

CONF-9504255-1

The Selective Removal of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  from Liquid  
Low-Level Waste at Oak Ridge National Laboratory

D. T. Bostick  
W. D. Arnold  
M. W. Burgess  
P. A. Taylor  
T. E. Kent

Prepared for the  
ESPIP Task Review Meeting  
Gaithersburg, Maryland  
April 25-26, 1995

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

---

<sup>1</sup>Managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400.

**MASTER**

# THE SELECTIVE REMOVAL OF $^{90}\text{Sr}$ AND $^{137}\text{Cs}$ FROM LIQUID LOW-LEVEL WASTE AT OAK RIDGE NATIONAL LABORATORY

D. A. Bostick, W. D. Arnold, M. W. Burgess, P. A. Taylor, and T. E. Kent

## ABSTRACT

Methods are being developed for the selective removal of the two principal radioactive contaminants,  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ , from liquid low-level waste generated and/or stored at Oak Ridge National Laboratory. These methods are to be used in a future centralized treatment facility at ORNL. Removal of  $^{90}\text{Sr}$  in the proposed treatment flashed (Fig. 1) is based on coprecipitation from strongly alkaline waste by adding stable strontium to the waste solution. Ferric sulfate, added with the stable strontium, improves the  $^{90}\text{Sr}$  removal and aids in the flocculation of the strontium carbonate ( $\text{SrCO}_3$ ) precipitate. After separation of the solids, the resultant supernate is adjusted to pH 8 for the cesium removal treatment. Upon pH adjustment, aluminum originally present in the untreated alkaline waste precipitates and sorbs an additional amount of  $^{90}\text{Sr}$ . Cesium is removed from the neutralized waste by two sequential treatments with potassium cobalt hexacyanoferrate (KCCF) slurry formed by the addition of potassium ferrocyanide ( $\text{K}_4\text{Fe}(\text{CN})_6$ ) and cobalt nitrate ( $\text{Co}(\text{NO}_3)_2$ ) solutions. The cumulative decontamination factors (DFs) for  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$  in bench-scale studies are 4900 and  $1 \times 10^6$ , respectively, if high speed centrifugation is used for the liquid/solid separations. Efforts are now underway to evaluate process-scale techniques to perform the liquid/solid separations required for removal of  $\text{SrCO}_3$  and  $^{137}\text{Cs}$ -bearing hexacyanoferrate solids from the treated waste solution.

## Strontium Coprecipitation Unit Operation

Table 1 summarizes the approximate composition of LLLW that is currently being generated at Oak Ridge National Laboratory. Decontamination factors of 80 and 1000 are required for the removal of  $^{90}\text{Sr}$  and  $^{137}\text{Cs}$ , resp., from the LLLW. Maximum  $^{90}\text{Sr}$  decontamination of the liquid low-level waste (LLLW) is obtained when at least 50 ppm stable strontium is added to the waste. Because the formation of the  $\text{SrCO}_3$  is very rapid, efficient mixing of the strontium carrier into the waste is required. The stable strontium must be dispersed throughout the waste to equilibrate with the active strontium before precipitation is completed. Precipitation of  $\text{SrCO}_3$  is most effective at pH 13 and decreases dramatically below pH 11. Ferric ion, 25 ppm Fe as  $\text{Fe}(\text{SO}_4)$ , and 2 ppm of Betz® 1138 polymer are added to the treated waste to aid in the physical

