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Treatment of ORNL High Level Waste
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FROM: I. R. Higgins

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1.0 INTRODUCTION

A common waste disposal practice is to neutralize acid waste with caustic and dump into an underground tank. The bulk of the fission products is deposited as sludge at the bottom of the tank. In order to conserve storage space, it is also a common practice to decant the supernate at a rate which the environment can tolerate. Cesium and strontium constitute the greatest hazard in the supernate and are fortunately adsorbed very well on soil.¹ Unadsorbed ruthenium and nitrate are then the major health hazards and the common remedy is dilution to acceptable levels. Recent results have shown that nitrate and ruthenium are passing through the soil pits at ORNL and may constitute a hazard to ground water. Consequently, a method for eliminating nitrate and ruthenium on ORNL wastes prior to discharge to the soil pits is required.

The proposed process for ORNL waste treatment follows the general pattern described above. The waste is neutralized with caustic and scavenged with any insoluble hydroxide which may be present. This provides a low temperature, noncorrosive method of concentrating fission products and separating the solid hydroxides from the nitrate-bearing solution. The supernate is then treated in an electrolytic cell to remove nitrate and ruthenium. Ion exchange sorption in a continuous contactor is proposed as an alternate for soil sorption for the isolation of long-lived isotopes.² In this case soil sorption would back up and reinforce ion exchange as an ultimate disposal method. In order to minimize discharge to the environment or storage of bulk salts, acid and alkali may be regenerated in the electrolytic cell. It is believed that laboratory development of this process is sufficiently advanced to warrant initial cost studies.

Other proposed waste treatment methods which should be considered accomplish concentration without addition of alkali. Nitric acid is easy to remove by evaporation or reduction with formaldehyde.

Nitrate salts may be decomposed by calcination. The acid approach has undisputed advantage as a one-step minimum-volume process, but does not denitrate the bulk radioactivity carriers as easily as the caustic neutralization method, as used at ORNL.

2.0 SUMMARY

It is proposed that neutralized ORNL waste be used as a feed for a waste processing development facility. Operation would start with storage tank supernates. An electrolytic cell would be installed to remove nitrate and ruthenium from the wastes prior to discharge to the soil disposal pits. This would eliminate the hazards of nitrate and ruthenium in the ORNL soil disposal pits. In addition, a continuous ion exchange unit could be installed to study the isolation of fission products from a portion of the waste stream. The total waste stream can be processed by ion exchange if desired. A six to eight inch diameter continuous ion exchange contactor² is considered sufficient to remove cesium, strontium, and rare earths from 5,000 to 10,000 gallons of waste per day. The estimated installed cost of such a unit is about \$16,000. The labor and chemical operating cost at 100% overhead is estimated at \$22.50 per day.

Three types of electrolytic cells have been considered. All of the cells remove about 90% of the ruthenium by plating on the cathode. It is expected that the degree of ruthenium removed may be increased by further laboratory development. The first cell type is the Ionics cell³ which converts NaNO_3 to NaOH and HNO_3 for recycle. The second is the nitrate reduction (or destruction) cell which produces caustic and ammonia gas, as studied by KAPL.⁴ The acid-base cell is favored because of nearly a factor of 8 lower power consumption, and the nitric acid may be reused as well as sodium hydroxide. An acid-base cell with rectifier for 5,000

gallons per day of 0.3 M NaNO_3 waste is estimated at about \$15,000. The operating cost with 100% overhead, including labor, electricity, and cell maintenance is estimated at \$47.72 per day. Operations may be credited with \$29 per day of caustic and \$86 per day of nitric acid.

If it is desired to isolate the ruthenium and not remove the nitrate, a simplified electrolytic cell may be used. Cell cost is estimated at $\sim 80\%$ of the acid-base cell and about one tenth the cost for a rectifier. About 90% of the ruthenium may be conveniently removed.⁵

Technetium is not considered a radioactive hazard, but recovery is considered because of its value and expected ease of recovery. Technetium is not scavenged and has a very great affinity for anion resin.⁶ At current prices it is estimated that 0.25 g per day of technetium is being discharged at ORNL, which at present prices is \$7,000/day.

3.0 THE BASIC FLOWSHEET

A flowsheet is presented which consists of two basic steps. The first is ion exchange or soil sorption of the long-lived isotopes, and the second is a method of diverting non-sorbed nitrate and ruthenium from discharge to the environment. The flowsheet starts with the alkaline supernate of neutralized wastes, where the fission products are in settled sludge (Fig. 1).

