferrites, respectively, during the calcination process [5–7]. The filtrate is treated with soda ash or carbon dioxide to yield the precipitates of $SrCO_3$ product. Nevertheless, this is the most widely used process, treating approximately 3 lakh tonnes annually [8]; the formation of $SrCO_3$ during calcination causing the insoluble loss of strontium during water leaching is the major disadvantage of this process. Moreover, an energy-intensive process generating the undesirable pollution by-products such as CO_2 and H_2S is also not favorable from operational and environmental aspects [9].

The occurrence of calcination reactions in the black ash process can be given as:

$$SrSO_4 + 2C \xrightarrow{\Delta} SrS + 2CO_2 \tag{1}$$

$$SrSO_4 + 3C \xrightarrow{\Delta} SrS + 2CO + CO_2 \tag{2}$$

However, the Gibbs free energy versus temperature data as shown in Fig. 2 for Eqs. (1) and (2) is thermodynamically possible at approximately 500°C; but if corroborated by the formation of CO and CO_2 from carbon, it can be depicted that

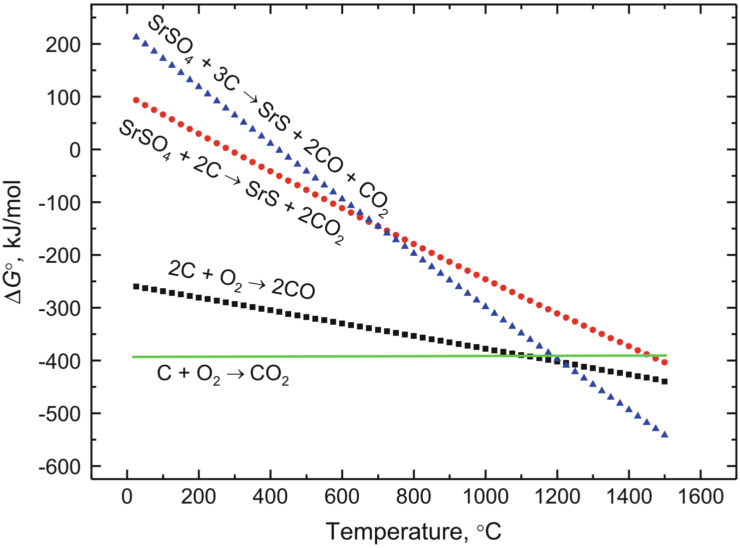


Fig. 2 Gibbs free energy versus temperature plot for celestite calcination with carbon

the occurrence of Eq. (2) is relatively more favorable than Eq. (1) at a temperature slightly below the 1200°C. Thus the formation of the calcined product according to Eq. (1) can be mainly due to often an increased temperature zone than the maintained value while dealing with carbon at high temperature.

The dissolution reaction of calcined product in water can be written as follows:

$$SrS + CO_2 + H_2O \rightarrow SrCO_3 + H_2S \tag{3}$$

Actually Eq. (3) occurs in two steps:

$$SrS + H_2O \rightarrow Sr(OH)_2 + H_2S \tag{3a}$$

$$Sr(OH)_2 + CO_2 \rightarrow SrCO_3 + H_2O \tag{3b}$$

Therefore, it has been found that the progress of Eq. (3) mainly depends on the solubility of $Sr(OH)_2$ by easier decomposition of SrS into hot water (as Eq. 3). The use of CO_2 instead of Na_2CO_3 and the introduction of oxygen in carbonation column can increase the yield and purity of the product within a shorter carbonation time [10].

2.2 *Extraction by Direct Leach Process*

Using the direct leach process in the commercial production of $SrCO_3$, the beneficiation of celestite simply involves crushing, sizing, acid washing (for dissolving impurities of $CaCO_3$, $BaCO_3$, and iron oxide), and sometimes flotation to obtain the concentrates that contain more than 90% $SrSO_4$ [5]. A typical example of celestite beneficiation is given in Table 1 [11]. Thereafter the concentrates are directly leached in carbonate solution using a mechanically stirred tank at moderate temperatures (90–95°C) to yield the $SrCO_3$.

Depending upon the celestite grade and the application, $SrCO_3$ can be used directly or subjected to further purification [6, 11, 12]. Dissolution in HCl followed by pH neutralization of the solution is carried out for removal of iron impurity as its precipitate along with silica. After filtration, the $SrCl_2$ solution is subjected to another precipitation with soda ash to yield $SrCO_3$ of high purity [7]. Alternatively, the impure $SrCO_3$ is calcined at 1400°C to obtain SrO, which is then dissolved in water to separate SiO_2, Fe_2O_3, $Ca(OH)_2$, and Al_2O_3. The filtered solution of $Sr(OH)_2$

Table 1 A typical composition of celestite mineral and concentrate after beneficiation works

Compound	Wt.% in raw mineral	Wt. % in concentrates
$SrSO_4$	76.43	97.85
$SrCO_3$	13.24	<0.01
$CaCO_3$	8.04	<0.01

Small quantities of $BaSO_4$, Fe_2O_3, Al_2O_3, K_2O, and MgO also remain with the mineral is treated with carbon dioxide to yield the $SrCO_3$ product. In the latter process of purification, the barium carbonate with a little tendency to decompose during calcination can also be eliminated. However, the direct leach process yields a relatively impure product (~95% $SrCO_3$) as compared to the black ash process; it has been considered the simpler process of low cost with by-products of commercial interest [6, 11]. The reactions involved in a direct conversion of celestite to carbonate species followed by purification steps can be given as below:

