HW--52824

DE92 003724

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21 pages. No. [redacted]

[redacted]. Series [redacted]

[redacted]

ULTIMATE DISPOSAL OF PUREX WASTES

by

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Classification Cancelled (Change to
declassified
By Authority of RLO-CG-4
C A Bauman 10/17/91
By D. G. Fischer 10/23/91
L. M. Lewis 10/23/91

Chemical Research
Chemical Research and Development
HANFORD LABORATORIES

September 26, 1957

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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INTRODUCTION

Since much Chemical Research and Development effort is being expended on the recovery of fission products from Purex waste streams, it seems well to simultaneously consider waste disposal practices, even though the two fields are quite different, with different goals. Recovery necessitates removal of fission products in a highly concentrated form, while disposal requires that most of the waste products be discarded with only minor amounts of fission product contamination. The high concentration of fission products required for recovery purposes is not consistent with the high decontamination factors required for disposal. Therefore economies in waste disposal as a result of recovery programs are unlikely, but not impossible. Of course, the fission products themselves must always be stored until they have decayed sufficiently to permit safe discard. The possible economies are in alternate methods of storage, the amounts of material to be stored, and in the utilization of radiation from the stored fission products.

Objectives and methods for waste disposal have been discussed by Glueckauf(1). He cites four primary principles for consideration in waste disposal; (a) protection of human food and water supplies from fission products; (b) protection of humans from over-exposure to radiation; (c) protection of mineral wealth, both above and below ground; and (d) economic consideration. He further cites three possible ways of satisfying the above requirements: (a) permanent storage in underground containers; (b) storage in less permanent containers in uninhabited desert and arctic regions; and (c) separation and storage of strontium and cesium, and disposal of the remaining fission products after several years of storage. In each case the fission products may be stored either wet or dry. If the fission products are in a non-leachable solid, they may be stored in simple containers; even pits may be adequate. These principles and possible solutions, though brief, should provide an adequate basis for discussion of the problem.

In all of the waste disposal plans cited above containment of the fission products in small volumes is required for maximum economy in container construction. In the second process, economical transportation also requires small volumes. The volumes attainable are limited by the total salt content of the wastes, and by the radiation from the concentrated fission products. The radiation causes problems of heating and radiation decomposition of the stored material. The primary problems to be considered in the ultimate disposal of Purex wastes are, therefore, the reduction of the amounts of inert solids to be stored, and containment of the fission products in a manner consistent with safety, economy, and radiation effects. This report will discuss primarily the chemical problems associated with adequate storage or discard of the major waste streams. Safe reduction of the amount of material to be stored, either in tanks or held in the soil, is the first goal, and other possible economies are secondary.

SUMMARY

The high-level waste streams from the Purex plant consist of the primary fission product stream (1WW), waste from organic recovery operations (1OW), and coating waste. The minimum volume of these streams for liquid storage is dependent on the concentration of ferric nitrate, sodium nitrate and sulfate in 1WW, sodium

carbonate and nitrate in 1OW, and sodium aluminate, hydroxide, nitrite, and nitrate in coating waste. The volume of 1WW is also limited by allowable fission product concentrations to prevent excessive boiling.

Because of these limitations, the current procedures for storage of liquid wastes can be improved only slightly by simple volume reduction techniques since self-concentration is already employed. Some decrease in stored salts is possible by flowsheet changes or by removing nitric acid from 1WW by means other than neutralization with sodium hydroxide. Nitric acid removal can be accomplished by evaporation, solvent extraction, chemical reaction, electrolysis, or anion exchange. The first three methods in particular are worth further investigation, but the last method does not appear very attractive. One or more of these methods can also yield additional nitric acid recovery, waste uranium and plutonium recovery, or removal of certain individual fission products.

After removal of nitric acid, the 1WW can be converted to a solid for storage either in underground containers or as a source of mixed fission product radiation. Recovery of individual fission products can be incorporated with these processes. The conversion to a solid can be accomplished by simple calcination, or by precipitation and calcination of the precipitate. Ruthenium volatilization may cause problems in disposal of gases with these processes. Liquids generated in these processes can probably be treated by recycle, or by ultimate disposal by established procedures for low level streams.

The volume of 1OW to be stored is small at present because of self-concentration in tanks containing 1WW. If the 1WW is stored as a solid, however, waste tanks will no longer be self-concentrating, and the stored volume of 1OW will increase unless new disposal methods are adopted. The volume may be reduced by evaporation before storage. An alternate is the removal of uranium, plutonium, and a few fission products from the 1OW, and cribbing the supernate. In this latter process, the value of recovered uranium and plutonium will be significant. Removal of uranium and plutonium can probably be accomplished by direct anion exchange, or by acidification and use of solvent extraction or precipitation techniques.

