

STRONTIUM REMOVAL FROM CAUSTIC CARBONATE WASTE SOLUTIONS USING CARRIER COPRECIPITATION

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ABSTRACT

A carrier coprecipitation procedure has been developed for the removal of radioactive strontium from caustic liquid low-level waste (LLLW) generated at Oak Ridge National Laboratory. The two-step treatment process involves the addition of normal Sr (as SrCl₂) to the waste matrix, which is composed primarily of 0.3 M NaOH and 0.6 M Na₂CO₃. The active Sr equilibrates with the normal Sr carrier and coprecipitates as SrCO₃ at pH 13. A liquid/solid separation is made before the pH of the supernate is reduced to pH 8 with sulfuric acid. During the neutralization step, the aluminum in the waste precipitates as Al(OH)₃. Further Sr decontamination is achieved as traces of active Sr sorb to the Al(OH)₃ that precipitates during the neutralization step. A final liquid/solid separation is made at pH 8 to remove the sorbed active Sr.

Maximum Sr decontamination of the LLLW is obtained when at least 50 ppm normal Sr is added to the waste. Because formation of the SrCO₃ is very rapid, efficient mixing of the Sr carrier into the waste is required. The normal Sr must be dispersed throughout the waste to equilibrate with the active Sr before precipitation is completed. Precipitation of SrCO₃ is most effective at pH 13 and decreases dramatically below pH 11. Ferric ion, 25 ppm Fe as sulfate, is added to the treated waste to aid in the physical separation of the fine SrCO₃ solids. Under optimum conditions, the Sr decontamination factor (DF) for the SrCO₃ precipitation unit operation is 135 in lab-scale samples.

Sorption of remaining active Sr on the Al(OH)₃ precipitate in the second unit operation of the process results in an additional decontamination factor of 3-5. Hence, the cumulative DF for the overall process is about 350. Sr removal increases linearly with the concentration of aluminum in the waste. Therefore, the overall DF of the process can be increased by adding aluminum to the LLLW to elevate the concentration above the 315 ppm level already present.

INTRODUCTION

A recent survey of liquid low-level (LLLW) waste generators at Oak Ridge National Laboratory indicated that the predominant activity of the waste generated over the next ten years will be due to the presence of ⁹⁰Sr, ¹³⁷Cs, and ^{103,106}Ru. (1) The anticipated activity of these radionuclides in the newly-generated liquid low-level waste (NGLLLW) will be a maximum of 19 mCi/L ⁹⁰Sr, 99 mCi/L ¹³⁷Cs and 130 mCi/L ^{103,106}Ru. The corresponding relative concentrations of these nuclides in the NGLLLW will be 0.14 ppm, 1.2 ppm and 0.033 ppm, respectively. The radionuclides will most likely be present in a matrix consisting primarily of 0.59 M Na₂CO₃ and 0.33 M NaOH at pH 13.1. A more complete description of the anticipated chemical composition of the NGLLLW is presented in Table I. The anticipated generation rate of this waste is 40,000 to 50,000 gal/yr.

Efforts are now underway to develop a treatment flowsheet for the NGLLLW that will provide a front-end decontamination of the waste to an extent that the treated NGLLLW can be accepted at a downstream treatment facility. The required decontamination factors (DFs) for the NGLLLW flowsheet will need to be greater than 78 for ⁹⁰Sr, 1320 for ¹³⁷Cs and 1.7 X 10⁵ for ^{103,106}Ru. A more detailed discussion of the DF requirements of the NGLLLW flowsheet is available (2).

Treatability studies have been initiated to evaluate the most effective strategy for the removal of the predominant radionuclides from the NGLLLW. Treatment methods for ¹³⁷Cs and ^{103,106}Ru are currently under review. This paper

describes the first unit operation of the NGLLLW flowsheet in which a carrier coprecipitation procedure has been selected as the most promising treatment technique tested to date for the removal of ⁹⁰Sr from the NGLLLW.

MATERIALS AND TEST PROCEDURES

A simulated waste solution, having the chemical composition presented in Table I, was prepared from reagent-grade chemicals dissolved in water. The initial NGLLLW simulant was prepared from deionized water and was filtered through 0.45 μm membranes before use. As the Sr coprecipitation unit operation became more defined, later simulant solutions were prepared from process water and were not filtered to more accurately reflect the composition of the anticipated matrix.