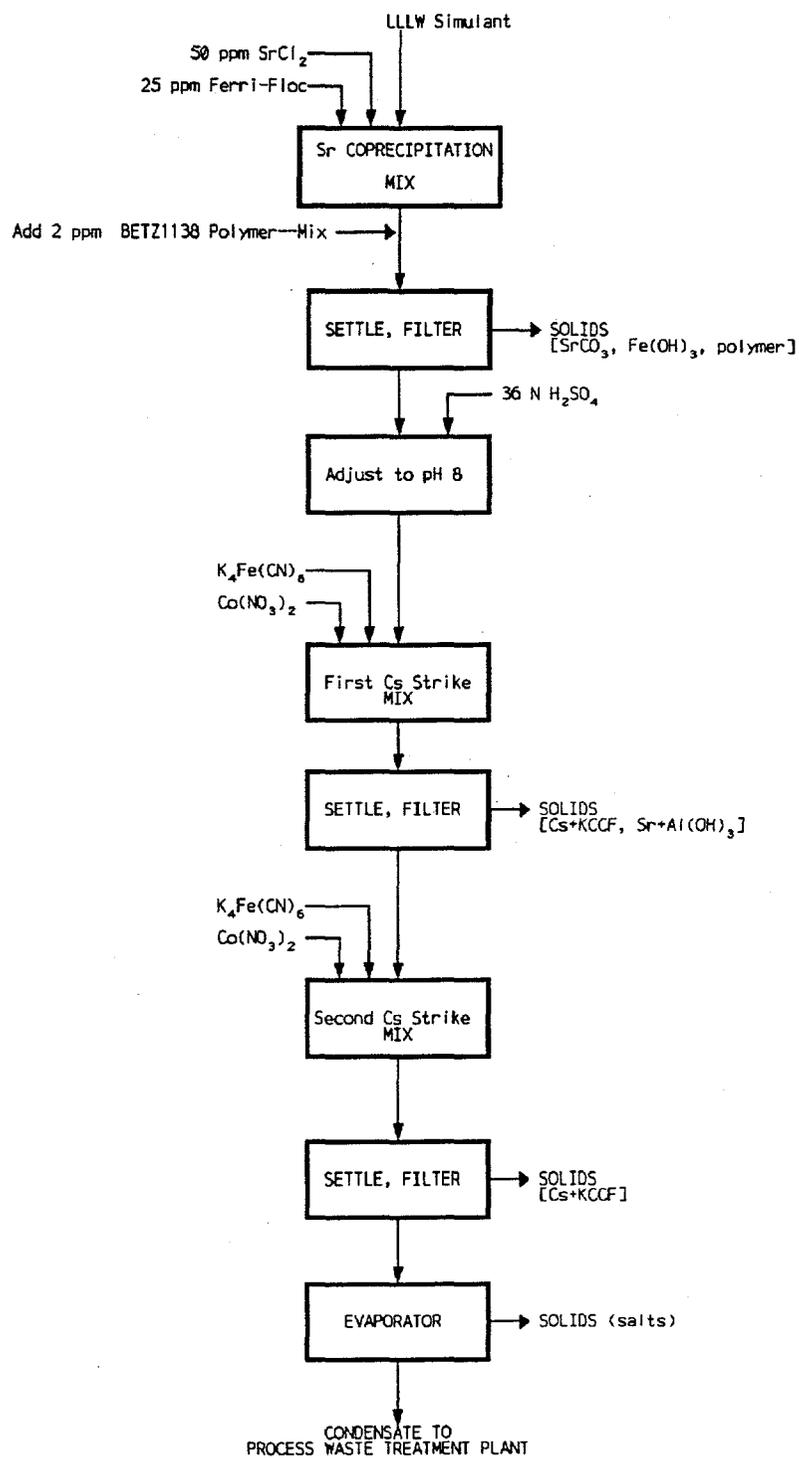


Fig. 1 Proposed Flashed for Treatment of LLLW Generated at Oak Ridge National Laboratory

Table 1. Composition of Simulated LLLW Generated at Oak Ridge National Laboratory

Component	Concentration (mol/L)	
	LLLW pH 13	LLLW* pH 8
NaOH	0.125	NP
Na <sub>2</sub> CO <sub>3</sub>	0.10	NP
NaHCO <sub>3</sub>	NP	0.096
NaNO <sub>3</sub>	0.061	0.059
NaCl	0.034	0.033
Na <sub>2</sub> SO <sub>4</sub>	NP	0.108
LiCl	0.025	0.024
NaAlO <sub>2</sub>	0.0117	NP
Al(OH) <sub>3</sub>	NP	0.0101
<sup>90</sup> Sr	19.4 mCi/L	
<sup>134, 137</sup> Cs	99.5 mCi/L	
<sup>103, 106</sup> Ru	132 mCi/L	
pH	12.7	8.0
Density (g/mL)	1.02	1.01

NP = not present

LLLW = low-level liquid waste

\*H<sub>2</sub>SO<sub>4</sub> used for neutralization of waste, dilution factor of 1.04

separation of the fine  $\text{SrCO}_3$  solids. Under optimum conditions, the  $^{90}\text{Sr}$  decontamination factor (DF) for the  $\text{SrCO}_3$  precipitation unit operation is 150 in lab-scale samples.