Coating waste cannot be cribbed directly because of the low adsorption of cesium and strontium on soil. If these elements are removed, coating waste can probably be cribbed safely. Alternate processes to improve storage of coating waste are conversion to a gel by addition of sodium silicate, or concentration by evaporation prior to storage in non-boiling tanks. Some saving can also be achieved by storing coating wastes in boiling waste tanks, but these savings are small, and will prevent future improvements in storage of these wastes by one of the other methods cited above.

DISCUSSION

Composition of Major Waste Streams

Major waste streams from the Purex plant consist of the primary fission product stream (1WW), waste from organic recovery operations (1OW), and coating waste (CRW). The approximate compositions of these streams are shown in Table I. Some unexpected or unlisted gross constituents may also be present. Mercury, for example, has recently

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been added to dissolver solution as an iodine control measure, and will be present in the 1WW while this practice continues. Unlisted minor constituents include fission products, corrosion products and impurities in uranium, aluminum, and process reagents, and organic decomposition products.

TABLE I

COMPOSITION OF HIGH-LEVEL PUREX WASTE STREAMS

	1WW			1OW		CRW
Constituent	HW #3	Two Cycle	Actual	HW #3	Two Cycle	HW #3
H, $\underline{M}$	7.6	6.2	5.6	---	---	---
Na, $\underline{M}$	0.48	0.32	*	0.43	0.30	3.7
U, $\underline{M}$	0.03	0.03	0.03	0.03	0.02	0.002
Fe, $\underline{M}$	0.1	0.36	0.32	---	---	---
Al, $\underline{M}$	---	---	0.06	---	---	1.2
NO_3^-, $\underline{M}$	8.0	6.4	*	0.07	0.05	0.6
$SO_4^=$, $\underline{M}$	0.2	0.6	0.4	---	---	---
$CO_3^=$, $\underline{M}$	---	---	---	0.21	0.15	---
OH^-, $\underline{M}$	---	---	---	---	---	1.0
NO_2^-, $\underline{M}$	---	---	---	---	---	0.9
$SiO_3^=$, $\underline{M}$	---	---	---	---	---	0.02
Pu, mg./l	3	2	10	2	1	0.2
γ curies/ ton U	$3x10^5$	$3x10^5$	$4x10^5$	20	20	100
Gal./ton U	150	40	100	270	310	240

1WW - Concentrated aqueous waste from extraction columns.
1OW - Aqueous waste from solvent recovery.
CRW - Coating waste.

HW #3 - Flowsheet HW #3 from Purex Technical Manual (2).
Two Cycle - Proposed flowsheet, Swift and Irish (3).
Actual - Sample of 1WW obtained from Purex on 11/9/56. Analyzed by Analytical Laboratories, HLO.

* - Not analyzed.
--- - Minor or unexpected constituent.

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The activities in 1WW and coating waste from the principal fission products of concern in waste disposal are listed in Table II. The activities were calculated for 600 MWD/T material, assuming 100 gal. of 1WW and 240 gal. of coating waste per ton of uranium processed, and a loss of 0.04 percent of the total activity to the coating waste. The activity in 10W will be less than that in coating waste, and will consist largely of ruthenium, zirconium, and niobium instead of mixed fission products as with the other streams. The radiochemical composition of 10W will be more variable than will the other two streams, and might increase markedly if waste streams are backcycled, since organic degradation products from the concentrator might cause an increase in the concentration of fission products in the organic phase.

TABLE II

FISSION PRODUCT ACTIVITY IN WASTE STREAMS

	Activity in 1WW, $\mu c/l \times 10^{-6}$			Activity in CRW, $\mu c/l$		
Nuclide	1 y.	10 y.	50 y.	1 y.	10 y.	50 y.
Sr^{90}	5.3	4.3	1.6	880	710	260
Y^{91}	6.9	---	---	1,200	---	---
Zr^{95}	9.9	---	---	1,600	---	---
Nb^{95}	22	---	---	3,600	---	---
Ru^{106}	6.8	0.013	---	1,100	2	---
Sb^{125}	0.19	0.018	---	32	3	---
Te^{127}	0.40	---	---	66	---	---
Cs^{137}	5.1	4.1	1.6	840	690	270
Ce^{144}	72	0.024	---	12,000	4	---
Pm^{147}	20	1.8	4×10^{-5}	3,300	300	---
Sm^{151}	0.10	0.092	0.065	17	15	11

Activities calculated from data in HW-48461(4), assuming 100 gal. of 1WW and 240 gal. of coating waste per ton of uranium, and a loss of 0.04 percent of the total activity to coating waste. Values not shown are less than 0.1 $\mu c/l$.

