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SUBJECT: REDUCTION OF RADIOACTIVE WASTE TO SOLIDS FOR ULTIMATE
STORAGE (To be presented at the A.C.S. Convention,
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ABSTRACT

A procedure is presented for processing high level radioactive wastes. The steps are: pot calcination of acid and neutral waste followed by separation by distillation of the fission products from effluent liquid and gaseous streams. The fission products would be recycled to the calcination pot. After calcination, the pot contents would be stored in a controlled area for cooling and accountability.

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SUMMARY

The ultimate disposal of liquid radioactive waste resulting from the reprocessing spent nuclear fuel elements is a serious problem facing the growth of the atomic power economy. One of the potentially safe methods of disposal of radioactive liquids is to reduce the waste to solids by heating and then decontaminating the resulting condensate and gases. The system that is proposed has been preliminarily scounted and several parallel paths of investigation will be discussed.

A procedure for processing high level radioactive wastes is: pot calcination of acid and neutral waste followed by separation of the fission products from effluent liquid and gaseous streams. The fission products would be recycled to the calcination pot. After calcination, the pot contents would be stored in a controlled area for cooling and accountability.

1.0 INTRODUCTION

One of the major problems to be satisfactorily solved before a nuclear power economy can survive is the disposal of unwanted fission product waste after maximum use has been made of the useful radioisotopes. Ultimate storage for fission waste should have two main goals: (1) the storage system must be safe, keeping fission products from the environment for at least 500 years, (2) fission products should be stored in such a manner so that they can be inspected and recovered if an economic market should arise.

The ideal process would have raw waste as the starting material and would expell decontaminated gases and liquid, a mixture of metal oxides and inert additives, and fission products suitably packaged as the finished material.

Some of the methods proposed for ultimate disposal of radioactive waste are:

1. Reduction to solids and dry storage.
2. Unlimited tank storage of a liquid or slurry.
3. Liquid disposal into salt formations.
4. Liquid disposal into pressure bearing sands.
5. Liquid or solids disposal into oceans.

Liquid disposal has the disadvantage that the high mobility of the fission products in liquids creates a severe safety hazard if the waste solutions inadvertently enter the ground water. Solid storage of fission product waste in water-tight containers reduces this hazard.

This paper will be limited to a discussion of one method of reduction of radioactive waste to solids by heating and storage of the waste in a suitable area. The steps in this disposal method are: (see Figure 1)

1. Pretreatment

General Flowsheet for Reduction of Radioactive Waste to Solids.

FIGURE 1

2. Calcination
3. Fission product off-gas treatment and fission product recovery
4. Cooling and ultimate storage

2.0 GENERAL FLOWSHEET

Consider for the sake of comparison two types of radioactive wastes (1) Purex waste, and (2) Darex waste. Purex waste is 5.5 molar nitric acid, 0.6 molar sulfuric acid and 0.15 molar ferric nitrate. The fission products concentration is 2.5 g/liter. The activity of the concentrated waste is about 1300 curies per gallon. The Darex waste is produced from dissolving stainless steel fuel elements in nitric and hydrochloric acid, after which the chloride is removed by distillation. The composition of the high level waste is 3 molar nitric acid, 0.7 molar ferric nitrate, 0.16 molar nitrate and 0.07 molar nickel nitrate. The activity may be about 1000 curies per gallon.

When this waste solution is discharged from the radioactive fuel processing plant, there are two alternatives for handling. The first alternative is to discharge the waste into a tank for long term tank storage. The second alternative is to process it immediately. First, consider tank storage (see Figure 2).

Nitric acid waste from fuel reprocessing plants may be stored as an acid waste in stainless steel tanks, or the waste can be neutralized with sodium hydroxide and stored in mild steel tanks. One of the problems encountered in tank storage is the heat evolved when the fission products decay. 22.7 Btu/hr (gal) are evolved from a waste which has an activity of 1300 curies per gallon. Heat may be released from the tank by allowing the radioactive waste to boil under conditions of total reflux. However, there has been some trouble with tanks in which the waste has been neutralized. Some of the solids have been difficult to maintain well dispersed and "bumping" has occurred resulting in a serious off-gas problem. One of the other disadvantages in tank storage may be the difficulty of removing the liquid and sludge from the storage tanks at a later date.