For leaching:

$$SrSO_4 + Na_2CO_3 \rightarrow SrCO_3 + Na_2SO_4 \tag{4}$$

For purification via acid treatment:

$$SrCO_3 + 2HCl \rightarrow SrCl_2 + H_2CO_3 \tag{5a}$$

$$SrCl_2 + Na_2CO_3 \rightarrow SrCO_3 + 2NaCl \tag{5b}$$

For purification via calcination:

$$SrCO_3 \xrightarrow{\Delta} SrO + CO_2 \tag{6a}$$

$$SrO + H_2O \rightarrow Sr(OH)_2 \tag{6b}$$

$$Sr(OH)_2 + CO_2 \rightarrow SrCO_3 + H_2O \tag{6c}$$

Further, the strontium metal can be produced either by the thermal reduction of strontium oxide and aluminum metal and distillation of elemental strontium on a cooled plate or by the electrolysis of a fused bath of $SrCl_2$ and ammonium/potassium chloride following the reactions [8, 13]:

$$Sr^{2+} + 2e^- \rightarrow Sr \tag{7a}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{7b}$$

It needs to be mentioned here that low recovery and purity are the main reasons for comparatively being the less industrial use of the direct leach process; hence, this process is widely being studied to understand the direct conversion phenomena of celestite to its high-yield product. Below some of the most influential factors are briefly discussed.

2.2.1 Aqueous Chemistry for Leaching the Strontium

A difference in solubility products between $SrSO_4$ (3.2×10^{-7}) and $SrCO_3$ (1.1×10^{-10}) is the main driving force for the leaching reaction of Eq. (4) [14]; hence, their apparent solubility in terms of Sr ion concentration can be expressed as:

$$\left[\mathrm{Sr}^{2+}\right] = \frac{3.2 \times 10^{-7}}{\left[\mathrm{SO}_4^{2-}\right]} \tag{8a}$$

$$\left[\mathrm{Sr}^{2+}\right] = \frac{1.1 \times 10^{-10}}{\left[\mathrm{CO}_3^{2-}\right]} \tag{8b}$$

The solubility calculated for a reaction system of Na_2CO_3: $SrSO_4$ from 1.0 to 1.2 (mole ratio) given in Fig. 3 indicates that regardless of the value of mole ratio, the solubility of $SrSO_4$ is maximum in absence of SO_4^{2-} ions and decreases with an increase in sulfate with the progress of leaching [11]. In contrast, the solubility of $SrCO_3$ increases with consuming the CO_3^{2-} ions. Leaching proceeds to the end of the reaction; the solubility of CO_3^{2-} eventually becomes similar to the SO_4^{2-} ions, which substantially decreases the driving force of leaching reaction. It can be handled by an excess of Na_2CO_3 in solution to keep leaching in progress.

The studies by Iwai and Toguri [15] and Sutarno et al. [7] have clearly established that the stoichiometric conversion of celestite to $SrCO_3$ (at Na_2CO_3: $SrSO_4$ = 1:1) occurs only above solution pH 9.0 (as shown in Fig. 4). The influential pH for carbonate leaching has been corroborated by the dissociation constant values of H_2CO_3 [7, 11, 15, 16]:

$$\mathrm{H_2CO_3} \leftrightarrow \mathrm{H^+} + \mathrm{HCO_3^-} \quad K_1 = 10^{-6.35} \tag{9a}$$

$$\mathrm{HCO_3^-} \leftrightarrow \mathrm{CO_3^{2-}} + \mathrm{H^+} \quad K_2 = 10^{-10.33} \tag{9b}$$

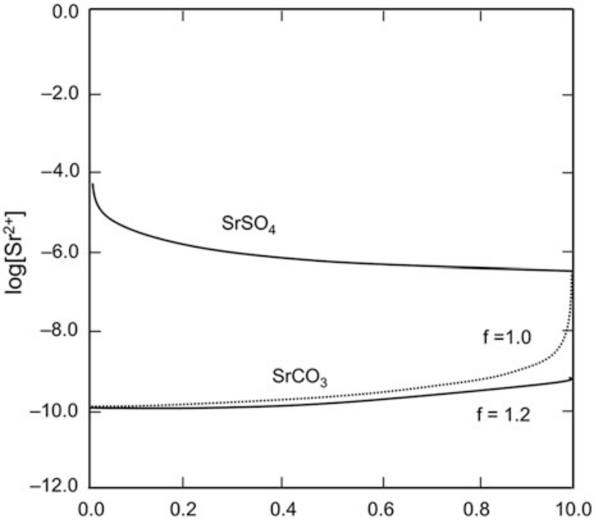


Fig. 3 Apparent solubility of celestite and $SrCO_3$ as a function of sulfate species by reaction with Na_2CO_3 and $SrSO_4$ at different molar ratios (Adopted with permission from Carrillo et al. [11])

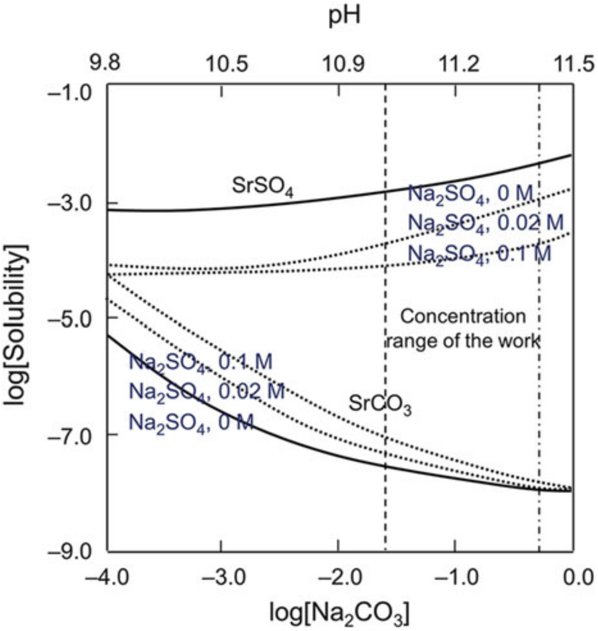


Fig. 4 Relationship between the apparent solubility of $SrCO_3$ and $SrSO_4$ with pH (Adopted with permission from Iwai and Toguri [15])

