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**Feasible Modifications for the  
Low-Level Waste Treatment Plant at  
Oak Ridge National Laboratory**

J. M. Chilton

**MASTER**

OPERATED BY  
MARTIN MARIETTA ENERGY SYSTEMS, INC.  
FOR THE UNITED STATES  
DEPARTMENT OF ENERGY

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**FEASIBLE MODIFICATIONS FOR THE LOW-LEVEL WASTE TREATMENT PLANT  
AT OAK RIDGE NATIONAL LABORATORY**

J. M. Chilton

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# FEASIBLE MODIFICATIONS FOR THE LOW-LEVEL WASTE TREATMENT PLANT AT OAK RIDGE NATIONAL LABORATORY

J. M. Chilton

## ABSTRACT

Aqueous, low-level, radioactive wastes at Oak Ridge National Laboratory (ORNL) contain small amounts of  $^{60}\text{Co}$ ,  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ , and trace amounts of other radionuclides. These wastes are processed by passage through beds of a strong-acid cation exchange resin, and the treated water is then discharged to the environment.

Studies show that pretreatment of the waste with a weak-acid cation exchange resin would result in a significant decrease in regeneration reagents and a saving of manpower. This can be accomplished in the present plant by piping changes on the existing columns.

The effluent from the cation treatment process contains all of the radionuclides that are present in anionic form. Routinely, this consists only of approximately one-half of the  $^{60}\text{Co}$ . Under certain conditions, other anions (such as  $^{131}\text{I}$ ) could be present. Studies show that these can be removed by use of an anion exchange resin bed at the end of the process. This would require the construction of an additional column, if the head-end treatment described above is also installed.

## 1. SUMMARY OF PLANT OPERATION

Aqueous wastes at ORNL that contain small amounts of radionuclides are collected in an open "equalization" basin. Since August 1981, these wastes have been processed in the Low-Level Waste Treatment (LLWT) Plant by passage through beds containing a strong-acid cation exchange resin (Dowex HCR-S). Prior to this, a "scavenging precipitation" ion exchange process was used.<sup>1</sup>

In the waste treatment process, water from the basin is pumped through one of two pressure-type filters containing a bed of 0.6- to 0.8-mm anthracite. The flow is switched to the second bed when the pressure drop increases by  $3 \times 10^4$  to  $4 \times 10^4$  Pa (5 to 6 psi), and the first bed is then backwashed.

From the filter, the stream passes downflow through one or more of four ion exchange columns containing 1275 L of hydrogen-form Dowex HCR-S resin. The beds are normally used consecutively, switching as  $^{137}\text{Cs}$  breakthrough exceeds a predetermined concentration. The maximum flow rate through a single bed is 380 L/min, but two beds may be operated simultaneously, in parallel.

To regenerate a resin bed, the column is eluted upflow with two batches (three bed-volumes each) of 3.5 M nitric acid. The first batch removes most of the radioactivity and hardness; this eluent is then concentrated by evaporation, neutralized with sodium hydroxide, and sent to the Intermediate-Level Waste Treatment Plant. The second batch is stored and used as the first batch for the next elution. After a final rinse with water, the bed is ready for reuse.

The waste stream leaving the ion exchange bed passes into the first compartment of the clearwell. This has a volume of 80,000 L and is divided into two sections by an overflow weir. Water from the first section, which holds two-thirds of the volume, is used to backwash the filters and to make the acid solution used for resin regeneration. An electrode continuously monitors the pH at the weir, and sulfuric acid or sodium hydroxide is added to maintain a pH of  $\sim 7$ . The neutralized waste then flows into White Oak Creek.

## 2. ADDITIONAL HEAD-END TREATMENT

### 2.1 PROPERTIES OF WEAK-ACID CATION EXCHANGE RESINS

Our studies indicate that there may be significant advantages to pretreatment of the low-level wastes with a weak-acid cation exchange resin. Properties of these resins and their potential benefits are discussed in this section.