Impurities in the uranium slugs will go to the 1WW and impurities in the aluminum cans will go to the coating waste. Some of these impurities will be radioactive since they have been irradiated in the pile along with the uranium. The amounts of the most important impurities per ton of uranium, and the activities expected in 1WW and coating waste are shown in Table III. Although these activities are small compared to the fission products, they must still be handled in a safe manner. Iron and cobalt are the only components of either stream which are expected to cause any trouble.

TABLE III

NEUTRON ACTIVATION OF IMPURITIES IN URANIUM AND ALUMINUM

Nuclide		Wt. of Element, Grams per ton U		Activity in 1WW, uc/l			Activity in CRW, uc/l		
Parent	Daughter	in U	in Al	1 y.	10 y.	50 y.	1 y.	10 y.	50 y.
Fe^{54}	Fe^{55}	50	160	5,000	580	---	6,700	770	---
Fe^{58}	Fe^{59}	50	160	5	---	---	7	---	---
Co^{59}	Co^{60}	<100	<0.2	$<2\times10^6$	$<5\times10^5$	$<3\times10^3$	<1,400	<420	<2
Ni^{62}	Ni^{63}	20	2	250	230	160	11	10	7
Zn^{64}	Zn^{65}	<100	<10	<26,000	<4	---	<1,100	---	---
Ca^{44}	Ca^{45}	<10	<1	<170	---	---	<7	---	---
Cl^{35}	S^{35}	<10	<1	<1,600	---	---	<70	---	---
S^{34}	S^{35}	<10	<1	<80	---	---	<3	---	---
Sc^{45}	Sc^{46}	<1	<0.1	<12,000	---	---	<500	---	---

Weights of impurities were calculated from data in the Purex Technical Manual(2). Activities were calculated for 600 MWD/T using the method outlined in HW-43461(4). Impurities in aluminum were assumed to go entirely to coating waste, and impurities in uranium were assumed to go entirely to 1WW. Volumes of 100 gal. of 1WW and 240 gal. of coating waste per ton of uranium processed were assumed. Values not listed are less than 0.1 uc/l.

Other common or expected elements, including B, C, N, O, Na, Mg, Al, Si, P, K, Ti, Cr, Mn, Cu, Ga, Sn, Cd, and Pb will not yield appreciable activities at the concentrations of these elements expected in uranium or aluminum.

Decontamination factors required to reduce the activity of the principal radioactive constituents of 1WW and coating waste to the maximum permissible concentration for water (MPC) are shown in Table IV. For cribbing waste streams, the required decontamination factors for all elements will depend on the behavior of wastes in the ground, and may be either higher or lower than those shown. Soil studies will be necessary before actual requirments can be defined. The concentrations must be lowered by at least the factors shown before the fission products reach water supplies.

TABLE IV

ACTIVITY IN WASTE STREAMS RELATIVE TO MPC

Nuclide	MPC*, μc/l	Activity in 1WW** 1 y.	10 y.	50 y.	Activity in CRW** 1 y.	10 y.	50 y.
Fe^{55}	5	1,000	100	----	1,000	200	----
Co^{60}	0.4	$<4\times10^{6}$	$<1\times10^{6}$	<6,000	<4,000	<1,000	<5
Sr^{90}	0.0008	7×10^{9}	5×10^{9}	2×10^{9}	1×10^{6}	9×10^{5}	3×10^{5}
Y^{91}	0.3	2×10^{7}	----	----	4×10^{3}	----	----
Zr^{95}	0.6	2×10^{7}	----	----	3,000	----	----
Nb^{95}	2	1×10^{7}	----	----	2,000	----	----
Ru^{106}	0.1	7×10^{7}	1×10^{5}	----	1×10^{4}	20	----
Sb^{125}	1	2×10^{5}	2×10^{4}	1	30	3	----
Te^{127}	0.7	6×10^{5}	----	----	90	----	----
Cs^{137}	2	3×10^{6}	2×10^{6}	1×10^{6}	400	300	100
Ce^{144}	0.1	7×10^{8}	2×10^{5}	----	1×10^{5}	40	----
Pm^{147}	2	1×10^{7}	9×10^{5}	20	2,000	200	----
Sm^{151}	8	1×10^{4}	1×10^{4}	700	2	2	1
U^{238}	0.002	2,000	2,000	2,000	200	200	200
Pu^{239}	0.003	2×10^{6}	2×10^{6}	2×10^{6}	2×10^{5}	2×10^{5}	2×10^{5}
Am^{241}	0.003	2×10^{5}	2×10^{5}	2×10^{5}	40	40	40
Cm^{242}	0.002	7×10^{5}	----	----	100	----	----

* Maximum permissible concentration in water, from HW-25457 Rev. 1 (5).

** Activity in waste stream divided by MPC. This gives the decontamination or dilution factor required for safe disposal of each nuclide.

Values not shown are less than 1.