If the radioactive waste solution is directly processed after it has been discharged from the fuel processing plant, the physical characteristics of the waste are easier to predict. The radioactive waste would be evaporated to produce a pumpable sludge. The vapor and noncondensables from the pretreatment evaporation step would pass to the off-gas treatment and fission product recovery system. The sludge from the evaporation step would be pumped into the furnace liner of a calciner. The furnace liner of the calciner would itself be the ultimate storage retaining vessel. The heating cycle would be programed so that the major portion of the water would be removed from the solids in the temperature range 100-200°C. After this the remaining waste would be increased in temperature to 600-800°C. The maximum temperature of the calcining step would be fixed as the maximum temperature that the solids will attain during ultimate storage.

Comparsion of Waste Processing Systems

FIGURE 2

The off-gas from the calciner would contain water, the decomposition products from nitric acid, and fission products. These constituents would pass through an off-gas treatment and fission products recovery system.

The purpose of the off-gas treatment and fission product recovery system is to release to the environment decontaminated gaseous and liquid streams and to recycle the fission products to the calciner. One chemical problem of the reduction of nitric wastes to solids is the decontamination of the nitric acid in the off-gas system. If nitric acid were recycled with the fission products there would be an acid build-up; therefore, the nitric acid must be decontaminated from the fission products and released to the environment. There are at least two methods for the decontamination of nitric acid. One method is chemical decontamination by the use of ion exchange or distillation. Another method is catalytic destruction of nitric acid to nitrogen, oxygen, and water, and then removal of fission products from the nitrogen-oxygen gaseous stream. Formaldehyde can be also used to destroy nitric acid, producing nitrous oxide, water, and carbon dioxide.

When the calciner contents have been cooled, the calciner liner which is the ultimate storage vessel would be removed and sent to an interim cooling facility. Interim cooling may be necessary because the fission product decay heat generation may cause the solids to reach a maximum temperature a few days after calcination. The temperature then decreases as a linear function of the fission product content (approximately exponential with time) in the waste solids. Forced cooling of these containers would be necessary to insure that the product never attains a temperature greater than the maximum processing temperature. If a greater temperature was permitted, there might be fission product off-gas which could rupture the container and contaminate the environment.

The storage vessel would then be shipped to some ultimate storage site. Probably the most expensive ultimate storage site is dry vault storage. However, dry vault storage has a major advantage in that the fission product wastes could be removed at a later date and reprocessed to recover the fission products when the market would bear the cost.

2.1 Pretreatment

The pretreatment step for waste before calcining includes evaporation and neutralization. The acid wastes could be evaporated and then neutralized if necessary. However, if the waste has been neutralized and stored for a period of time, evaporation could be carried out with the neutral slurry. In general the acid waste can be evaporated to a smaller percentage of the original value than can neutralized waste. Darex acid waste can be evaporated to 20-25% of its original value before the resulting slurry solidifies at room temperature. Purex waste can be evaporated from 10 to 15% of its original value before any precipitation occurs. When a stoichiometric amount of formaldehyde is added to Darex waste before evaporation, the resulting slurry has a lower viscosity and is easier to handle than the normal evaporated acid waste.

One of the problems encountered in reducing nitric waste to solids is the recycle and build-up of nitrate ion with the fission products from the condenser and the scrubbing system. The effect of NaOH on this build-up was determined by adding 38 g NaOH/200 ml (resulting in a pH of 9) to "25" waste before evaporation. The "25" waste has the following composition:

$\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$	1.6 <u>M</u>
$\text{Hg}(\text{NO}_3)_2$	0.01 <u>M</u>
NH_4NO_3	0.03 <u>M</u>
HNO_3	0.50 <u>M</u>

Two samples were heated to 140°C. The condensate from the acid sample was 0.59 M HNO_3 while the condensate from the neutralized sample was 0.47 HNO_3 (see Table I). While there was only little difference in the acidity of the condensate, the corrosion of the calciner should be less with the neutral waste.

TABLE I

Evaporation of "25" Waste to 10% of Original Volume

Feed - 200 ml	"25" Waste	
Maximum Temp	NaOH, g	Condensate Molarity (HNO_3)
140	0	0.59
140	38	0.47

2.2 Calcination

The reduction of the radioactive waste to solids by calcination is the most important step in the present process. As the water is distilled into the off-gas system, the thermal decomposition products of nitric acid and nitric salts ($\text{Fe}(\text{NO}_3)_2$) are evolved and are transferred to the off-gas system. The maximum calcination temperature used for the experiments was 850°C; the normal calcination temperature was 700°C. The reduction in volume was 5 to 10 fold at 700°C (see Table II).

TABLE II

Volume and Bulk Densities of Calcined Waste

<u>Feed</u>	<u>% of Original Volume</u>	<u>Bulk Density</u>
Darex acid	10	0.80
Neutralized	23	2.0
Purex acid	6	0.80
Neutralized	?	?