2.2.2 Parametric Influences on Direct Leach Process of Celestite

Castillejos and co-workers [16] have shown that the rate of reaction significantly increases with increasing carbonate concentration in solution. The fitted parabolic rate constants indicated the leaching is controlled by the diffusion of $NaCO_3^-$ into the pores of the thickening product layer. Notably, leaching celestite in >0.1 M Na_2CO_3 solution at 10 g L^{-1} pulp density caused a decrease in reaction rate due to a lower diffusivity with an increased dense product layer [15, 16]. It has been observed that under a stoichiometric Na_2CO_3 dosage and mild temperature, large conversion fractions are achievable, but not all. An entire conversion has found to be possible with a risen temperature (from 25 to 75°C) under the similar condition (as shown in Fig. 5). The calculated activation energy of 64.1 and 70.05 kJ $mole^{-1}$ in different studies has revealed the transport through chemically controlled conversion reaction [17] and the effective diffusivity of carbonate ions fell in the range of 1.2×10^{-9} to 6.7×10^{-8} cm^2 s^{-1}. Studies on the effect of stirring speed and particle size have favorably demonstrated a high speed (>550 rpm) and small particle size (58 μm) follows shrinking-core model leaching is controlled by product layer reaction [16].

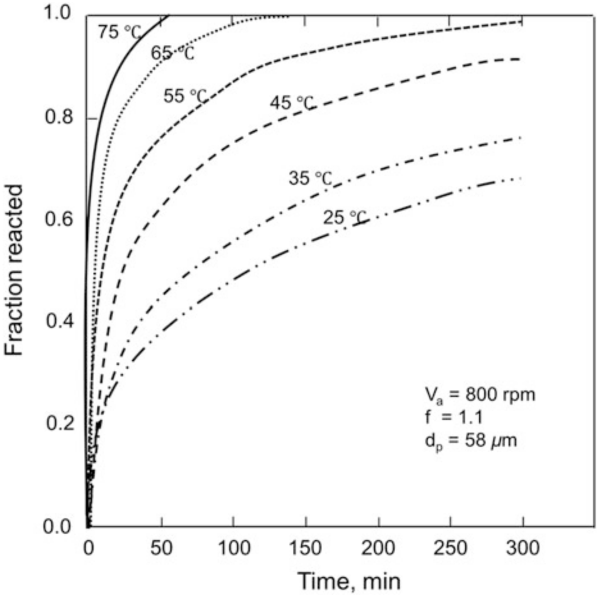


Fig. 5 Rate curve for the conversion of celestite to strontium carbonate as a function of time with different temperatures (Adopted with permission from Castillejos et al. [16])

2.2.3 Other studies

Besides the direct soda ash leach process of celestite, several alternatives have been explored either to increase the yield or purity of $SrCO_3$ product. HCl leaching of celestite showed the activation energy of 68.8 kJ $mole^{-1}$ for the process in 8.25×10^{-3} M $BaCl_2$ solution equilibrated with 0.5 M HCl, and the reaction rate has found to be inversely proportional to the particle size which increases as 0.19, 0.70, and 0.73 powers of the Ba^{2+}, Cl^-, and H^+, respectively [18]. A high purity of 98% celestite has been achieved by Dogan et al. [19], while a Turkish concentrate (~95% $SrSO_4$) cleaning was performed with 50% H_2SO_4 and 1–3% HNO_3 at 40–50°C. Using dry mechanochemical conversion of celestite with Na_2CO_3 in a planetary-type ball mill indicated the degree $SrCO_3$ formation increased (>90%) with milling time above 30 min [20]. The milled powders leached in water at room temperature followed by washing with 1 M HCl give a desirable product of $SrCO_3$, whereas Bingol et al. [21] used the activated $SrSO_4$–$(NH_4)_2CO_3$ mixtures to yield the conversion product of 98.1% $SrCO_3$ [21].

3 Extraction of Radionuclide ^{90}Sr from the HLW of Fission Products

In the processing of spent fuel of nuclear fission, the majority of heat load and radiation in the repository is mainly due to the high-level waste (HLW) of fission products. Approximately 27 tonnes of spent fuel is taken annually from the core of 1000 MWe nuclear reactor [22] that can be regarded entirely as waste (in the USA and Canada) or can be reprocessed (up to 97% in Europe and Japan). ^{137}Cs and ^{90}Sr with their relatively short half-lives of 30 and 28.8 years, respectively, contribute a larger heat load in HLW [23–25]. Therefore, the separation of ^{137}Cs and ^{90}Sr is potentially required to allow their management as a single product with reduced waste volume, saving repository capacity, and shortened the time for subsurface storage until they have decayed sufficiently to be disposed of as low-level waste (LLW). Additionally, the recovered ^{137}Cs and ^{90}Sr can be used as a radiation source in radiotherapy and micropower generator [26, 27]. Various methods (like solvent extraction, ion exchange, adsorption, precipitation, and membrane technology) have been studied and upscaled for the separation of ^{137}Cs and ^{90}Sr from HLW [24, 26–30]. Each of them has own limitations in their application, as given in Table 2 [31, 32]. In terms of stability and applicability for handling a large amount of radionuclide waste, below the prominent one, solvent extraction is being discussed in this chapter (for biosorption studies on strontium, please see Chap. 4).