Strong-acid cation exchange resins are generally composed of sulfonic acid groups attached to a styrene-divinylbenzene matrix. Weak-acid cation resins are composed of carboxylic acid groups on a similar matrix. In comparison with strong-acid resins, they have the following characteristics:

1. They are less efficient in removing cations from a feed solution. This results in the weak-acid resin's ability to remove polyvalent cations (e. g., calcium, magnesium, and strontium) while allowing monovalent ions to pass through.
2. The total exchange capacity is significantly higher. A weak-acid resin will load a maximum of 3.0 eq/L under ideal conditions, compared to a 1.8 eq/L load for strong-acid resins.
3. The weak-acid resins can be regenerated to the hydrogen form very easily. Only 110% of the theoretical acid volume required is generally used in a typical operation.

### 2.2 ADVANTAGES OF USE IN THE LLWT PLANT

At the present time, the LLWT Plant uses only beds of Dowex HCR-S resin, a strong-acid cation resin. This treatment effectively removes all cations from the plant stream. The ionic constituents in the feed vary widely in concentration, and hardness may range from ~60 to >500 ppm  $\text{CaCO}_3$ . The total of monovalent cations typically varies from ~1.0 meq/L to 5 or 6 meq/L. During our observations over several months, these values averaged ~160 ppm hardness and 1.5 meq/L monovalent cations.

If a bed of weak-acid resin (such as Dowex CCR-2) were placed in the process line prior to the strong-acid resin (Dowex HCR-S) beds, two distinct advantages would be realized. The polyvalent cations would be sorbed on the weak-acid bed, and only the monovalent cations would reach the second bed. With the higher exchange capacity of this weak-acid resin, fewer bed regenerations would be required to process a given volume of feed. In addition, less acid is required to regenerate the weak-acid resin, and the use of less regenerant solution would have both economic and environmental benefits.

Table 1 illustrates the efficiency of a two-bed operation compared to that of the present one-bed system. Calculated results for waste streams with hardness values ranging from 75 to 570 ppm and with monovalent cations ( $M^+$ ) ranging from 1 to 4 meq/L are presented.

### 2.3 LABORATORY DEMONSTRATION

In order to obtain experimental verification of this two-bed operational concept, a simulation was run on a laboratory scale. A 19-L sample of the waste feed solution was obtained from the LLWT Plant on June 14, 1983. Analyses of this feed indicated 230 ppm hardness and 5.4 meq/L of monovalent cations. This feed was passed simultaneously, and at equal flow rates, through a column containing 15 mL of Dowex HCR-S resin and through a column containing 15 mL of this resin preceded by 15 mL of Dowex CCR-2 resin. Samples of the effluents from both columns were monitored for  $^{137}\text{Cs}$  content.

The bed with the single resin showed cesium breakthrough >20 Bq/L after ~3400 mL, while the bed containing both resins showed breakthrough only after ~5400 mL. Details of this run are shown in Fig. 1. These results are in reasonable agreement with the predictions in Table 1.

Table 1. Calculated operating parameters for a 1250-L column of Dowex HCR-S, with and without pretreatment with a 1250-L column of Dowex CCR-2

(2,500,000 L treated; 378 L/min flowrate)

CaCO <sub>3</sub> (ppm)	Feed M <sup>+</sup> (meq/L)	Bed volumes regenerated		Bed life, h		Elution 3.5 M HNO <sub>3</sub> <sup>b</sup> (L)	Concentration factor <sup>a</sup>
		Resin A <sup>a</sup>	Resin B <sup>b,c</sup>	Resin A <sup>a</sup>	Resin B <sup>b,c</sup>		
75	1	1	1.1 (2.8)	110	99 (40)	5,405 (10,395)	462 (240)
150	1	2	1.1 (4.4)	55	99 (25)	6,653 (16,632)	375 (150)
300	1	4	1.1 (7.8)	28	99 (14)	9,148 (29,106)	273 (86)
570	1	7.6	1.1 (13.8)	15	99 (8)	13,638 (51,559)	183 (48)
75	2	1	2.2 (3.9)	110	50 (28)	9,563 (14,553)	261 (171)
150	2	2	2.2 (5.6)	55	50 (20)	10,810 (20,790)	231 (120)
300	2	4	2.2 (8.9)	28	50 (12)	13,305 (33,624)	188 (85)
570	2	7.6	2.2 (14.9)	15	50 (7)	17,796 (55,717)	140 (45)
75	3	1	3.3 (5.0)	110	33 (22)	13,721 (18,711)	182 (133)
150	3	2	3.3 (6.7)	55	33 (17)	14,969 (24,948)	167 (100)
300	3	4	3.3 (10.0)	28	33 (11)	16,330 (37,422)	153 (67)
570	3	7.6	3.3 (16.0)	15	33 (7)	21,954 (59,875)	114 (42)
75	4	1	4.4 (6.1)	110	25 (18)	17,879 (22,869)	140 (109)
150	4	2	4.4 (7.8)	55	25 (14)	19,127 (29,106)	130 (86)
300	4	4	4.4 (11.1)	28	25 (10)	21,620 (41,580)	115 (60)
570	4	7.6	4.4 (17.1)	15	25 (7)	26,112 (64,033)	96 (39)