Disposal of 1WW

Removal of Nitric Acid

Although much of the potential salt storage problem is already eliminated by recovery of nitric acid from wastes, one of the main salt limitations for liquid storage is still caused by neutralization of the remaining nitric acid. Further removal of nitric acid is therefore desirable in order to reduce the amounts of salts to be stored. Alternatively, the sodium nitrate formed by neutralization of the acid may be converted to innocuous products. Removal of additional nitric acid may be accomplished by (a) additional evaporation, (b) extraction into organic solvents, (c) chemical reaction to give water and gaseous products, (d) electrolysis, and (e) ion exchange.

Evaporation

Further evaporation of the 1WW is limited partly by the possibility of ruthenium volatilization. As long as the temperature of the 1WW remains below 140°C and the nitric acid concentration remains below 8 molar, little ruthenium volatilization is expected. Even with the present knowledge of ruthenium behavior during evaporation, additional concentration of 1WW appears possible without appreciable complication from ruthenium. The addition of reagents to suppress ruthenium volatilization could further increase the amount of concentration possible. Other limitations on the amount of nitric acid removed in this manner are the possibility of formation of solids in the evaporator, and corrosion of the evaporator. Current operations are limited becuase of possible formation of solids in the evaporator. Since determination of dissolved salt content is not accurate at present, a safety factor in amount of concentration is allowed. Better determination of salt content could permit additional evaporation of the 1WW.

Solvent Extraction

Many organic solvents, such as hexone, ether, organic amines, and triglycol dichloride, extract nitric acid from aqueous solutions. The nitric acid can be stripped from the organic phase with water, and the organic phase can be re-used. Depending on the amount of fission product activity extracted, the recovered nitric acid could be sent to the 1WF or the 2WF for further purification. The uncertainties associated with this process include possible radiation decomposition of the solvent, possible reactions between nitric acid and the solvent, and possible extraction of materials other than nitric acid from the 1WW. Under proper conditions, this approach can probably be used for recovery of uranium and plutonium, by extraction into the organic phase. The material stripped from the organic phase could then be sent to the dissolver or to the HAF. The concentration of nitric acid remaining in the 1WW could be reduced to below one molar, and the volume of 1WW would be reduced by the extraction step. Thus about 90 percent of the nitric acid would be removed from the 1WW, and could be recovered for re-use. Probably the solvent can be re-used and the aqueous strip can be recycled, so that no storage problems would result. This process appears to be technically feasible, and does not require any reagents other than water and occasional replenishment of the organic phase.

Chemical Reaction

Nitric acid reacts with formaldehyde, paraformaldehyde, or formic acid to give only gases and water as reaction products(6). The approximate stoichiometry of the reactions is indicated by the following equations:

$$2\ HNO_3 + HCHO \longrightarrow NO + NO_2 + CO_2 + 2\ H_2O$$

$$2\ HNO_3 + 2\ HCHO \longrightarrow NO + NO_2 + 2\ HCOOH + H_2O$$

$$2\ HNO_3 + 2\ HCOOH \longrightarrow NO + NO_2 + 2\ CO_2 + 3\ H_2O$$

The decomposition reaction is fairly rapid at the boiling point, even for concentrations of nitric acid below one molar. Little change in concentration can be expected after one hour. A concentration of 0.5 molar acid remaining appears readily attainable, which corresponds to over 90 percent removal of the nitric acid. Since the reaction produces only gases and one mole of water per mole of nitric acid consumed, the only increase of volume will be the amount of water added along with the reagents. This volume can be quite small since little water is associated with paraformaldehyde. With formaldehyde, the volume increase will be about 20 percent. Because of the simple nature of the process, no problems with fission products are expected. At reagent costs of 15 cents per pound for paraformaldehyde and four cents per pound for sodium hydroxide, the paraformaldehyde will cost 50 percent more than the cost of the sodium hydroxide currently used. The additional reagent cost could be recovered, however, if waste volumes after self-concentration were reduced to 0.86 times their present value.

Electrolysis

The removal of nitric acid by electrolysis has been investigated by D. L. Barney of KAPL(7). With a solution approximating 1WW, he obtained a minimum nitric acid concentration of 1.6 molar, with only 1.5 percent of the acid converted to ammonium ion. Even lower acid concentrations could probably be obtained if the voltage and current density were reduced. Experiments with two molar nitric acid showed that final acid concentrations of less than 0.5 molar can be achieved with copper catalysis, with about 15 percent of the acid being converted to ammonium ion. Four to five faradays were required per mole of acid destroyed in each case. A process of this type for nitric acid removal would require no process reagents other than electricity. Any ammonium nitrate formed in the solution would have to be stored in the same manner as sodium nitrate, and would contribute to salt limitations in stored waste. Some removal of fission products by electrodeposition is possible, but is not expected to change waste storage requirements appreciably. The off-gas produced by any electrolytic process must naturally be decontaminated to a large extent to permit disposal. This decontamination might require filtration, scrubbing, or condensation of the off-gas, and possible re-distillation of liquids generated in the scrubbing or condensation steps.