Table 2 Features and limitations of each process applicable to radioactive waste treatments (After [31, 32])

Technique	Key features	Operational limitations
Precipitation	Handling of large volume and high salt content waste is non-expensive	Low decontamination factor and efficiency is dependent on the filtration rate
Evaporation	Suitable for a variety of radionuclides with decontamination factor $>10^4$ to 10^6	High operational cost with scaling, corrosion, and volatility problems
Ion exchange	The high chemical and thermal stability of long-range resin beads ensure high selectivity	Higher salt concentration affects adversely with blockage and poisoning effect of resin beads
Reverse osmoses	Economical for large-scale operation with decontamination factor 10^2 to 10^3	Fouling and high-pressure system
Ultra filtration	Higher separation ability even for colloidal material	Fouling and radiation damage of membrane are possible
Microfiltration	High recovery, low fouling	Very sensitive to impurity types
Solvent extraction	Large volume operation with high selectivity yields; removal, recovery, and recycling of actinides and solvent itself	Generates aqueous effluent after metal removal often needed a treatment step

3.1 Solvent Extraction

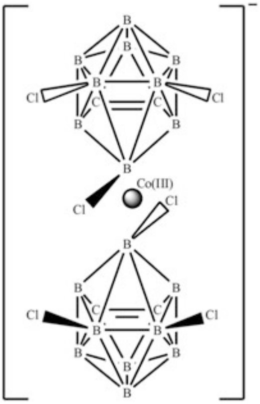
The flexibility in stage design and regeneration of organic, convenience in combining with other processes, and easiness to be scaled up are the inherent properties of solvent extraction (SX) to gain more attention in fuel reprocessing, which in fact is invariably being used at present [33]. Selection of appropriate extractant is the vital factor of SX; hence, below the SX of ^{90}Sr is divided on the basis of extractant used in the separation and recovery process. The compounds developed and widely used in strontium extraction have been given in Fig. 6 [30].

3.1.1 Crown Ethers

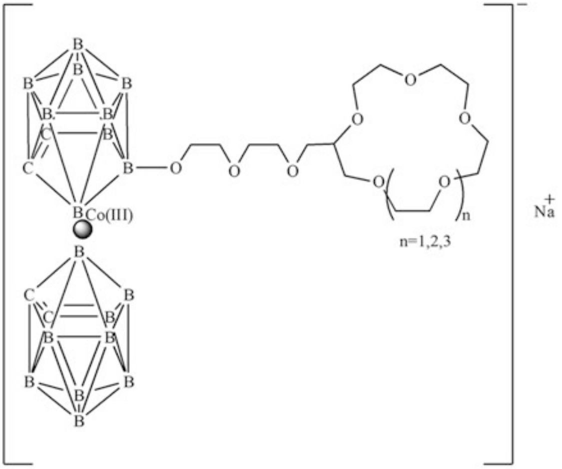
Crown ethers are highly selective compounds to interact with metal ions, which arise due to the interactions between the charged metal ion and dipole from the donor atom of crown ether [33]. The selectivity is primarily dependent on the suitability of the size of metal ions with the cavity of particular crown ether. The effect of electrostatic induction as the additional electron withdrawing or donating groups, the presence of altering heteroatoms (P, S, N, and O) within the crown ether, and types of solvents have the major role in the extraction process. Various electron donating and withdrawing substituents, including the alkyl groups (like halogen, methyl, nitro, and amine groups), have been introduced to modify the properties (like solubility and electronic property) of crown ether and are used in the extraction of ^{90}Sr [25, 34]. For instance, 15-crown-5 (15C5) or 18-crown-6 (18C6) are strongly hydrophilic; hence, aryl or alkyl group must be added to enhance their lipophilicity for making them suitable to be used in SX, e.g., dicyclohexano-18-crown-6 (DC18C6) or dibenzo-21-crown-7 (DB21C7) [35]. The extraction of strontium from a nitrate solution by crown ethers can commonly be presented as below (where m and n are an integer value):

$$\mathrm{Sr(NO_3)_2} + \overline{m\mathrm{C}n} \rightarrow \overline{\mathrm{Sr(NO_3)_2} \cdot m\mathrm{C}n} \tag{10}$$

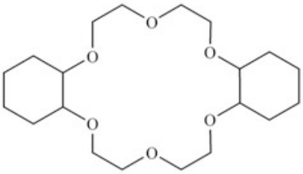
The rigid benzocrown ethers are effective in the extraction of monovalent cations, whereas the cyclohexano crowns are more suitable for divalent cations. The cis-syn-cis, cis-anti-cis, and trans-syn-trans isomers of DC18C6 exhibited the most efficient extractant ($D_{\mathrm{Sr}} = 24.8$) from nitric acid solution. The trans-syn-trans of DC 18C6 yields maximum extraction at a higher acidity, however, with only a 14.3 value of distribution coefficient. Using DC18C6 (0.1 M in chloroform) and DB21C7 (0.1 M in nitrobenzene with the addition of phosphomolybdic acid), the extraction of strontium and cesium could be quantitatively achieved, respectively [36]. The value of distribution coefficient decreases more with an increase in nitric acid concentration in the aqueous solution, as the D_{Cs} and D_{Sr} with *bis*-(4,4′(5′)-[1-hydroxy-2-ethylhexyl]-benzo)-18-crown-6 and *bis*-(4,4′(5′)-[1-hydroxyheptyl] cyclohexano)-18-crown-6 (0.02 M concentration of both crown ether in the mixture



