PROCESS SELECTION FOR THE REMOVAL OF RADIO-
NUCLIDES FROM LOW-LEVEL WASTES AT
OAK RIDGE NATIONAL LABORATORY*

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Introduction

Low-level wastes, which are produced at many atomic research and production installations, contain low concentrations of the mineral salts commonly found in natural waters and are contaminated with small amounts of radionuclides. Decontamination of these wastes prior to discharge to the environment is usually necessary. The methods currently used for decontamination include scavenging-precipitation, ion exchange, and evaporation. At Oak Ridge National Laboratory, the major radioactive contaminants that must be removed from the low-level waste are ^{90}Sr and ^{137}Cs . The waste contains about 100 ppm of total hardness (dissolved calcium and magnesium) and is discharged at the average rate of 100 gpm.

We have made a study of various processes that could be used to replace a lime-soda precipitation plant currently in use at ORNL. Decontamination factors (expressed as inlet-to-product-concentration ratios) of greater than 500 for ^{90}Sr and 100 for ^{137}Cs were used as the criteria for this study. Problems associated with the disposal of solid and liquid wastes generated by the processes themselves were also considered.

Two processes, developed specifically for the decontamination of ORNL low-level wastes, were evaluated. Both contain precipitation and ion exchange steps; however, they differ with regard to the point at which the bulk of the hardness is removed from the water. The first process, known as the Scavenging-Precipitation Ion-Exchange Process (SP-IX), has been demonstrated on a pilot-plant scale using ORNL process waste.^{1,2} The second process, known as the Clarification Ion-Exchange

Process (C-IX), is an adaptation of the work by Yee³ on a water recycle process for ORNL. A third process, evaporation, is currently being investigated, but relatively high fuel costs may make it somewhat more expensive to operate.

Scavenging-Precipitation Ion-Exchange Process

The first slide shows the flowsheet for the Scavenging-Precipitation Ion-Exchange Process (SP-IX). In the precipitation or head-end step of this process, the pH of the waste is increased to about 11.8 by making the waste 0.01 N in NaOH and, at the same time, adding 5 ppm of Fe^{2+} as copperas. The Fe^{2+} promotes the formulation of a large floc from the dissolved calcium and magnesium present in the waste. Most of the calcium and magnesium precipitate as the carbonate and the hydroxide, respectively. Dirt, algae, and radionuclides are also carried down during this precipitation step. Coagulation of the precipitates occurs in the flocculator, where the mixture is gently agitated at 1 rpm for 15 min. At the end of this time, the floc leaves the bottom of the flocculator and enters the bottom of the clarifier vessel, where separation of the solids is achieved by feeding the mixture through a 4- to 5-ft-high sludge blanket. The sludge blanket consists of fluidized particles of precipitate that trap the floc and furnish additional nuclei to aid in the precipitation of additional solids by crystal growth. In our pilot plant, we have found that it is necessary to gently agitate the clarifier in order to maintain a uniform sludge blanket. As particles in the sludge blanket agglomerate, they settle in the water until they form a slurry in the bottom of the vessel. Some of this slurry is recycled to the flash-mixer to provide "seed" nuclei to promote precipitation. The slurry to be disposed of may be concentrated to 30% by centrifugation, which will make it suitable for disposal via burial or hydrofracture. However, if pit disposal is used, the slurry will be

discharged at a concentration of about 4% by weight. The effluent from the clarifier is further clarified by passage through a polishing filter containing a fixed bed of anthracite.

After filtration, the clarified effluent (whose hardness content is less than 10 ppm) is fed to a cation exchange column containing sodium-form Duolite CS-100 resin. This is a phenolic-carboxylic cation exchange resin (a weak-acid type), which was selected because of its high preference for sorbing cesium over sodium present in the liquid phase. Breakthrough of cesium does not occur until 2000 bed volumes of waste have been fed to the column. To regenerate the resin, the column is removed from service; then the bed is washed with one-half bed volume of water and is subsequently eluted in an upflow mode with five volumes of 0.5 N HNO_3 remaining from a prior regeneration. This quantity of acid effectively removes almost all the sorbed hardness and radioactivity; it is evaporated to permit recovery of part of the nitric acid and then discarded. An additional five volumes of fresh 0.5 N HNO_3 are used to complete the elution; however, this acid effluent is routed to a storage tank, where it is retained until it is reused during the first half of the elution cycle on the next regeneration. The bed is finally rinsed with water and converted to the sodium form by feeding 20 volumes of 0.1 N $NaOH$ upflow through the resin. The rinse water and the 0.1 N $NaOH$ are recycled and used for adjusting the pH of the feed to the flash-mixer.