Another electrolytic scheme for removal of nitric acid is to neutralize the 1WW with sodium hydroxide, and electrolyze the sodium nitrate to produce ammonia and sodium hydroxide(8). The sodium hydroxide thus formed can be concentrated and recycled to neutralize additional 1WW. Current consumption observed was about ten faradays required per mole of sodium nitrate destroyed. Because of the highly basic nature of the final solution, no ammonium ion would remain after the electrolysis. Since the process involves recycle of sodium hydroxide, the precipitate formed on neutralizing the 1WW would have to be removed before electrolysis. This process, therefore, is more attractive with solid storage of gross fission products than with liquid storage. If complete recycle can be achieved, only electricity is added as a process reagent. Constituents of 1WW which are not removed from the solution before recycling will increase in concentration, so occasional disposal of the solution to be recycled may be required. Therefore, proper operation of this type of process requires that very little material, either radioactive or inert, be recycled without at least partial removal from the solution.

Acid can also be removed by electrolysis through an anion semi-permeable membrane(9). The anions move through the membrane into the anode compartment, and hydrogen ions are reduced at the cathode to form hydrogen gas. Thus acid is removed from the cathode compartment and concentrated in the anode compartment without the addition of chemicals. The process can be used to deplete the acid concentration in the cathode compartment to a very low level. However, some of the fission products are transferred to the anode compartment, along with nitrates and sulfates. Also the life of the membrane may not be very long, because of both chemical and radiation instability.

Ion Exchange

When nitric acid solutions are passed through an anion exchange resin in the hydroxide form, nitrates are retained by resin and hydroxyl ions are liberated to the solution. The result is a reduction in the acid content of the solution. If the column is sufficiently large, basic precipitates such as ferric hydroxide may form and plug the column. The column in the nitrate form may be washed with sodium or ammonium hydroxide to regenerate the resin. The salt produced will probably not be sufficiently decontaminated from fission products to permit uncontrolled disposal. Therefore the salt must either be stored or decontaminated sufficiently for disposal. The process may not even be technically feasible because of the instability of resins in high radiation fields. Therefore removal of nitrates by anion exchange does not appear promising.

Storage as a Liquid

Limitations

1WW is currently being neutralized with sodium hydroxide and stored in boiling waste tanks along with the 1OW. The minimum volume obtainable with liquid storage is usually determined by the quantity of inert constituents in the waste, but for very concentrated solutions, radiation effects such as the rate of heating and radiation decomposition become limiting. The present minimum volume of 1WW after self-concentration is determined by the amount of sludge, and an upper limit of ten molar sodium ion concentration. These limits yield about 65 gallons of 1WW per ton of uranium processed, depending in part on the volume and concentration of nitric acid before neutralization.

Major ions present in 1WW are nitrate, sulfate, sodium, iron(III), aluminum, and uranium(VI). Removal of these ions will permit concentration of 1WW to smaller volumes. Most of the nitrate ion comes from nitric acid, but some of the nitrate and all of the sodium come from sodium nitrite added as an oxidant. The removal of nitric acid was previously discussed. The sodium can be eliminated by the use of different oxidants such as nitrogen dioxide or nitrous acid. Sulfate can be eliminated by the use of a different reductant in the process (e.g., hydrazine), by precipitation, or by electrolysis through a semi-permeable membrane.

Aluminum is not intentionally introduced into the process, but some aluminum is introduced by incomplete dissolution of cans and the bonding layer prior to acid dissolution of the slugs, and by corrosion of aluminum tanks and piping in the demineralized water system. Aluminum can be eliminated, or at least reduced in concentration, by better control of dissolving operation, and by replacement of aluminum equipment.

Iron is introduced into the process as an impurity in uranium and process reagents, as a process reagent, and as a corrosion product. The amount of iron introduced can be reduced, (e.g., by using a different reductant, and using titanium tube bundles in concentrators), but iron cannot be completely eliminated. Some uranium will also be present in 1WW. These elements must be stored since uranium is radioactive, and the iron introduced as an impurity in uranium will be radioactive because of neutron activation. Since liquid wastes must be stored as basic solutions to minimize corrosion, hydrous ferric oxide and sodium diuranate will be present as a slurry in stored wastes. The amount of this slurry is important for boiling waste tanks since it affects the temperature distribution and boiling characteristics. The amount of these precipitates present in a tank furnishes a serious limitation to the minimum volume of 1WW stored as a liquid.