<sup>a</sup>Resin A = weak-acid resin, Dowex CCR-2.

<sup>b</sup>Resin B = strong-acid resin, Dowex HCR-S.

<sup>c</sup>Values in parentheses were calculated for processing without Resin A pretreatment.

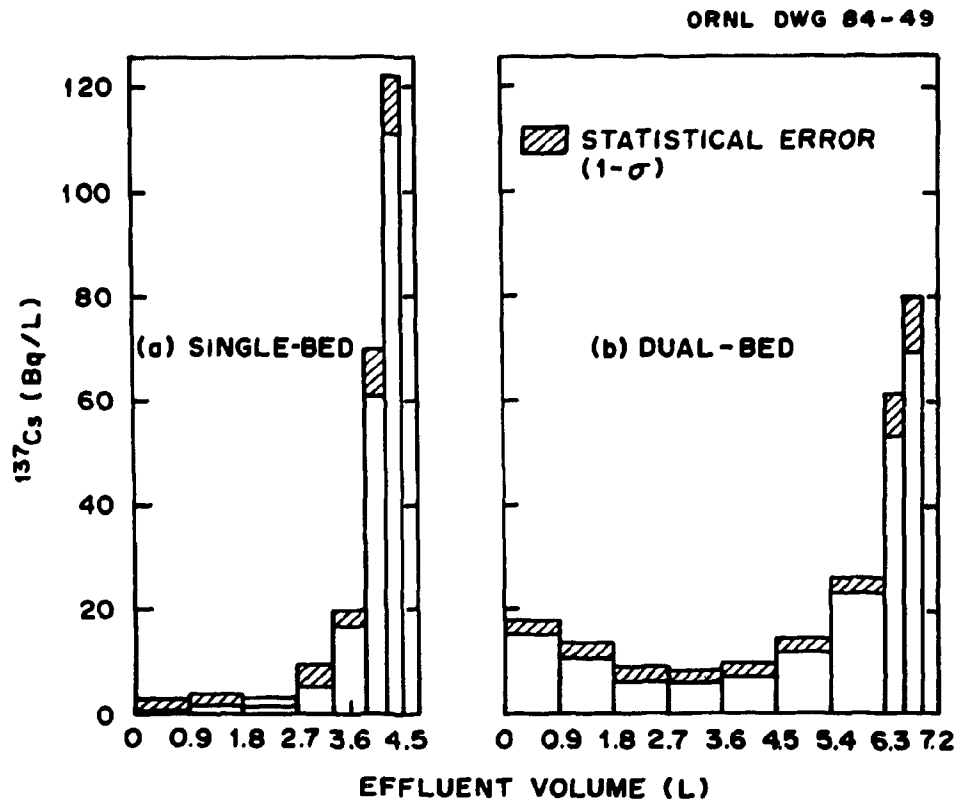


Fig. 1. Cesium breakthrough with (a) single-bed and (b) double-bed cation exchange processing.