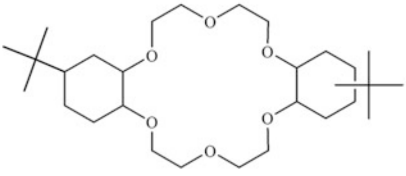
1. Chlorinated cobalt dicarbollide



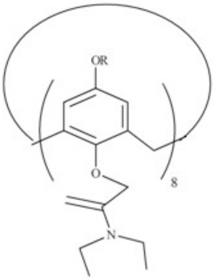
2. Crown ether substituted cobalt bis (dicarbollide)



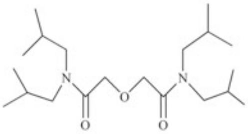
3. Dicyclohexano-18-crown-6 (DCH18C6)



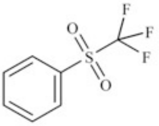
4. di-*tetra*-butylcyclohexano-18-crown-6 (DtBuCH18C6)



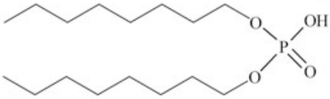
5. Calix[8]arene octamides



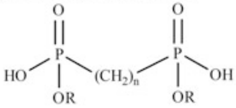
6. *N,N,N',N'*-tetraisobutyl-3-oxa-gluteramide (TiBOGA)



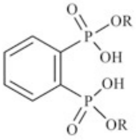
7. Phenyltrifluoromethylsulfone (FS-13)



8. di-*n*-octylphosphoric acid (HDOP)



(R = 2-ethylhexyl)
9. P,-P'-di(2- ethylhexyl) alkylenediphosphonic acids



10. P,-P'-di(2- ethylhexyl) benzen-1-2-diphosphonic acid
(H_2DEH[1-2-BzDP]

Fig. 6 Various compounds used for solvent extraction of strontium extraction (Adopted with permission from Xu et al. [30])

of 0.1 M nonyl-naphthalenesulfonic acid or TBP–kerosene) were only 1.6 and 1.98 from a 3 M HNO_3 solution. The back-extraction of both metals required multiple stages of stripping with a dilute HNO_3 solution [37–39]. In a similar type of studies by Dietz et al. [40, 41] with a higher acidic solution (4 M HNO_3), the most efficient result ($D_{Cs} = 4$) was with 0.1 M di-*tert*-butyl-benzo-21C7 diluted in methylpentanone and, as for the strontium, evidenced the role of dissolved water therein the diluents. The highest selectivity for cesium over sodium was with 21C7 derivatives; however, the efficient extractant was 4,4′-(5′)-di-[(1-hydroxy-ethylhexyl)-benzo]-18C6 associated with 0.2 M TBP, yielding $D_{Cs} = 30$. It showed that none of the investigated compounds gave the desired combination of selectivity, efficiency, solubility, and stability. The examined dependency on nitrate ion for strontium extraction with various crown ethers revealed the contribution of two moles NO_3^- and the relation with associated cations found in the order of $Mg^{2+} > Al^{3+} > Na^+$ [42]. The extraction behavior of crown ethers from a lower 1.0 HNO_3 solution to the higher 10.0 M HNO_3 solution is given in Table 3.

Horwitz et al. [43–45] used DC18C6 and its dimethyl or di-*tert*-butyl derivatives in various oxygenated and aliphatic diluents, for the SX of strontium from acidic solutions. The highest D_{Sr} obtained with *n*-pentanol and *n*-hexanol could be corroborated to the metal cation extraction with the water contents combined in the diluent. Due to this, the diluent does not require the complete removal of the hydration shell of the nitrate associated with strontium for its mass transfer in the organic phase. Subsequently, the process, namely, "SREX" (stands for strontium extraction) was proposed using the di-*tert*-butyl-cyclohexano-18C6 diluted in 0.2 M 1-octanol from >1 M HNO_3 solution. A good chemical and radiochemical stability showed by the organic constituents required three extraction stages for quantitative extraction (99.7%) of strontium in the SREX process. A trial on Na-bearing waste solution revealed that the interferences caused by the alkali and alkaline earth cations (like Na^+, K^+, Ca^{2+}) did not affect the extraction efficiency of Sr^{2+}. Nevertheless taking the di-*tert*-butyl-cyclohexano-18C6 (0.15 M) in 1.2 M TBP/Isopar L as (diluents), the co-extraction of strontium and lead followed by their selective stripping (using 16 centrifugal contactors) did not give the desired results. A poor selectivity and low extraction were observed due to the building up of metal cations into the organic phase as their insufficient stripping from the loaded organic after the extraction stages.

Combining the Cs extraction (CSEX) with SREX process using the *bis*-4,4′(5′)[(2-hydroxy-alkyl)-benzo]-18-crown-6 and *bis*-4,4′(5′)[(*tert*-butyl)cyclohexano]-18-crown-6 diluted in the mixture of 1.2 M TBP, lauryl nitrile, and Isopar-L, the

Table 3 The behavior of Sr^{2+} extraction by different crown ethers from the feed aqueous solution of 1.0 and 10.0 M HNO_3