For storage as a very concentrated solution, cooling must be provided to prevent excessive boiling, and water must be added to replace that which is removed by distillation and by radiation decomposition. If the volume of 1WW after self-concentration is reduced much beyond the present figure, the waste tanks will continue to boil for many years because of the heat liberated by strontium and cesium. Excessive heating rates are undesirable since storage of boiling or specially cooled wastes is more expensive than storage of less active wastes, both from initial construction and operating expense considerations. Another effect of radiation is the decomposition of nitrates to form oxides of nitrogen. If nitric oxide reacts with water to form acids in the vapor space above the solution, the life of the tanks may be reduced. Radiation effects are not quite limiting factors in determining waste volumes at present, even though the stored liquid does boil for some time, and some oxides of nitrogen are formed.

Possible Improvement

Since the minimum volume for liquid storage is limited in three ways (soluble salt, precipitate, and radiation) as mentioned above, liquid storage cannot be greatly improved under present operating conditions. Improvement can be achieved only by changing both the amount of stored salts and the rate of energy release. Removal of nitric acid by means other than neutralization would reduce the salt content. However, the precipitate volumes and rate of heating limitations would require a volume almost as large as currently achieved. Savings by reduction of the salt content could be achieved, however, if low exposure material were being processed, or if the long lived fission products were removed from the waste (e.g., by adopting cesium and strontium recovery processes). Another possibility is the removal of some salts from 1WW and combination of the 1WW with other stored wastes. The only wastes available for this type of treatment are 10W and coating waste. 10W is currently being treated this way, and other satisfactory methods for disposal of coating waste are possible, as will be discussed later.

Removing fission products, plutonium, etc., from the 1WW to a sufficient extent to permit cribbing the supernate is unlikely because of the high decontamination factors required. Solid wastes generated would include not only the uranium, plutonium, and fission products, but also the scavenging agents and all of the iron introduced into the 1WW. The isotopic dilution of the radioactive iron by the natural element may increase the MPC somewhat, but some control of the iron from 1WW will be necessary. Solid waste volumes are thus likely to be excessive, even if adequate decontamination factors can be achieved.

Storage as a Solid

Storage Limitations

Storage in waste tanks, even as liquids, is generally regarded as satisfactory permanent storage at Hanford, since even in the event of a tank rupture, the soil under the tanks will retain the waste on a specific retention basis. Greater safety can be achieved by storage as solids in closed containers, or as non-leachable solids in open containers or even simple pits. Storage of leachable solids in unconfined containers would be quite similar to storage of liquid wastes in soil on a specific retention basis, although migration of the waste is much less likely in the solid storage case. In any case the stored material will be hazardous after even hundreds or thousands of years since cesium and strontium decay very slowly, and uranium and plutonium remain for even much longer periods of time.

Safety in storage will be dependent on the effects of radiation on the stored material. The volume of material, heat transfer rate, and radiation effects will be largely determined by the inert constituents. With confined solids, sufficient cooling must be provided to prevent rupture of the container, and pressure relief must be provided unless many precautions are taken to prevent formation of gases by heating and radiation decomposition. If a pressure relief system is provided, highly efficient decontamination of the gases released will be required to prevent excessive release of radioactive materials. If the solids are non-leachable, the effects of prolonged standing in a radiation field must be evaluated. With all solid storage, therefore, radiation damage and heat transfer studies must be made before safety in storage can be assured.

Utilization as Radiation Sources

Utilization of stored solids as radiation sources may be accomplished with either a gross mixture or individual fission products. The sources must be confined to insure

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that no radioactive material enters the material being irradiated. Source preparation may be by the techniques of fission product recovery, or by the methods for gross fission product sources described below. Utilization of packaged fission products for radiation sources does not eliminate the storage problem, but merely shifts the responsibility for storage to the purchaser. Safe handling of the sources during use, and safe disposal after partial decay must be possible. Fission product utilization as currently envisioned is thus merely a special case of disposal of fission products as confined solids.

Preparation by Calcination

An obvious method for converting the 1WW to a solid for storage is to concentrate the 1WW by evaporation, and to calcine the bottoms from the evaporator. The distillate could be treated via the acid recovery system. The most significant chemical problem expected in this process is the volatilization of ruthenium as the tetroxide during the late stages of evaporation, and during calcination. Many possible solutions to this problem are being considered at Arco, in connection with their program for calcination of aluminum nitrate wastes. The volatilized ruthenium is expected to be extremely difficult to remove from the off-gas. Therefore, the general approach is to reduce the amount of ruthenium volatilization by elimination of nitrates from the material, or by having an excess of innocuous reducing agents present during calcination. Similar work with Hanford waste streams will be required to determine the feasibility of calcination. If the ruthenium volatilization problem can be overcome, this approach to ultimate disposal appears quite feasible technically. Additional problems may be caused by organic materials in the waste stream.