### 3. ADDITIONAL TAIL-END TREATMENT

#### 3.1 PROPERTIES OF STRONG-BASE ANION EXCHANGE RESINS

As now operated, the LLWT Plant removes only cations from the waste stream. Under usual conditions, almost all of the radionuclides are in cationic form. However, about one-third to one-half of the  $^{60}\text{Co}$  is in anionic form and passes through the plant. This activity is generally  $\sim 10$  to  $30$  Bq/L, and is a very small fraction of the maximum permissible concentration in water ( $\text{MPC}_w$ ). Table 2 summarizes these permissible nuclide concentrations.<sup>2</sup>

In addition to the cobalt, under abnormal conditions it is possible for other radioactive anions to be present in the waste. Of particular concern would be  $^{131}\text{I}$ . This is not a customary constituent, but it has been detected on rare occasions.

A strong-base anion resin will remove essentially all anions in a stream, just as a strong-acid cation resin removes all the cations. These anion resins usually are in the chloride or hydroxide form, and, for our applications, the hydroxide form is preferable. Such a bed could be maintained on standby to treat the effluent from the cation bed when necessary, although it might not be used routinely.

Table 2. Maximum permissible radionuclide concentrations in aqueous waste streams

Nuclide	$\text{MPC}_w$ (Bq/L)
$^{60}\text{Co}$	1850
$^{90}\text{Sr}$	11.1
$^{131}\text{I}$	11.1
$^{137}\text{Cs}$	740

#### 3.2 ADDITIONAL DECONTAMINATION USING ANION RESIN COLUMN

A number of laboratory experiments have been done to prove the effectiveness of adding an anion column to decontaminate waste streams. In one run, feed from the LLWT Plant contained 137 Bq/L of  $^{60}\text{Co}$ . After passage through a cation column, the level decreased to 76 Bq/L; further processing through an anion column of Dowex I-X8 reduced the  $^{60}\text{Co}$  activity in the effluent to only 13 Bq/L.

Since the feed stream does not usually contain any radioactive iodine,  $^{131}\text{I}$  from the TRU processing operation was added to a test sample of feed from the LLWT Plant. The spiked feed was passed through a cation column and then through a hydroxide-form anion column. The feed contained 80 Bq/L  $^{60}\text{Co}$ , 1406 Bq/L  $^{131}\text{I}$ , and 248 Bq/L  $^{137}\text{Cs}$ . Analysis of the effluent from the cation column showed 54 Bq/L  $^{60}\text{Co}$ , 1336 Bq/L  $^{131}\text{I}$ , and 12 Bq/L  $^{137}\text{Cs}$ . After processing the effluent through the additional column containing a strong-base anion exchange resin, values were  $<6$  Bq/L  $^{60}\text{Co}$ , 13 Bq/L  $^{131}\text{I}$ , and 12 Bq/L  $^{137}\text{Cs}$ . These iodine values are adjusted for decay (half-life = 8 d).

Elution of the anion resin is done with sodium hydroxide solution. Laboratory results show that resin regeneration requires  $\sim 10$  bed-volumes of 1.0 M NaOH,  $\sim 8$  bed-volumes of 1.5 M, and  $\sim 6$  bed-volumes of 2.0 M. Use of a 2.0 M NaOH solution in plant operation might result in the resin washing out in an upflow elution. For this reason, a solution

of 1.5 M, or more dilute, NaOH is suggested. As with the regeneration of the cation resin, the second batch of regenerant solution could be saved and used for the first half of the subsequent elution.

### 3.3 FLOWSHEET USING DOWEX SAR RESIN

Currently, the LLWT Plant uses four, stainless steel, ion exchange columns, each containing 1250 L of resin. If one of these is converted for use as a weak-acid cation bed, an additional column would be required for an anion exchange bed. Three columns of strong-acid resin are required for normal operation since, at times of maximum flow, two columns must be operated in parallel.

The proposed modification would add a column containing a strong-base anion exchange resin such as Dowex SAR (commercial-grade Dowex-2) to the treatment process. If the anion column elution is done in two batches, two additional tanks would also be required to hold the regenerant solutions. The first batch in each cycle could be pumped to the evaporator.

