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TREATMENT OF WASTE
SOLIDIFICATION CONDENSATES

By

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Water and Land Resources Section
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ABSTRACT

The Waste Solidification Engineering Prototypes program is a comprehensive research and development plan undertaken to provide the nuclear industry with methods for long-term storage of highly radioactive wastes. During the solidification of highly radioactive wastes, some low and intermediate level condensates are encountered as secondary effluent streams. For complete demonstration of the solidification processes, these condensates must be effectively treated so that any potential for release to the environment is avoided. This report describes the research performed in exploring methods for attaining this objective. Two types of condensates requiring treatment were identified as (1) glass melter condensate, and (2) nitric acid fractionator condensate. In the first case, 10 potential treatment methods were investigated with emphasis on those offering the most promise, i.e. scavenging, volatilization, precipitation, distillation, and asphalt incorporation. In general, the methods fit categories designated as (1) separation of sulfates, and (2) conversion to solid forms. In treating acid fractionator condensates, methods such as adsorption, electrodialysis, ion exchange, and oxidation were explored. As a result of this research, alternatives considered to be the most effective for treating these condensates have been selected and described herein. In the case of glass melter condensate full-level radioactive demonstration is planned.

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TREATMENT OF WASTE
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INTRODUCTION

WASTE SOLIDIFICATION ENGINEERING PROTOTYPES

The Atomic Energy Commission estimates that by 1980, nuclear power plants in the United States will have a generating capacity of 120,000 to 170,000 MW_e.⁽¹⁾ Virtually all will be from light-water reactors using slightly enriched uranium fuel. As a result of this use of nuclear power, the annual demand for chemical processing of irradiated nuclear fuels will be about 300 to 400 metric tons of reactor-discharged uranium. The present processing demand is under 30 tons.

During chemical processing of irradiated nuclear fuels, most of the highly radioactive fission products are accumulated as waste. Since even minute quantities of fission products are highly toxic to mankind and other life, exceedingly careful storage and control of these materials must be maintained for centuries.

While the present practice of storing these wastes as concentrated solutions in underground tanks has been demonstrated to be economical and safe, a more permanent solution will be necessary as the relatively young atomic energy industry expands.

Fortunately, those who have been associated with the environmental and waste disposal aspects of the nuclear industry have anticipated the requirement for a more permanent solution. As a result, a comprehensive research and development plan was undertaken to provide the nuclear industry with methods for long-term storage of highly radioactive wastes.

The culmination of this plan is the Waste Solidification Engineering Prototypes (WSEP) program at Battelle-Northwest.

The objective of the WSEP program is the demonstration of processes for the solidification of highly radioactive wastes. The processes selected for demonstration are (1) spray solidification, (2) pot solidification, and (3) phosphate glass solidification. While the bulk of the radioactive fission products in each of the three processes are fixed in stable, solid form, some low and intermediate level radioactive wastes are encountered as relatively minor effluent streams. In all cases, these effluent streams appear as condensates.

A truly complete demonstration of the solidification processes requires that these low and intermediate level radioactive condensates be effectively treated in order to eliminate the potential for release to the environment. The research performed in conjunction with this report has explored methods whereby this objective will be attained.

SOLIDIFICATION PROCESSES

The previously referenced spray, pot, and phosphate glass solidification processes were selected for final demonstration in the WSEP program based on prior research at Hanford Laboratories (now Battelle-Northwest), Oak Ridge National Laboratory, and Brookhaven National Laboratory.

The spray solidification process developed at the Hanford Laboratories employs a spray calciner coupled to a continuous melter which converts the radioactive waste to a chemically inactive solid for reliable permanent storage.⁽²⁾ The major features of the spray solidification process are shown in Figure 1.⁽³⁾ During operation of the process, radioactive liquid waste is sprayed into the top of a calciner through an atomizing nozzle. The waste is then finely atomized by steam

FIGURE 1. The Spray Solidification Process

or air addition. The spray, as it falls through the calciner, is progressively dried and calcined to powder by electrically heated walls. The calcined powder falls directly to the melter below, while the gas passes to a filter chamber. An optional scheme includes a concentric internal draft tube in the spray calciner reactor chamber.

In the electrically heated continuous melter, the calcined powder is heated from 700 to 1200 °C until a melt is formed. The melt then flows to a storage pot where the contents cool to form a glassy or crystalline solid. Just as in the other solidification processes, the solid is sealed in the pot and transported to the designated storage area. At present, the storage area is expected to be similar to those described in Reference 4, e.g., vaults in underground salt or crystalline rock formations.