One possible disadvantage is that the material is never obtained in a form sutiable for recovery of individual fission products. This can be overcome by dilution after evaporation to remove nitric acid, or by removing nitric acid by one of the other methods previously described. The solution after acid removal would be suitable for many fission product recovery operations. Uranium and plutonium could be recovered either by individual operations, or along with nitric acid removal if solvent extraction is used.

Preparation by Recycle Methods

Another modification is to remove nitric acid, fission products, and inert constituents to a sufficient extent to permit concentration and recycle of the remaining material. If over half of all constituents were removed, the steady state concentrations would be less than twice the present concentrations. However, removal of half of the sodium and sulfate is not easy. Use of calcium hydroxide to neutralize the solution would probably result in adequate removal of all major ions except sodium. Sodium ion could best be eliminated by using a different oxidant than sodium nitrite; or the sodium could be recycled until the concentration became excessive, and then the supernate could be stored. Since the initial sodium ion concentration is below 0.5 molar, about ten recycles may be possible before discard is necessary. This would reduce the volume of stored 1WW almost tenfold. Also the concentrated sodium nitrate solution could possibly be used in coating removal, if the amounts of fission products and plutonium are sufficiently low. Of course, the problem of storage of the solid would remain. With this process, or in fact any time solids are taken to dryness, there is a possibility of ruthenium volatilization. Because of the reduced nitrate concentration in the precipitate, this loss should be smaller with this process than with simple calcination as described above.

R. H. Moore(10) proposed a similar process, based on KAPL work(8) with electrolysis of sodium nitrate solutions. The electrolytic portion of this process was described briefly under nitric acid removal. The process as conceived by Moore involves neutralization of 1WW, removal of fission products, and electrolysis to ammonia and sodium hydroxide. The sodium hydroxide would then be concentrated and recycled to neutralize more 1WW. Again the problems are sodium and sulfate in the liquid portion, and ruthenium in the solid portion of the waste. Also a new problem is introduced in the ammonia off-gas from the electrolysis cell. Redistillation may be required before ammonia can be safely discarded to air as a gas, or to ground as an aqueous solution. It is possible that ruthenium may be partially electrodeposited during the sodium nitrate destruction step if conditions are carefully chosen. Ruthenium volatilization will probably still be a problem in the drying of solids, even if partial removal of ruthenium is accomplished by electrodeposition.

Disposal of Organic Recovery Wastes

The waste from organic recovery is primarily an aqueous solution of sodium carbonate and sodium nitrate, with smaller amounts of uranium and plutonium present as carbonate complexes. (The following discussion relates to pooled wastes from organic recovery, whether this be 1OW only as with flowsheet HW #3, or 1OW plus 2OW as with the two cycle flowsheet.) This solution is currently combined with 1WW in boiling waste tanks to concentrate it from its initial volume of about 300 gallons per ton of uranium processed to a volume after concentration of about 12 gallons per ton of uranium. As long as present operating conditions are maintained, there is little economic incentive for cribbing the 1OW. However, if 1WW storage is altered to eliminate boiling waste tanks, there is considerable incentive to reduce the stored volume of 1OW. This can be accomplished either by distillation to reduce the volume, or by scavenging and cribbing. The technology for distillation is rather simple, and will not be considered here.

The major radioactive components of 1OW are plutonium, uranium, ruthenium, zirconium, and niobium. Other fission products are present in the 1OW to a much smaller extent since they are less readily extracted from aqueous solution. Since the amount of fission products in 1OW is even less than with coating waste, and most of the fission products in 1OW are short lived, the major limitation on cribbing of 1OW will be plutonium. The amounts of uranium and plutonium expected in 1OW under Flowsheet HW #3 conditions about 15 pounds and two grams respectively per ton of uranium processed. Further incentive for removal of these elements from 1OW is their economic value if they can be recovered.

As mentioned above, uranium and plutonium are expected as carbonate complexes, which do not precipitate readily from aqueous solution. If this is the case, they can probably be recovered by anion exchange to remove the carbonate complexes, or the waste can be neutralized with nitric acid to destroy the carbonate complexes. After acidification, the elements may be recovered by more standard precipitation, solvent extraction, or ion exchange processes. Destruction of carbonates and re-neutralization would probably improve retention of both elements by the soil, thus facilitating cribbing possibilities. Unless cribbing is possible, the recovery operations will not improve waste storage costs. However, because of the better retention on the soil after carbonate removal, waste storage will be safer after recovery of the uranium and plutonium from this waste.