Crown ether	Distribution ratio (D_{Sr}) in acidic solution	
	1.0 M HNO_3	10.0 M HNO_3
12C4	0.0009	0.0038
15C5	0.026	0.089
18C6	0.114	0.63
DB18C6	0.0036	0.013

process enables 99.99% cesium and strontium recovery from the waste solution containing 3.78 M HNO_3, 0.486 M Al, 0.778 M Ca, 0.225 M Zr, and 0.015 M Na [46]. Lumetta et al. [47, 48] used di-*tert*-butyl-cyclohexano-18C6 in octanol for selective extraction of strontium after the extraction of lanthanides and actinides by CMPO (Octyl-phenyl-*N*,*N*-diisobutyl carbamoyl methyl phosphine oxide) yielding the decontamination factors that exceeded 7800. A relation between D_{Sr} and water contents into the various organic phases (constituted of DC18C6 in alcohols and DB18C6 derivatives in nitrobenzene 4,4′(5′)-dinonaoyl-dibenzo-18C6, 4,4′(5′)-dihexanoyl-benzo-18C6, 4,4′(5′)-di-acetyl-benzo-18C6, di-*tert*-butylbenzo-18C6, dibenzo-18C6) revealed the highest D_{Sr} with the mixture of butanol and octanol in a ratio of 80:20 [49, 50], whereas the highest D_{Cs} could be achieved with di*tert*-benzo-18C6 in addition with phosphotungstic acid albeit the low solubility of it in nitrobenzene is disadvantageous. Strontium extraction carried out with 15C5/dicarbollide diluted in nitrobenzene from $HClO_4$ with dibenzo-18C6/dicarbollide also diluted in $C_6H_5NO_2$ enabled to get the extraction constants of metal-organic complexes [51, 52]. Also, the highest D_{sr} and selectivity on the extraction of strontium over calcium was obtained with 15-crown-5 and with 15-benzo- and dibenzocrown-5; 12C4 and 18C6 have found to be less effective.

Extraction Influenced by the Diluents and Irradiation Effect

In most of the cases, the diluents comprise the larger part of a solvent. Therefore, proper selection of diluents is almost as crucial as selecting a suitable extractant because of the physical and chemical effects that the diluents can exhibit and also meet the environmental and safety requirements in an SX process [53]. Using the DtBuCH18C6, Mohapatra et al. [54] have investigated the effects of several diluents (including toluene, *n*-octanol, benzene, *t*-butyl benzene, *o*-dichlorobenzene, *n*-dodecane, chloroform, *n*-hexane, and the binary mixtures) on strontium extraction from a nitrate solution. A correlation between the Sr extraction and Schmidt's diluent parameter has been determined, which is formulated by the various physical properties of the diluents (polarizability, H-bonding, viscosity, polarity, Hildebrand's solubility parameter, etc.). Using DCH18C6 with several diluents (chlorobenzene, chloroform, dichloroethane, carbon tetrachloride, *n*-octanol, nitrobenzene, and its mixtures with benzene), Gupta et al. [55] found higher D_{Sr} values for aromatic and chlorinated diluents with their higher dielectric constants. But due to safety concern in the nuclear process, these diluents are not recommended to be used, and, alternatively, a diluent mixture of TBP + dodecane + *n*-octanol (in the proportionate ratio of 30:20:50 vol.%) can be used. Use of dinitriles (glutaronitrile, succinonitrile, malononitrile, and adiponitrile) and diluents with DCH18C6 leads to form the solvated cationic complexes into the organic phase, resulting in an increased efficiency of strontium extraction [56].

The strong radiation by the ^{90}Sr, ^{137}Cs, and other radionuclide elements of the nuclear waste solution, exhibiting the irradiation effect on SX system during the operation, must be addressed [57]. The extractant and diluents in contact with the

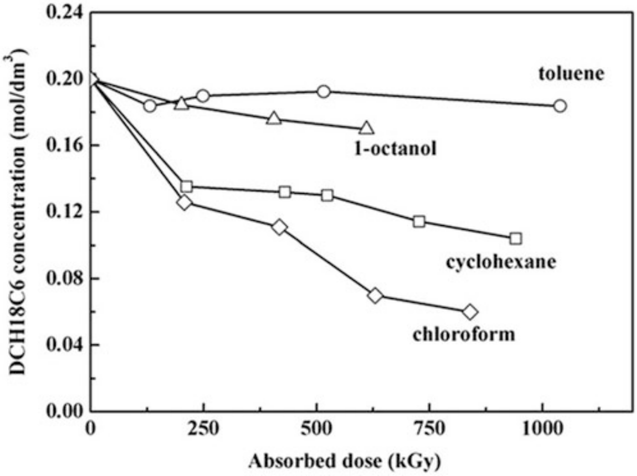


Fig. 7 DCH18C6 concentrations remaining in selected solvents after irradiation (Adopted with permission from Takagi et al. [58])

radioactive waste adversely affect the performance of organic that includes the efficiency, distribution, and separation factors and the recyclability of the organic solvents. The investigated irradiation effect on DCH18C6 with different diluents (chloroform, *n*-octanol, toluene, and cyclohexane) has been given in Fig. 7 [58]. The radiolytic degradation of DCH18C6 in all of the diluents, certainly with different degree, was observed, in which it was least in toluene and highest in chloroform. Exposure to γ-radiation could cause a darkening of solvent (0.12 M HCCD and 0.027 M PEG-400 in phenyltrifluoromethylsulfone) due to the formation of a water-soluble radiolytic product [59]. The value of D_{Sr} gets decreased with an increasing absorbed dosage; however, stripping was unaffected. In a study with the organic phase (0.025 M DtBuCH18C6 in *n*-octanol or in the mixture of 20:80 vol% *n*-octanol/toluene), the irradiated organic phase with diluent mixture showed an improvement in strontium extraction up to a dose of 40 mrad, due to the increased uptake of acid into the organic phase [60]. A reduction in partitioning of Sr^{2+} to crown ether ionic liquids, [C(4)mim][PF6] and [C(4)mim][NTf2] phase, has been observed due to the formation of proton ion during γ-radiation of the ionic liquids, which can be handled by additional water washing step [61–63]. Interestingly, all the removal of Sr^{2+} ions from nuclear waste solution occurs via the irradiated [C_4mim][NTf_2] and via precipitation not by extraction with the organic phase. The precipitates as irradiation product identified as $SrSO_3$ and/or $SrSO_4$, depending on the contact time [63].