Clarification Ion-Exchange Process

The next slide shows the chemical flowsheet for the Clarification Ion-Exchange process. The processing steps are similar to those used in the SP-IX

process. The main difference between the two processes involves the location at which the bulk of the hardness is removed from the process waste. In the SP-IX process, removal is accomplished in the head-end step at a high pH; in the C-IX process, it is accomplished in a cation exchange column at a pH near neutral. The head-end step in the C-IX process serves only to remove algae, colloids, and solids that may contain activity from the process waste. Removal of such materials is accomplished through the use of coagulants, followed by clarification to remove the precipitated solids from the system. In the C-IX process, fewer solids are produced during the head-end step, but more eluate is produced by the ion exchange step.

Raw waste is fed to the C-IX process and blended with alum and activated silica in the flash-mixer. The amounts of coagulants used are established by measuring the zeta potential of the floc resulting from coagulation of the colloids present in the process waste. Zeta potential measurements determine the electrophoretic mobility of the floc immediately after the flash-mixing step.

The flash-mixer provides a 15-sec holdup time for mixing the coagulating chemicals with the waste. Flocculation and clarification take place in the agitated flocculator during a 20-min period; then clarification is accomplished in a sludge blanket clarifier having a holdup time of about 60 min. Solids removed from the clarifier could be centrifuged if they are to be drummed and shipped; however, the recommended procedure involves dissolution in the ion exchange column eluate, which results in only one waste stream for the process. Clear water leaving the sludge blanket clarifier is pressurized and then clarified further by passage through an anthracite-bed polishing filter. A bed of Dowex 50W-X8 resin (strong-acid type) effectively decontaminates the waste with regard

to ^{137}Cs and ^{90}Sr and removes the hardness at the same time. Regeneration of the cation bed requires elution with three bed volumes of 4 N HNO_3 remaining from the prior regeneration, followed by elution with three bed volumes of fresh 4 N HNO_3 . The latter three bed volumes are retained for use in the subsequent regeneration. Since only a portion of the nitric acid is used for removing salts from the bed, the first fraction must be evaporated in order to recover most of the unused acid for subsequent regenerations. This removal of nitrate reduces the quantity of waste salts significantly because all wastes to be disposed of must be neutralized first, and any excess nitric acid in the waste stream would be converted to sodium nitrate in our waste storage system.

Capital Costs

The capital costs for the SP-IX and C-IX processes at a 200-gpm capacity have been estimated as part of the overall study. (These estimates were prepared for a plant installed at ORNL in 1971 and do not include any escalation, which could increase the costs significantly.) The SP-IX process had the lowest capital cost (\$894,000), but the C-IX process was only about \$24,000 more expensive (\$918,000). We estimated that a continuous ion exchange contactor for the C-IX process would increase the cost of this process to \$964,000.

Operating Costs

The operating costs for each of the processes under consideration should include the costs for disposal of the wastes generated by the process. However, methods to be used for disposing of these wastes can only be suggested at the present time, and the costs associated with them can only be roughly estimated. Possible methods include pit disposal of sludge, hydrofracturing, burial of

concentrated sludge in drums, or shipment of the sludge to a National Repository. Hydrofracturing refers to a process in which radioactive solutions are mixed with concrete grout and then pumped at high pressure into a fractured stratum of shale about 1000 ft underground. Ecological considerations will certainly play an important role in the ultimate decisions that will be made concerning this problem.

Two of the several possible modes of operation were selected, and costs were estimated for operation under the corresponding conditions. The first assumes that all sludges are buried in the waste pits and that the eluate is disposed of by hydrofracturing or some other procedure having a cost comparable to that of hydrofracturing. The cost assumed for pit disposal was 3 ¢ per gallon of sludge; the cost for hydrofracturing was assumed to be 30 ¢/gal. The second mode assumes that all wastes, including the sludges, are hydrofractured or disposed of in a comparable manner. For this mode, it was assumed that the sludges could be hydrofractured at a 10% (by weight) concentration and that the cost of hydrofracturing would again be 30¢/gal.

The operating costs for the two processes include: (1) fixed charges, calculated at 10% of the original investment per year; (2) labor and supervision, (3) utilities, (4) chemical costs, and (5) waste handling costs.