The cationic species, cesium, strontium, and rare earths may be sorbed on phenolic ion exchange resin with distribution coefficients of about 100. This favorable ion exchange equilibria combined with efficiencies obtained by continuous countercurrent ion exchange represents an effective treatment step. The elution step can be chosen depending on the final cesium handling method.

Fig. 1 ORNL WASTE TREATMENT FLOWSHEET

Hydrochloric acid is recommended because it is a volatile acid and cesium sources are prepared as CsCl. For ORNL wastes, sulfuric acid is preferred because the quantity of cesium is not sufficient for sources and sulfate is more compatible for return to the tank farm or diversion to the cesium alum process (Fig. 2).

Extensive studies have been made of soils for the adsorption of long-lived isotopes.¹ About 45 yd³ per year of shale will immobilize all the cesium from ORNL waste. The greatest disadvantage to the present pit system is channeling, or poor seepage distribution through the pits. As an alternate to the continuous ion exchange method, it is suggested that a cheap impervious-lined pit (concrete or asphalt), filled with ground and graded shale, be considered.

The supernate from the ion exchange or soil adsorption contains practically all the nitrate and ruthenium. Nitrate has a 44 ppm tolerance level in wastes, and ruthenium is dangerous because it is unadsorbed. Two electrolytic methods have been developed for nitrate removal from radioactive waste. One is nitrate migration³ (Fig. 3), and the other a nitrate destruction by reduction to ammonia⁴ (Fig. 4). Each regenerates caustic for reuse, and the migration cell also delivers nitric acid for reuse. The acid-base cell construction is more complicated because it requires membranes and cell compartments. The nitrate reduction cell is simple in construction but requires a power source 5 to 10 times greater. The power consumption is correspondingly greater and more heat exchange capacity is required for cooling.

In either electrolytic cell, ruthenium is plated on the cathode. It may be desirable to disregard the nitrate and use a cell designed for ruthenium alone. About 90% of the ruthenium is deposited under present conditions, but this may be improved after further laboratory study.⁵

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Fig. 2 CONTINUOUS CONTACTOR FOR ORNL WASTE

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Fig. 3 ACID-BASE CELL FOR ORNL WASTE

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Fig. 4 NITRATE DESTRUCTION CELL FOR ORNL WASTE

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A fixed bed anion exchange column can be used before the electrolytic cell treatment to recover technetium. In the oxidized state and in alkaline solution, practically all the technetium is soluble.⁶ Technetium has an extremely high affinity for anion resin, similar to rhenium, and this seems to be a simple method of recovery. A distribution coefficient greater than 200 has been demonstrated. If the cesium discharged at ORNL represents 100% and the technetium is 100% soluble, there is 1/4 gram of technetium lost per day.

4.0 ORNL WASTES

There are two major liquid waste sources at ORNL. One is 5×10^6 gallons of process water per day, which averages 25-50 cts/min/ml and occasionally jumps to a few thousand counts. This source is not considered for treatment in this proposal. The second is the chemical waste, which runs about 5,000 to 10,000 gallons per day. This waste may vary considerably, but typical analysis is about 0.3 M nitrate, 0.5 M sodium, 30 curies of cesium per day, 30 millicuries of strontium, and 1.5 curies of ruthenium. About 4,000 to 4,500 gallons of 50% caustic is used for neutralization per month. The bulk of the radioactivity is scavenged by hydroxide precipitates and settles to the bottom of underground tanks. The strontium, cesium, rare earths, zirconium, and niobium are completely immobilized in open seepage pits. The 0.3 M nitrate and 1.5 curies per day of ruthenium empty into White Oak Creek, which finally dumps into the Clinch River. The river flow is about 4,000 ft³ per second.