Figure 2 shows a schematic diagram of the flow patterns that would result if the proposed modifications to the LLWT Plant are made, adding both the weak-acid cation bed and the strong-base anion bed. The bed of Dowex CCR-2 resin would be bypassed during periods of regeneration, as would the bed of Dowex SAR. The anion bed could be reserved for use only in situations where it was deemed necessary.

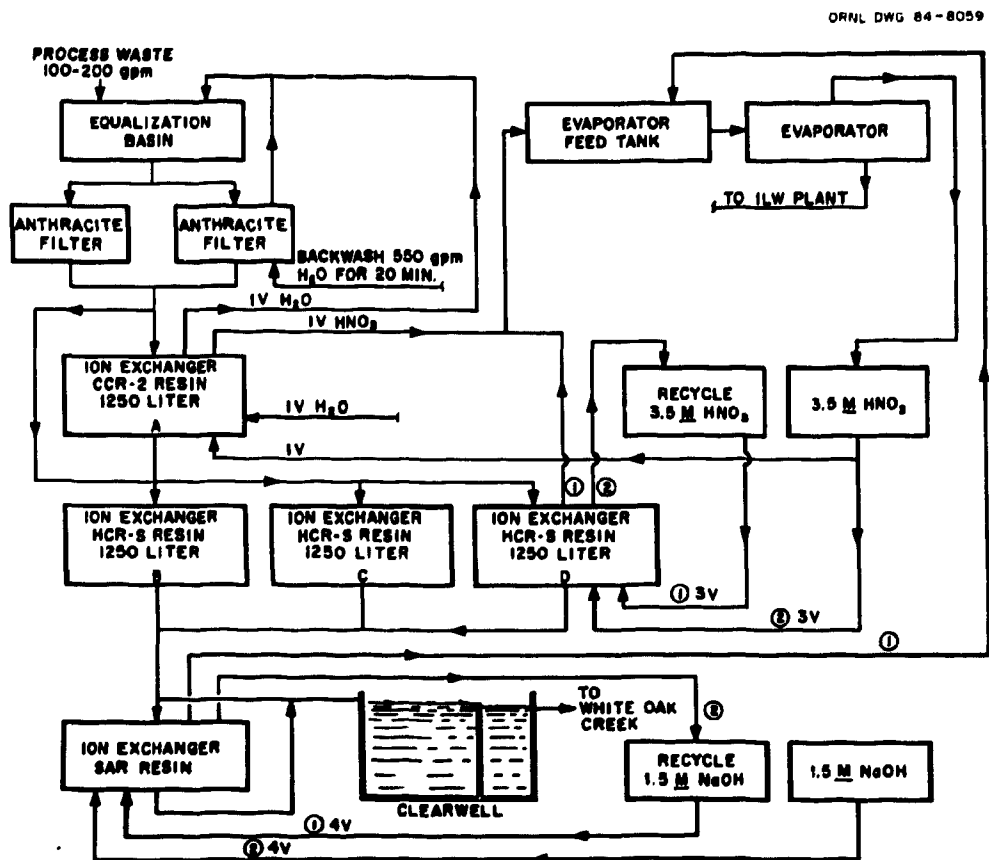


Fig. 2. Proposed flowsheet for the LLWT Plant.

#### 4. RECOMMENDATIONS

Based on the findings of this study, the author recommends that the present flowsheet of the LLWT Plant be modified to allow pretreatment of the waste by passage through a weak-acid cation exchange bed before processing by the strong-acid cation exchange resin. This would result in a significant reduction in the amount of regeneration reagents used and a saving of manpower. The modification can be done at minimal cost, since only minor changes in piping on the existing treatment columns are required.

As presently operated, the LLWT Plant removes from the waste only those radionuclides that are in cationic form. A feasible process modification to handle the occasional wastes containing anionic radionuclides (such as  $^{131}\text{I}$  and anionic forms of  $^{60}\text{Co}$ ) would be the addition of a tail-end treatment column containing a strong-base anion exchange resin; this could be maintained on a standby basis for use when needed. Since such modification would require an additional column and one or two holding tanks for regenerant solutions, a cost-benefit analysis should be conducted to determine whether this is a desirable method for handling the infrequent occurrences of anionic radionuclides in the waste streams.

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