A hot cell experiment was performed to determine the amount of fission products evolved when Darex and Purex wastes were calcined to dryness. The amount of fission products reporting to the condensate and the amount removed by the caustic scrubbers down-steam of the condensate receiver were determined.

A thin walled stainless steel cup of 600 ml capacity was placed within a stainless steel bomb which was heated in a programed manner to first boil the 200 ml of waste solution to dryness and subsequently calcine it at 700°C. The bomb was vented to an off-gas train which collected the activity; however, the system had little or no leakage. A condenser removed the condensibles which were collected. The non-condensibles were passed to a packed bed caustic scrubber and then through three caustic bubblers in series. Finally the off-gas was passed to the plant hot off-gas which operated at 3 to 10 inches of water vacuum (see Figure 3).

Darex waste was simulated by dissolving the appropriate metal powders in Purex waste (6.0 M HNO_3 , 0.5 M H_2SO_4). The activity of waste was 2×10^{11} count/min/ml β and γ respectively. Some of the waste was diluted with synthetic waste for lower activity level studies.

At the lower activity level there were slightly less fission products evolved from the neutralized waste as compared to the acid waste. However, at higher level approximately the same amount was evolved from neutralized or acid waste; however, this evolution represented a lower proportion of the total fission product than was evolved from the lower level waste (see Table III).

The calcination vessel, which is the final storage container, should have these requirements; it should be easily filled and vented during calcination, should have a positive closure for storage, and should be constructed from corrosion compatible material (see Figure 4). Stainless steel would be acceptable for acid waste, while mild steel might be serviceable for neutralized waste.

Experimental Setup For Radioactive Waste Reduction to Solids.

FIGURE 3

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AMOUNTS OF FISSION PRODUCTS EVOLVED FROM THE REDUCTION OF WASTE
TO SOLIDS BY HEAT

FEED TYPE		FEED ACTIVITY COUNTS/MIN/MI		COUNTS/MILLION COUNTS IN FEED			
				CONDENSATE		OFF-GAS	
		β	γ	β	γ	β	γ
DAREX	NEUTRALIZED	9×10^9	9×10^9	20	60	0.5	0.5
PUREX	NEUTRALIZED	8×10^9	8×10^9	30	20	0.3	0.8
PUREX	ACID	8×10^9	8×10^9	400	600	1.0	2
PUREX	NEUTRALIZED	2×10^{11}	2×10^{11}	50	100	0.07	0.2
PUREX	ACID	2×10^{11}	2×10^{11}	10	10	1.0	2.0

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Remote Furnace for Drying Radioactive Waste.

2.3 Off-Gas Treatment and Fission Product Recovery

The off-gas treatment and fission product recovery section of the process is concerned with two problems. The first problem is to remove the fission products from the gaseous phase and to isolate them into a minimum liquid volume. The second problem is to remove all of the nitrate from the fission product liquid phase and discharge the nitrate or its decomposition products to the environment decontaminated. When the fission products have been separated from the gaseous and liquid phases and have been concentrated they are returned with the feed to the calciner. The volume of liquid condensed in the off-gas treatment is approximately 80-90% of the original waste volume charged to the calciner. The acid concentration for the neutralized waste condensate is 0.2 - 11.4 molar and 0.7 - 0.5 molar for the acid waste condensate (see Table IV). The difference in nitrate ion is due largely to amount of nitrate converted to NaNO_3 . The waste condensate contains a complete spectrum of fission products, i.e., cesium, strontium, cerium, ruthenium, and zirconium - niobium (see Table V). If the fission products are to be concentrated and returned to the calciner, a normal method would be to evaporate the condensate to a minimum volume and return to the calciner.

Two methods for removing the nitric acid have been proposed. They are distillation and ion exchange (see Figure 5). If the ion exchange process is chosen the fission products in liquid phase would be loaded on cation resin from a nitric acid stream ranging in concentration from about 1.0 molar to 4.0 molar and would be stripped with a small volume of 8-10 molar nitric acid (approximately 10% of feed volume).

If distillation is used to remove the nitric acid from the fission product liquid phase, the procedure will be as follows. The nitric acid and fission product concentrate would be fed into the still pot of a distillation system which would be operating at or near to total reflux. Formaldehyde would be fed into the still pot to reduce the nitric acid to NO and CO_2 ($4 \text{HNO}_3 + 3 \text{H}_2\text{CO} \longrightarrow \text{CO}_2 + 4 \text{NO} + 3 \text{H}_2\text{O}$). These gaseous compounds would be scrubbed as they went up the distillation column and would be discharged through the condenser system along with the distilled decontaminated water. The bottoms containing the fission products are returned to the calciner at their maximum concentration.