The effectiveness of the carrier coprecipitation process was evaluated through a series of bench-scale sample tests. Small volume (5-20 mL) samples were mixed in polyethylene vials using a magnetic stirrer; reagent additions were made by pipeting solutions directly into the stirred samples. In most cases, triplicate samples were included in each data set to estimate the variability in sample treatment. The sample solutions contained stable SrCl₂, CsCl and RuCl₃ equivalent to the molar concentration of the radionuclides expected in the actual waste. The amount of Sr removed from a sample was determined by adding ⁸⁵Sr tracer as the chloride salt to the NGLLLW simulant prior to sample processing. The Sr strike was performed by pipeting 0.1 mL of a 10g Sr/L solution and 0.05 mL of 10g Fe(III)/L solution into 20 mL of the traced NGLLLW simulant. At the end of a one-hour mixing time, a

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TABLE I
Composition of Simulated Waste Solutions

Component	Concentration (mol/L)	
	NGLLLW pH 13	NGLLLW* pH 8
NaOH	0.335	NP
Na ₂ CO ₃	0.587	NP
NaHCO ₃	NP	0.506
NaNO ₃	0.061	0.053
NaCl	0.034	0.030
Na ₂ SO ₄	NP	0.401
LiCl	0.025	0.022
NaAlO ₂	0.0117	NP
Al(OH) ₃	NP	0.0101
⁹⁰ Sr	19.4 mCi/L	
^{134, 137} Cs	99.5 mCi/L	
^{103, 106} Ru	132 mCi/L	
pH	13.1	8.0
Density (g/mL)	1.074	1.059

*H₂SO₄ used for neutralization of waste, dilution factor of 1.15
NP = not present

portion of the sample solution was withdrawn and centrifuged for thirty minutes at 5000 rcf. Two milliliters of the supernate were transferred to a counting tube; the ⁸⁵Sr sample activity was counted for 1000s on a Canberra Series 90 Gamma Spectrometer. The remaining supernate was neutralized with the addition of 5.4 N sulfuric acid and mixed for 1 hour; centrifugation was again used to remove the Al(OH)₃ solids. A final 2-mL aliquot of the supernate was collected and counted for ⁸⁵Sr activity. The DF of each processing step was calculated as the ratio of the initial ⁸⁵Sr activity in the traced sample divided by the activity of the processed sample. Thus, the stated DF of each treatment reflects the reduction of ⁸⁵Sr activity by both removal of Sr-bearing precipitates and by sample dilution as a result of reagent addition.

RESULTS AND DISCUSSION

Several sorbent and ion-exchange treatment procedures have been reported for the removal of ⁹⁰Sr from caustic waste. These include the use of zeolites (3), o-titanates (4-6), the resorcinol-formaldehyde resin developed at Savannah River Site (SRS) (7) and calcium coprecipitation (8). Application of zeolites to ⁹⁰Sr removal is limited by the interference of large amounts of sodium ion in the waste. Sodium titanate, purchased from several vendors, was evaluated in a powder form and as a slurry for the treatment of the NGLLLW simulant. The presence of a few ppm calcium was found to severely depress Sr sorption on the sodium titanate. In addition, inconsistent Sr decontamination results were observed from different suppliers and from different batches from the same supplier. Slight Sr sorption was observed on the SRS resin when the NGLLLW was contacted batch-wise with the exchanger. Sr sorption results were similar to the less effective batches of sodium titanate.

Sr decontamination factors high enough to allow discharge to the downstream treatment facility were obtained

using calcium coprecipitation for the treatment of NGLLLW. The waste treatment included two strikes of 80 ppm Ca (as CaCl₂) added to the NGLLLW at pH 13.1, followed by a liquid/solid separation after each strike. The pH of the final supernate was then adjusted to 8; remaining Sr-bearing solids were then removed by centrifugation. The cumulative Sr DF after each successive step in the CaCl₂ treatment process was 3 after the first CaCl₂ strike, 10 after the second strike, and 164 after pH adjustment. A more in-depth discussion of the testing procedures and Sr decontamination for the above treatment methods is described elsewhere (2).