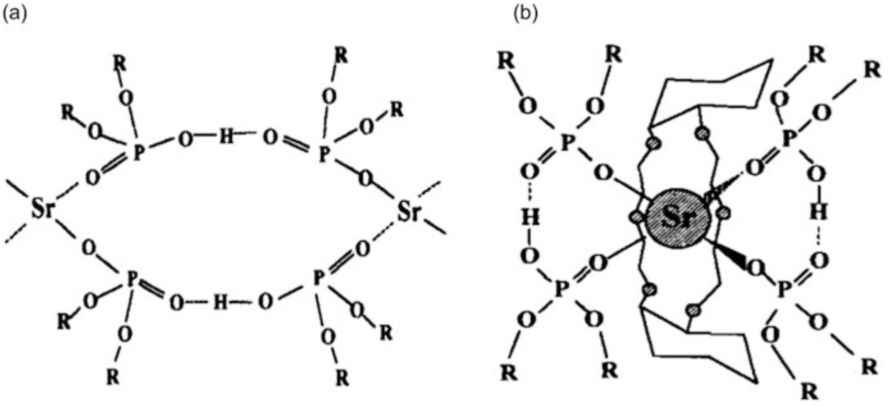


Fig. 8 The structure of Sr complexes (Adopted with permission from Thiyagarajan et al. [65])

Complexed Structure into the Organic Phase

For a better understanding of extraction mechanism, the study on structure formation of metal ion complexed with the organic extractant can be helpful. Adopting the small-angle neutron scattering (SANS) methodology, Chiarizia et al. [64] investigated the extraction behavior of strontium from a $LiNO_3$ solution by using the di-*n*-octylphosphoric acid (HDOP) and compared with HDOP/DCH18C6 mixture in toluene. The addition of DCH18C6 showed a synergistic effect on extraction with increased efficiency than that of with HDOP alone. The SANS analysis revealed that the extraction with HDOP alone in large stoichiometric excess predominantly forms the $Sr(H(DOP)_2)_2$ complex solvated into the organic phase (as shown in Fig. 8a). It is similar to the structure that was reported for the aggregates formation with HDEHP [65]. When Sr^{2+} is wrapped by the DCH18C6 ligand, its interaction with the next two dimmers of HDOP becomes more difficult and prefers to reorient itself as the mononuclear complex schematically is shown in Fig. 8b for the *cis-syn-cis* isomer of DCH18C6. Hence, the addition of crown ether takes part in the complex formation in the ratio of 1:2 for DCH18C6: HDOP while extracting one molecule of Sr^{2+}. The large aggregates by HDOP alone could not be observed in both the *cis-syn-cis* and *cis-anti-cis* isomers of DCH18C6. The structure shown in Fig. 8b is quite supporting to that of the structural study carried out by Burns and Kessler [66] for the bis(dibutylphosphato)aquastrontuim-18crown-6, in which, the 9-coordinated Sr^{2+} ion is revealed to be complexed with six oxygen atoms of the crown ether, two monodentate dibutyl phosphato ions, and one molecule of H_2O. Although a 10-coordinated Sr^{2+} can be found in [Sr(*cis-syn-cis*-DCHI8C6)$(NO_3)_2$]·CCI_4 and [Sr(*cis-syn-cis*-DCHI8C6)$(TMA)_2$]·H_2O [67], the 9-coordinated Sr^{2+} ion appears to be more suitable for accounting the orientational flexibility of solution complexes [64].

3.1.2 Dicarbollides

Dicarbollide is a boron cluster with a π-bonded cobaltic ion. It was originally prepared by Hawthorne in 1965 and studied for cesium extraction, later used in the extraction of strontium by adding the polyethylene glycols (PEGs) to yield the synergistic effect [23, 29, 30]. The chemical and radiation stability possess the uses of dicarbollides in radionuclide's extraction even from the waste solution of very high acid concentration [68]. The poorly hydrated anions of dicarbollide associated with cations forming the ion-pair neutral compounds have greater solubility in polar-dissociating diluents like nitrobenzene than the water [30]. Its lipophilic anion is difficult to protonate and allows metal cations to be discriminated by their Gibbs energies of transfer. The extraction of strontium from a highly acidic solution can commonly be presented as below (where, *m* and *n* are an integer value):

$$\mathrm{Sr}^{2+} + \overline{n\mathrm{H}^{+}} + \overline{n\mathrm{CoB}_2^{-}} \rightarrow n\mathrm{H}^{+} + \overline{\mathrm{Sr}^{2+}} + \overline{n\mathrm{CoB}_2^{-}} \tag{11}$$