### **pH Adjustment Unit Operation**

The LLLW contains approximately 335 ppm aluminum which precipitates as  $\text{Al}(\text{OH})_3$  as the pH of the waste is reduced from pH 13 to pH 8. Sorption of remaining  $^{90}\text{Sr}$  from the strontium coprecipitation unit operation is achieved by sorption onto the  $\text{Al}(\text{OH})_3$  precipitate. The decontamination factor for the pH adjustment unit operation is typically 30. Hence, the cumulative DF for the overall process is about 4500. 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 335 ppm level already present. The solids generated from this unit operation are not removed until the LLLW is treated for the removal of cesium in the first KCCF strike unit operation.

### **First and Second KCCF Strike Unit Operations**

Cesium removal in the flashed is based on treatment at pH 8 with a slurry of 100 ppm KCCF, formed in-situ by the sequential addition of equimolar amounts of  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $\text{Co}(\text{NO}_3)_2$  solutions to the waste. The  $\text{Al}(\text{OH})_3$  that precipitates from the LLLW during the pH adjustment unit operation aids in the flocculation of the KCCF-cesium complex. A DF of about 1000 is obtained in the first strike with 100 ppm KCCF when high speed centrifugation is used to separate the cesium-bearing solids. Additional  $\text{K}_4\text{Fe}(\text{CN})_6$  and  $\text{Co}(\text{NO}_3)_2$  solutions are added to the clarified LLLW in the second KCCF strike to form a 50 ppm KCCF slurry. The cesium DF for the second unit operation is typically 3000, so that the cumulative DF for both KCCF strike operations is greater than  $1 \times 10^6$ .

### **Summary**

The DFs for each unit operation is given in the table below. These values are obtained for bench-scale samples in which the liquid/solid separation is accomplished using a high speed laboratory centrifuge. Efforts are now underway to identify liquid/solid separation methods that will be appropriate to clarify the treated LLLW in process scale applications.

UNIT OPERATION	Sr Decontamination Factor*	Cs Decontamination Factor*
Sr Coprecipitation	150	1
pH Adjustment	30	1
First KCCF (100 ppm) Strike	1	1000
Second KCCF (50 ppm) Strike	1	3000

\*Liquid/solid separation performed by high speed centrifugation

Attributes of the strontium coprecipitation unit operation for the removal of <sup>90</sup>Sr include:

separation of the fine SrCO<sub>3</sub> solids. Under optimum conditions, the <sup>90</sup>Sr decontamination factor (DF) for the SrCO<sub>3</sub> precipitation unit operation is 150 in lab-scale samples.

- The process uses a readily available reagent, SrCl<sub>2</sub>, and 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.
- The addition of 50 ppm Sr to the waste should not impact further processing of the LLLW. The residual Sr concentration after SrCO<sub>3</sub> precipitation at pH 13 is only about 4 ppm, which is at a concentration typically present in natural waters.
- Finally, the overall decontamination of the carrier coprecipitation process can be increased as needed by the addition of aluminum to the LLLW.

Attributes of in-situ potassium hexacyanoferrate (KCCF) treatment for  $^{137}\text{Cs}$  removal include:

- In-Situ treatment with KCCF has greatest  $^{137}\text{Cs}$  decontamination efficiency of any method tested thus far for the processing of the LLLW generated at Oak Ridge National Laboratory
- The cumulative DF for two KCCF strikes is greater than  $1 \times 10^6$
- KCCF treatment, unlike other available cesium treatment technologies, is unaffected by the presence of potassium in the waste
- Highest loading, smallest secondary waste volume.

#### DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.