The most effective method tested in our laboratory for Sr removal from simulated NGLLLW was a treatment procedure including 1) coprecipitation of ⁹⁰Sr with stable (i.e., natural) Sr, followed by a liquid/solid separation at pH 13 and 2) acid neutralization of the supernate to pH 8 and a final liquid/solid separation (Fig. 1). The cumulative Sr decontamination factor for this process is several times the needed DF of 78 required for waste discharge to the downstream treatment facility. Typical DFs of 30 are obtained for a 50 ppm stable Sr strike. When 25 ppm Fe, added as ferric sulfate, is also added to the Sr strike solution to aid the flocculation of the Sr-bearing solids, Sr decontamination is further improved by 2-3 times. The remainder of the Sr in the clarified supernate is removed by sorption onto the Al(OH)₃ that forms during acid neutralization. The cumulative effect of the Sr strike and pH adjustment steps decontaminate the NGLLLW simulant by a factor of over 350. The effect of several processing parameters were evaluated to determine the optimum operating conditions for the Sr strike and pH adjustment operations.

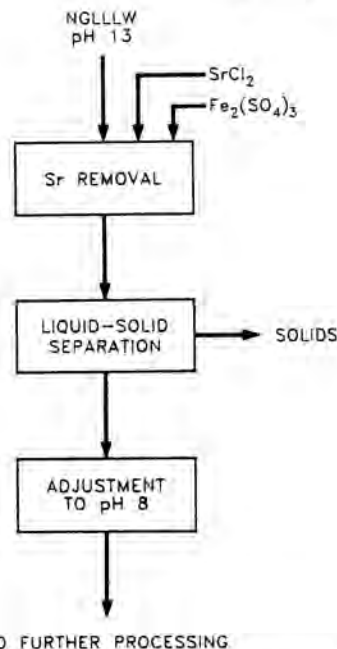


Fig. 1. Flowsheet for ⁹⁰Sr coprecipitation treatment in NGLLLW.

Strontium Strike Unit Operation

The solubility of strontium carbonate in the NGLLLW simulant was determined experimentally to be about 4 ppm. By adding stable Sr to the NGLLLW simulant in excess of this concentration, the radioactive Sr coprecipitates with the stable Sr from the caustic carbonate matrix. The solids formed

in the coprecipitation process have been identified by x-ray diffraction analysis as strontianite, SrCO_3 . As seen in Figure 2, maximum Sr removal by coprecipitation requires the addition of as little as 50 ppm stable Sr to the NGLLLW simulant. The critical control parameter in the coprecipitation treatment is that of rapid mixing. The stable Sr must be dispersed throughout the waste solution prior to the formation and precipitation of SrCO_3 . Insufficient equilibration of the stable Sr with ^{90}Sr results in localized precipitation of the stable Sr and, thus, limited decontamination of the waste. Adding larger volumes of more dilute stable SrCl_2 to the NGLLLW did not reduce the need for fast mixing rates during the introduction of the Sr strike solution. The duration of mixing beyond the one hour equilibration time also had no effect on the Sr DF of the Sr strike treatment.

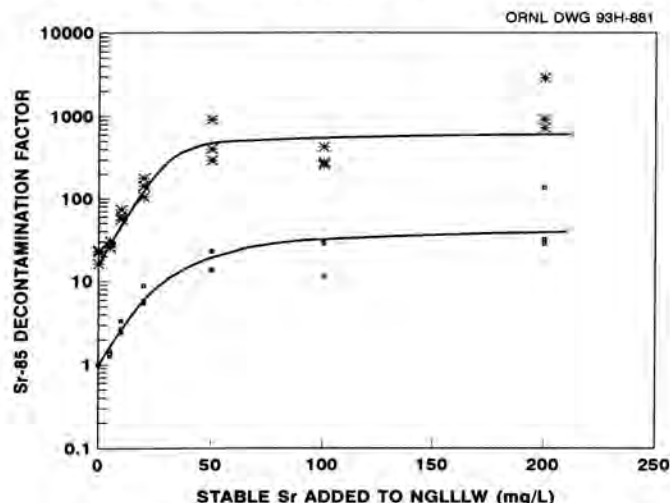


Fig. 2. Effect of added stable Sr on the coprecipitation of ^{85}Sr from simulated NGLLLW (■ Sr DF of SrCl_2 strike unit operation; * Cumulative Sr DF for SrCl_2 Strike and pH Adjustment/ $\text{Al}(\text{OH})_3$ precipitation unit operations).