The extraction of ^{90}Sr from the nitric acid medium is carried out by dicarbollide anion $\{[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Co\}$ diluted in polar nitrobenzene. The addition of polyethylene glycol (PEG, HO–$(C_2H_4O)_n$–H mainly the lipophilic *p*-nonylphenyl-nonaethylene glycol, Slovafol 909 HO–$(C_2H_4O)_9$–C_6H_4–C_9H_{19}) to the dicarbollide can remove the water molecules surrounding the metal cations to improve its transfer to the organic phase. Dicarbollides display good stability toward irradiation; however, only effective in diluents of toxic nature like nitrobenzene and releasing halides during the reprocessing can raise the corrosion problem for the system. Using a diluent without nitro group, diethylene glycol ditetrafluoropropyl is proposed; Slovafol addition can lead to the extraction of ^{90}Sr and ^{137}Cs from 2 M HNO_3 solution. Tetrahexyl-dicarbollide in aromatic hydrocarbon diluents exhibits comparable distribution coefficients to that of the dicarbollide in nitrobenzene. With a negligible loss into the aqueous phase, the equilibrium constant value of 1.7 was obtained for strontium, which was 800 and 0.5 for cesium and sodium ions, respectively [69–71]. Using tetrahexyl-dicarbollide in diethylbenzene for extracting the cesium and strontium from alkaline media yielded a diminished distribution coefficient with respect to increasing alkalinity of the solution. The value of D_{Sr} could be changed from 30 to 7 when NaOH concentration varied from 0.01 to 1.0 M. Using the chlorinated cobalt dicarbollide in nitrobenzene and carbon tetrachloride mixture, with the addition of 1 vol.% Slovafol 909, a 99.8% recovery for ^{90}Sr yielded the decontamination factor of above 500 [72].

Notably, the extracted ^{90}Sr and ^{137}Cs from the HLW are usually taken together for the final geological disposal; hence, their co-extraction can be advantageous [30]. The Universal Extraction (UNEX) process is a relatively well studied co-extraction process using dicarbollide and phosphorylated polyethylene glycols (PPEGs) diluted in *m*-nitrobenzotrifluoride (MNBTF) [73–75]. The organic phase constituted of the mixture of dicarbollide, PEG, and carbamoylmethyl phosphine oxide (CMPO) diluted in phenyltrifluoromethyl sulfone can be adopted for the simultaneous extraction of ^{90}Sr and ^{137}Cs from highly acidic media, along with the lanthanides and

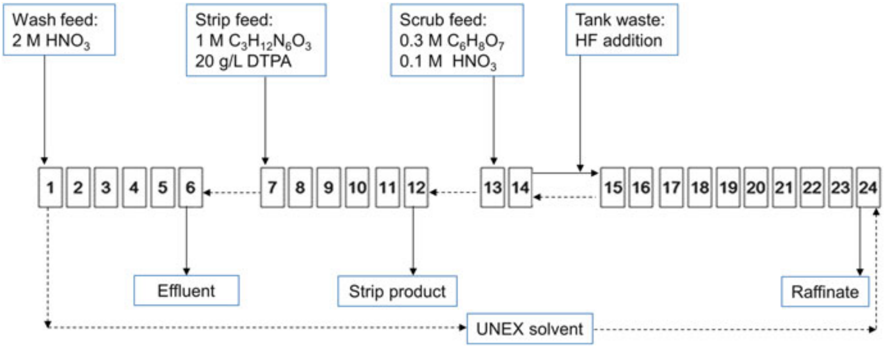


Fig. 9 Flowsheet for the demonstration of the UNEX process. (Adopted with permission from Law et al. [77])

actinides. Diethylenetriaminepentaacetic acid (DTPA) or the guanidine carbonate solution can be used for the effective stripping of extracted metals [76]. Law et al. [77] demonstrated the improved UNEX process with simulated and genuine acidic liquid tank waste, as shown in Fig. 9, in which the suppression iron and zirconium in co-extraction with the strontium and cesium was achieved by adding a certain amount of HF, yielding efficiencies of 99.4% ^{90}Sr and 99.99% ^{137}Cs along with >99% actinides. But looking on the requirement of actinide separation for transmutation in the process of advanced nuclear fuel cycling, the co-extraction of actinides is not preferable; hence, the later use of FS-13 with 0.08 M dicarbollide +0.6 vol.% PEG-400 could significantly suppress the actinide over co-extraction of 99.9% strontium and 97.4% cesium [78].

4 Conclusions

Celestite ($SrSO_4$) and strontianite ($SrCO_3$) are the main mineral source of strontium and predominantly being recovered as its carbonate salt by following the black ash or direct leach process. Nevertheless, the black ash process is widely used; the formation of $SrCO_3$ during calcination leads to the strontium loss, while leaching in water is found to be disadvantageous for the energy-intensive process. On contrary, the direct leach process yields a relatively impure product (~95% $SrCO_3$) as compared to the black ash process, but it is a low-cost simple process with by-products of commercial interests. There has been a plenty of researches devoted to strontium extraction from minerals; however, a high yield with the increased purity has still many scopes for new research to extract strontium from geo-environment.

At the same time, removal of radioactive and heat-emitting ^{90}Sr and ^{137}Cs from nuclear wastes and spent-fuel solutions is of great importance not only for the spent-fuel reprocessing and sustainable management of nuclear but also for the recovery of these two metals. As the requirement of radionuclide removal is still under discussion with respect to its economic aspects, the R&D on their recovery as value-added products will surely be beneficial for a further technical road map of the spent-fuel reprocessing. The solvent extraction has been potentially demonstrated for the simultaneous separation of cesium and strontium, mainly the CSEX/SREX process, and a combined crown ether/calixarene process. The stability of CSEX crown ether in HNO_3 solution, however, limits its use in an industrial process, and without any further development, the CSEX/SREX process is not a feasible option for advanced fuel cycle initiatives. An improved stability of the extractant in presence of HNO_3 must be addressed by the new research on these processes. In summary, the solvent extraction is a reasonable choice for strontium separation and recovery in advance fuel cycling, and more developments in this area can be well-expected in the near future.

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