Disposal of Coating Waste

The current volume of coating waste is about 240 gallons per ton of uranium processed, and this volume can be reduced to only about 90 gallons by evaporation of the solution to ten molar sodium and 3.2 molar aluminate. One evaporation method is to store coating waste with the other high level wastes in boiling tanks. The savings achieved will be largely offset by the higher unit costs of storage in boiling tanks. The volume limitation for storage in boiling tanks is determined by the salt content and by the concentration of radionuclides in the waste. Combination of 1WW with coating waste will yield a volume limitation of 155 gallons because of the dissolved salt content, while smaller volumes would be allowed from radionuclide concentration considerations. If the dissolved salt content of 1WW was reduced by nitric acid removal, the permissible volume of combined wastes would be reduced to about 100 gallons per ton of uranium processed. Since the present volume of stored 1WW is about 65 gallons per ton of uranium, the contribution from coating waste in the above scheme would be only about 35 gallons per ton of uranium, as opposed to 90 gallons by simple evaporation, or 240 gallons per ton of uranium at present. Sludge volume limitations may also reduce the possible savings by this process.

Cribbing of the coating waste after scavenging to remove objectionable radioactive constituents appears to be technically feasible, even though processes have not been fully developed as yet. The high salt content of coating waste reduces the amount of retention of most nuclides on the soil. Therefore scavenging techniques must reduce the concentrations of the most important nuclides to a very low value, perhaps even approaching MPC. Most of the objectionable nuclides can be removed adequately by a simple centrifugation of the waste to remove the basic precipitate. Strontium, cerium, and plutonium are largely removed in this manner, but the high decontamination factors required (see Table IV) may necessitate a second precipitation with a suitable carrier.

Cesium is not removed well by simple precipitation of the hydroxides, but may be removed by other techniques. The removal of cesium from coating waste by ion exchange has been investigated by Barney et. al. (11). They conclude that decontamination factors of 100 for cesium can be readily obtained by using phenolic methylene sulfonic resin. Another method for removal of cesium from highly alkaline solutions is precipitation with sodium tetraphenyl boron. The precipitate when formed by itself does not have good settling, centrifugation, or filtration characteristics, but these may possibly be improved by the use of coagulants, or by mixing with other basic precipitates. The cesium tetraphenyl boron precipitate can also be removed by solvent extraction (12).

The economics of cribbing coating waste are difficult to assess since they involve the current storage costs, cost of cribbing, cost of scavenging, cost of storing and scavenged materials, and possible savings on present costs by other storage techniques. It is unlikely that any of the materials removed from coating waste can be recovered economically to help offset the cost of cribbing.

An additional problem with coating wastes, both in storage and in cribbing, is the precipitation of aluminum from the solution. The precipitate, which forms slowly on prolonged standing, could lead to excessive volumes of scavenged solids in cribbing procedures, plugging of cribs, or excessive volumes of solids in tank storage. While the amount of precipitate is not critical at present, it could become important if the coating wastes are cribbed or stored in boiling tanks.

Active investigation is in progress by Chemical Effluents Technology(13) on the problem of converting coating waste to a non-leachable solid by gel formation with sodium silicate. The major advantage of such a process would be to reduce the hazard and cost of storage. Volumes would not be changed appreciably, although some shrinking of the gel upon long standing is possible. Disposal costs by this method are estimated to be about ten cents per gallon.

RECOMMENDATIONS

1. Develop a systematic program to determine actual waste stream compositions. Present work and planning are based only on nominal or flowsheet compositions, and individual samples of 1WW and coating waste are known to differ substantially from the nominal compositions. Additional variations will probably occur with conversion to a two cycle flowsheet.

2. Devise flowsheets for the Purex process which will minimize the amounts of acid and other inert materials (i.e., sodium, iron, aluminum, uranium, and sulfate) in 1WW. Elimination of these materials will improve storage as a concentrated liquid, reduce volumes required for storage as a solid, and facilitate recovery of additional values (e.g., plutonium and fission products) from waste streams.

3. Initiate or expand laboratory investigations on the removal of nitric acid from 1WW by further distillation, solvent extraction, and chemical reaction. Examine electrolytic and ion exchange methods for removal of nitric acid, considering both economic and technical questions, to determine whether further work on these methods is advisable. Removal of nitric acid from 1WW by means other than neutralization with sodium hydroxide will improve current liquid storage, and facilitate conversion of 1WW to a solid for storage.

4. Continue work on methods to remove cesium and strontium from 1WW. Removal of these elements will reduce the hazards involved in storage of gross fission products, and provide valuable by-products.

5. Investigate the conversion of 1WW to a solid by both direct calcination and precipitation-calcination flowsheets. This should include investigation of ruthenium behavior, and determination of radiation and themal stability, physical and chemical properties and heat transfer characteristics of the solid.

6. Develop flowsheets for the recovery of plutonium and uranium from organic recovery wastes and determine the economics of these flowsheets.

7. From the analyses mentioned in recommendation 1, determine which nuclides are limiting in the disposal of organic recovery wastes to ground (cribbing). Develop flowsheets for the adequate removal of these nuclides and determine the economics of these flowsheets.

8. Evaluate the proposed methods of coating waste disposal, and further develop the methods which offer the greatest economic incentive consistent with safety requirements.

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