The SrCO_3 solids formed during coprecipitation range in size from 1-3 μm in diameter. Although the DF obtained with the SrCl_2 strike is most effective at pH 13, the settling properties of the fine solids are more favorable at pH 11. The reason for the improved settling is unclear. Ferric ion has been used in the previous applications to improve solids separation in the coprecipitation of Sr with alkaline earth elements (8). Similar improvements in Sr decontamination were observed in our laboratory when 5-100 ppm $\text{Fe}(\text{III})$, as ferric sulfate, were added to a treatment process in which the active strontium was coprecipitated from NGLLLW simulant with calcium chloride (2). The effect of ferric ion addition, in conjunction with SrCl_2 coprecipitation in NGLLLW, was tested at pH 13 and pH 11. SrCl_2 (50 ppm Sr) and 25 ppm $\text{Fe}(\text{III})$ were added simultaneously to two sets of NGLLLW samples. The pH of one sample set was maintained at the original pH of 13.1; this sample set was then mixed one hour before the solids were removed by centrifugation. After adding the stable Sr and $\text{Fe}(\text{III})$ at the an initial pH value of 13.1, the pH of the second sample set was reduced to pH 11 prior to sample equilibration and solids removal. The sample supernates from both sample sets were then adjusted to pH 8 following the SrCO_3 removal. Ferric ion improved the efficiency of the SrCl_2 strike; the Sr DF at pH 13.1 was 84 as

compared to 30 without iron addition. Although the settling properties of the Sr strike solids are more favorable at pH 11, SrCO_3 is more soluble at lower pH values (Fig. 3). Thus, the Sr DF of the sample set containing ferric ion at pH 11 was only 67. It is therefore preferable to make the Sr strike in the presence of 25 ppm ferric ion at pH 13, provided that the solids can be adequately separated. If the solids can only be removed efficiently at pH 11, care must be taken not to overshoot the pH 11 set point. If the waste is acidified beyond pH 11, the Sr DF of the Sr strike cannot be totally recovered by simply adding caustic to readjust the pH of the waste to 11.

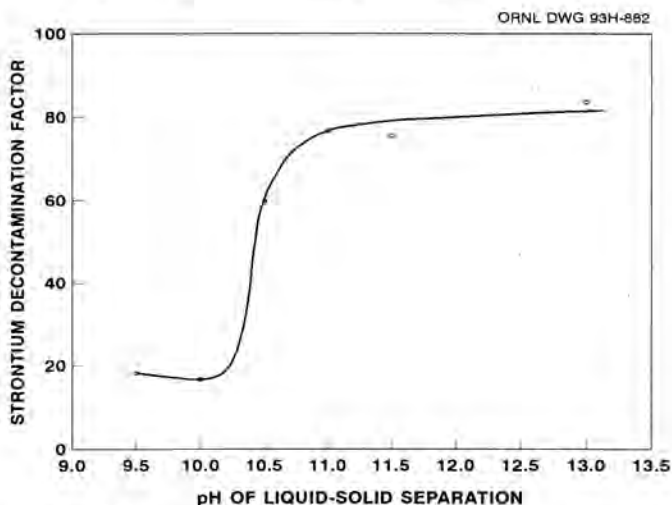


Fig. 3. Effect of pH of liquid/solid separation on ^{85}Sr coprecipitation from simulated NGLLLW with stable Sr.

Rather than relying on the settling properties of SrCO_3 , a polymeric settling agent was tested for a 0.5 L/min pilot-scale operation of the flowsheet at pH 13. When 2 ppm of an emulsion polymer (Calgon® Pol-E-Z 2466) is added after the 1 hour mixing time to the treated NGLLLW at pH 13, the solids removal is more effective and the Sr strike DF improves from 84 to 130 in lab-scale samples.