5.0 LABORATORY RESULTS

Scavenging, along with ion exchange sorption of rare earths,

strontium, cesium, and technetium, are being studied in the laboratory. Electrolytic cell studies include electrolytic nitrate migration and reduction, and ruthenium plating. Studies are not complete at present, but results are as follows: Cesium, strontium, and rare earths have a distribution of greater than 100 for Duolite C-3 resin from 0.5 M Na^+ , 0.3 M NaNO_3 , and 0.1 M NaAlO_2 solution. For cesium the distribution is >60 from 0.9 NH_4NO_3 -0.1 M N_2OH and from 3 M NaNO_3 -0.1 M NaOH . These tests indicate that cesium loading conditions are favorable for continuous ion exchange from severe and varied feed conditions. Hydrochloric acid is considered for stripping because it can be recycled by evaporation. A distribution coefficient of 5 and <1 was observed for cesium and sodium, respectively in 3 M HCl and Duolite C-3 resin. A laboratory 1 1/2-in.-dia continuous contactor has been run at rates up to 800 gal/hr/ft² with cesium cts/min/ml reduced from 3.5×10^4 to 0-50 at a feed to resin ratio of 60 in a 3 ft loading section. The cesium product stream was decontaminated from sodium by a factor of 10^4 .

The acid-base cell has been studied most thoroughly by Ionics, Inc. in connection with similar studies for BNL.³ They indicate 1 M HNO_3 may be produced at 100% current efficiencies in a membrane cell and 8 M at 50%. On ORNL waste about 90% migration of nitrate was accomplished in a single stage at about 60% current efficiency. Much more extensive testing of this cell is planned.

Considerable work has been done at KAPL on the electrolytic destruction of nitrate.⁴ With ORNL waste, 18 g/l nitrate has been reduced to ~ 0.01 g/l at 60% current efficiency. An iron cathode and a stainless steel anode were used as recommended by KAPL. During an extended run on ORNL waste, a stainless steel anode completely dissolved in less than 24 hours.

Ruthenium plating was observed in the nitrate destruction cell.

About 80 to 90% of the ruthenium can be depended on to deposit on the cathode and appears to be a time dependent phenomenon. Mercury and lead cathodes initially appeared superior to iron, but the final amount deposited was the same in 3 to 4 hours.

6.0 COST ESTIMATE FOR MAJOR EQUIPMENT AND OPERATING ITEMS

6.1 Cost Summary

Installed Capital Cost

Ion exchange contactor	\$ 16,000
Acid-base electrolytic cell	<u>15,000</u>
Total	\$ 31,000

Operating Costs Per Day

Ion exchange	\$ 22.50
Electrolytic cell	<u>47.72</u>
Total	\$ 70.22

Product Credit Per Day

NaOH	\$ 29.00
HNO ₃	<u>86.00</u>
Total	\$ 115.00

6.2 Ion Exchange Costs

Ion exchange contactor (Fig. 2)	\$ 10,000
Installed cost (40%)	4,000
Piping (10%)	1,000
Instrumentation (10%)	<u>1,000</u>
Total Capital Cost	\$ 16,000
Labor (1/2 man-day)	\$ 10.00
Chemicals (125 lb H ₂ SO ₄ /day)	<u>1.25</u>
	\$ 11.25
Overhead (100%)	<u>11.25</u>
Total Operating Cost	\$ 22.50

6.3 Acid-Base Electrolytic Cell Costs (Fig. 3)

Anodes (platinized tantalum)	7 at \$275	\$ 1,920
Cathodes (iron, 1/16-in. plate)		50
Ion exchange membranes	28 at \$15	420
1-in. Redwood spacers and filter press frame		1,000
Feed pumps	3 at \$400	<u>1,200</u>
Total		\$ 4,590
Installation cost (40%)		1,820
Piping (50%)		2,245
Instrumentation (10%)		<u>459</u>
Total Capital for Cell		\$ 9,114
Power supply at \$100/kw (6 volts at 90% CE)		\$ 4,200
Installation cost (40%)		<u>1,680</u>
Total Power Supply Cost		\$ 5,880
Total Capital Cost		<u>\$14,994</u>
Labor (1/2 man-day)		\$ 10.00
Electricity at 1¢/kwh		10.00
Membrane replacement (6 mo)		2.30
Anode replacement (6 mo) (\$40 worth of Pt on each electrode)		<u>1.56</u>
		\$ 23.86
Overhead (100%)		<u>23.86</u>
Total		\$ 47.72

6.4 Product Recovery Credit Per Day

Assume 0.3 M NaNO_3	
500 lb of 100% NaOH - 2.9¢/lb as 50%	\$ 29.00
800 lb of 100% HNO_3 - 6 $\frac{1}{4}$ ¢/lb as 60%	<u>86.00</u>
Total Credit	\$ 115.00

7.0 REFERENCES

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