The distillation procedure has some advantages over the ion exchange procedure. There are no moving parts to be serviced in a hot cell containing a distillation column and there are no materials which are subject to radiation degradation such as ion exchange resin.

2.4 Cooling and Ultimate Storage

The cooling and ultimate storage of calcined solids has been a subject for much conjecture and discussion. So far, very little work has been done on this subject. A conservative method is here proposed for cooling and ultimate storage. The requirement that the solid cannot attain a temperature in cooling or storing which exceeds the maximum calcined temperature must be

TABLE IV

Condensate Resulting From Calcination of Acid and Neutralized "25" Waste

Neutralized with NaOH 1900 g/liter

Calcine

Temperature	Volume	Condensate	Molarity
°C	ML	Acid	Neutral
0-425	40	0.7	0.2
425-475	40	2.0	0.9
475-520	40	6.3	5.2
520-650	46	11.5	11.4
Recovery of (NO ₃)		86%	76%

TABLE V

Fission Products In Condensate After Pot Calcination of Purex Waste.

Vol ml	Gross β c/m/ml	Gross γ c/m/ml	Sr c/m/ml	Ce c/m/ml	Cs c/m/ml	Ru c/m/ml	Zr-Nb c/m/ml
Feed 100 hot 200 cold	4×10^{11}	4×10^{11}	1×10^{10}	4×10^{10}	4×10^9	2×10^{10}	1×10^{11}
Conden- sate							
1 30	3×10^7	6×10^7	1×10^5	9×10^4	3×10^6	5×10^7	5×10^6
2 70	4×10^6	6×10^6	4×10^4	1×10^4	5×10^5	5×10^6	1×10^5
3 70	1×10^6	4×10^6	3×10^4	8×10^3	2×10^5	3×10^6	3×10^5
4 70	9×10^6	2×10^7	1×10^5	4×10^5	4×10^5	1×10^7	9×10^5

Comparison of Fission Product Recycle Systems.

FIGURE 5

observed. The calcined waste which is enclosed in the calciner vessel can be cooled either with air or water for a period of time in a controlled environment until the heat due to fission product decay is reduced to a point at which they can be safely stored in their ultimate site. A boiling water cooler may be the most easily constructed and maintained cooling equipment (see Figure 6).

In picking a storage site many things must be considered - the nearness to a processing site, the cost of handling and shipping, the population in the area, and all economic factors that go into establishing a plant site. The most conservative type of ultimate storage is the vault type storage. The fission product containers are stored in an area in which they can be monitored, accounted for, and at later date removed if the fission product market can support the reprocessing of the calcined wastes for the fission products of value.

One other procedure for this ultimate storage site would be to mine a series of shafts and side shafts either in stone or in salt (see Figure 7). These hollow shafts and side shafts would be designed for self-shielding. The calcined storage vessel would be shipped in carriers and lowered into a canal. From the canal they would be loaded remotely into a frame which would hold a number of containers. The frame could be transported by a shielded lift truck into the storage area. The storage area can be so designed that all the heat generated from the fission product decay could be dissipated into the immediate surrounding mass eliminating the need for air or water cooling.

A machine calculation has been performed for infinite vertical cylinder of waste in a hole with an air space between the cylinder and an infinite salt medium into which the fission product heat is dissipated. (see Figure 8). For the case of a 9-in. radius cylinder of waste generating 100 Btu/hr-gal (1 yr cooled), a 1-in. air space, an allowable temperature increase of 1200°F (650°C) and an air film coefficient of 0.7 - 1.3 Btu/hr-sq ft-°F, the minimum acceptable thermal conductivity for the solid waste would be 0.15 Btu/hr-ft-°F.

3.0 CONCLUSION

One attractive method for ultimate disposal of radioactive waste resulting from the reprocessing of reactor fuel elements is reduction of the radioactive fission product waste to a solid and subsequent storage in a dry shielded area. In this process the gaseous and liquid components of the waste are decontaminated and are discharged to the environment.

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Interium Cooling Tank For Solid Waste Containers.

FIGURE 6

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Ultimate Storage of Radioactive Solid Waste.

FIGURE 7

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FIGURE 8

CALCULATION OF MINIMUM ACCEPTABLE
THERMAL CONDUCTIVITY FOR WASTE SOLIDS

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