The declining decontamination of the NGLLLW simulant with lower pH values further illustrates the need to make two separate liquid/solid separations at pH 13 and pH 8, rather than collecting the solids generated by both the SrCl_2 strike and the acid neutralization/ $\text{Al}(\text{OH})_3$ precipitation operations in a single combined phase separation. The increasing solubility of SrCl_2 at lower pH and the consumption of free carbonate ion during acid neutralization reduce the amount of solid SrCO_3 formed.

pH Adjustment/ $\text{Al}(\text{OH})_3$ Precipitation Unit Operation

The NGLLLW flowsheet relies on the precipitation of $\text{Al}(\text{OH})_3$, present at 315 ppm in NGLLLW, to sorb ^{90}Sr remaining in the clarified supernate after Sr coprecipitation. The aluminum in the waste begins to precipitate as the pH drops below 11 during acid neutralization. A profile of Sr DF as a function of pH in the range of 7-13 indicates that the maximum $\text{Al}(\text{OH})_3$ precipitation and, thus, active Sr removal occurs at and below pH 8. The typical Sr DF for this unit operation is about 3-5; the cumulative Sr DF for both the Sr strike and pH adjustment operations is generally above 350.

Strontium decontamination in the pH adjustment unit operation increases linearly with the amount of aluminum initially present in the waste (Fig. 4). In these tests, the Sr DF

of the pH adjustment operation increased to 120 when an additional 1000 ppm Al was added to the waste. A sorption isotherm plotted from these results indicates a maximum Sr loading on the $\text{Al}(\text{OH})_3$ of at least 30 meq/kg and indicates a sorption ratio for $\text{Al}(\text{OH})_3$ of about 25000. This value is slightly higher than the sorption ratios measured by Shiao, et al, (9) for the distribution of Sr on absorption grade Al_2O_3 from NaCl solutions. Addition of the aluminum to previously neutralized NGLLLW does not substantially improve Sr removal. Efficient Sr sorption appears to occur only if the aluminum is initially dissolved at pH 13 so that the $\text{Al}(\text{OH})_3$ forms during the neutralization process.

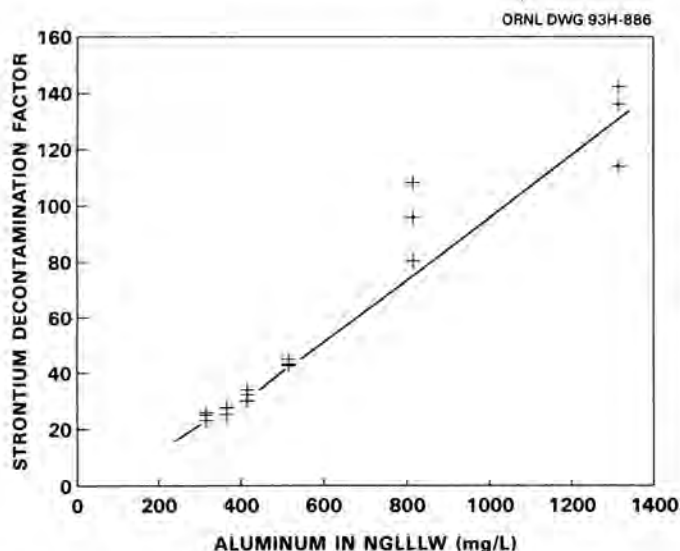


Fig. 4. Effect of Aluminum Concentration on ^{85}Sr Removal from Simulated NGLLLW with Stable Sr.

Because the aluminate is soluble above pH 10, the DF of the 50 ppm Sr strike unit operation is unaffected by the total Al concentration in the caustic waste. However, the cumulative decontamination of the full treatment process is heavily influenced by the $\text{Al}(\text{OH})_3$ sorption. Therefore, the efficiency of Sr removal can be optimized with addition of Al to the NGLLLW before processing. This must be weighed against the resulting increase in secondary waste solids, however.

CONCLUSION

There are several advantages in using the carrier coprecipitation process to remove active Sr from caustic NGLLLW. The process uses a readily available reagent, SrCl_2 , and takes advantage of the waste matrix components to

effect decontamination of the waste. Therefore, the cost and quantity of solid wastes generated by the process are minimized. The chemistry of the process is simple, with little potential for interferences from the diverse components that may be present in the waste. Finally, the overall decontamination of the carrier coprecipitation process can be increased as needed by the addition of aluminum to the caustic NGLLLW.

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