The results for pit disposal of the sludge are given on the next slide. Note that the waste handling costs for the C-IX flowsheet are more than twice those for the SP-IX flowsheet. The reason for this is that the C-IX flowsheet produces only an eluate solution (the sludge is dissolved in the eluate in the C-IX process), which is more expensive to handle. The resulting high waste handling costs tend to make the C-IX process more expensive than the SP-IX process.

The data on the next slide indicate that, if all of the wastes are hydrofractured, the SP-IX process may be somewhat more expensive than the other process. The reasons for this are twofold: (1) the SP-IX process must include a centrifuge to concentrate the sludge if it is to be hydrofractured; and (2) the sludge-plus-eluate volumes are still greater than the eluate volumes for the C-IX flowsheet. Therefore, it appears that, at the present time, the SP-IX process should be installed if pit disposal of the sludge is used. However, over the long term, consideration should be given to changing to the C-IX process if more expensive methods such as hydrofracturing become necessary for both the sludges and the eluate.

Comparison of Processes

An overall comparison of the SP-IX and C-IX processes installed at ORNL is shown on the next slide. Both processes have adequate decontamination factors for ^{90}Sr and ^{137}Cs . If pit disposal of sludge is assumed, the capital and operating costs for the SP-IX process are somewhat lower; however, if hydrofracturing is used, the C-IX has a lower operating cost. The SP-IX process adds far more salts to the product stream because it operates at a pH of 11.7 and requires neutralizing before discharge to the environment. The SP-IX process discharges a greater waste volume unless the sludge is concentrated, but the volume could be reduced by centrifuging the sludge. Finally, we have developed the SP-IX process to the pilot-plant stage, whereas the C-IX process has only been demonstrated in a bench-scale experiment.

Conclusions

The results of this study indicate that the choice of a particular process will strongly depend on the methods used for disposal of the wastes from the plant.

The choice may also be sensitive to the concentration of salts desired in the product water streams since the two processes differ by a factor of 22 in this respect. If the C-IX process is selected, further development on a pilot-plant scale will probably be necessary.

References

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2. L. J. King and M. Ichikawa, Pilot Plant Demonstration of the Decontamination of Low-Level Process Wastes by a Recycle Scavenging-Precipitation Ion-Exchange Process, ORNL-3863 (December 1965).
3. W. C. Yee et al., Low-Level Radioactivity Waste Treatment: The Water Recycle Process, ORNL-4472 (July 1970).
4. I. R. Higgins, "Pilot Plant Test of Continuous Ion Exchange Treatment of Low Level Waste at Oak Ridge National Laboratory," USNC Order 834 47027, October 1963.

SCAVENGING-PRECIPITATION ION-EXCHANGE FLOWSHEET

CLARIFICATION ION-EXCHANGE FLOWSHEET

COMPARISON OF OPERATING COSTS, ASSUMING PIT DISPOSAL
OF THE SLUDGE AND HYDROFRACTURING OF THE ELUATE

	PROCESS	
	SP-IX	C-IX
OPERATING COSTS, ¢ PER 1000 GAL OF FEED		
FIXED CHARGES	113.3	116.5
LABOR AND SUPERVISION	53.9	53.9
UTILITIES	2.5	5.9
CHEMICALS	23.2	21.9
WASTE HANDLING		
SLUDGE DISPOSAL	11.5	
ELUATE DISPOSAL	<u>1.9</u>	<u>30.8</u>
TOTAL OPERATING COST	206.3	229.0

COMPARISON OF OPERATING COSTS, ASSUMING
HYDROFRACTURE DISPOSAL OF ALL WASTES

	PROCESS	
	SP-IX	C-IX
OPERATING COSTS, ¢ PER 1000 GAL OF FEED		
FIXED CHARGES	116.3	116.5
LABOR AND SUPERVISION	53.9	53.9
UTILITIES	2.5	5.9
CHEMICALS	23.2	21.9
WASTE HANDLING	<u>48.1</u>	<u>30.8</u>
TOTAL OPERATING COST	244.0	229.0

COMPARISON OF THE SP-IX AND C-IX PROCESSES

	SP-IX	C-IX
DECONTAMINATION FACTORS		
^{90}SR	1500	1950
^{137}CS	920	200
CAPITAL COST	894,000	918,000
OPERATING COST, ¢/1000 GAL		
PIT DISPOSAL AND HYDROFRACTURING	206	229
HYDROFRACTURING	244	229
SALT CONCENTRATION IN PRODUCT WATER, PPM	710	32
WASTE VOLUMES, GAL/DAY		
SLUDGE	1110	0
ELUATE	54	363
SCALE OF DEVELOPMENT	PILOT PLANT	BENCH SCALE