The pot solidification process was developed at the Oak Ridge National Laboratory.⁽⁵⁾ The process is a batch scheme in which liquid waste is added to a pot heated by a multiple-zone furnace until the waste becomes a salt cake. At this point, the feed stops and heating is continued until the salt cake is denitrated and a porous calcine is formed. The calcine forms at about 900 °C. A flow diagram for this process is shown in Figure 2.⁽³⁾

Vapors generated in this process are partially refluxed to keep the off-gas line clean. The refluxed vapors are collected in a condensate tank along with the rest of the vapors already condensed in the process condenser. Noncondensable vapors are scrubbed and filtered before release.

Since sulfate can be retained in the calcine at low temperatures, with proper feed formulation, processing can be performed in stainless steel containers. Hence, for this method, the processing vessel is also the storage vessel.

FIGURE 2. Pot Solidification Processes

The third solidification process to be demonstrated is the phosphate glass process developed by Brookhaven National Laboratory.⁽⁶⁾ A simplified flow diagram is shown in Figure 3.⁽³⁾ Basically, three steps are employed to form phosphate glass in this process. In the first step, phosphoric acid is added to the liquid radioactive waste. During the second step, most of the water and nitric acid is removed in an evaporator to concentrate the mixture into a thick slurry. In the third step, the slurry is fed to a continuous melter where final evaporation and glass formation occurs at 1000 to 1300 °C. Volatile materials, including sulfuric acid are driven off during this final step.

The vapors from the denitration evaporator and the glass melter are then condensed and collected, the phosphate glass flows from the melter into a storage container where it cools, and the solidified glass is packaged and transported to a designated long-term storage site. Figure 4⁽³⁾ is a flow sheet summarizing each of the waste solidification methods.

SOLIDIFICATION CONDENSATES

The previous general discussion of solidification processes identified the four condensates to be encountered in the WSEP demonstration program. These are:

- Spray calciner condensate
- Pot calciner condensate
- Phosphate glass melter condensate
- Nitric acid fractionator condensate.

Both the spray and pot calciner condensates will be recycled to the waste evaporator because of low sulfate content. Phosphate glass melter condensate, on the other hand,

FIGURE 3. The Phosphate Glass Process

FIGURE 4. Waste Solidification Engineering Prototypes

contains nearly all of the sulfate from the feed and cannot be recycled. In addition, up to 10% of the ruthenium, about 0.1% of the remaining fission products, <5% of the nitric acid, and <1% of the phosphoric acid are contained in the phosphate glass melter condensate. Although the melter condensate was placed in the intermediate level waste category early in the waste solidification program, changes in the composition since have made it a high level waste more appropriately called a secondary waste. Detailed compositions of the glass melter condensate appear in the following section of this report.

The reason that essentially all of the sulfate is volatilized in the phosphate glass process is due to high melter temperature. The solubility of phosphate glass prepared in this manner is much lower than in the case where sulfates are incorporated in the phosphate melts at lower temperature.

The largest volume condensate arises from the nitric acid fractionator. This condensate contains low level fission product concentrations, principally ruthenium in a dilute nitric acid solution ($<0.1 \text{ M HNO}_3$). This condensate appears in all of the solidification alternatives.

OBJECTIVES

PROGRAM PLANS

The basic objective of this program was to identify and characterize the intermediate and low level radioactive wastes of concern in the WSEP program, and to recommend

treatment methods for these wastes for disposal and/or recycle. The term disposal connotes either direct discharge to the environment in conformance with the most rigorous safety standards, or long-term storage in a solid form with the same adherence to environmental protection considerations.

Initially, a survey of potential methods for treating these wastes was conducted.⁽⁷⁾ Over 20 separate techniques and variations were investigated as possible methods for treating the condensates. As expected, certain of the methods offered considerably more promise than others. As these methods were identified, the nature of the research shifted from a survey to a detailed study of the most promising schemes. Research became even more defined as the WSEP program progressed and data became available on waste stream characteristics.

The two-fold objective of this report is first to recommend the most effective alternatives for treating glass melter condensate so that full-level radioactive demonstrations can be implemented, and second to recommend the most effective method for treating nitric acid fractionator condensate.

Subsequent to the issuance of this report, research will continue on the optimization of the glass melter condensate treatment method selected for full-level demonstration. The most effective method for treating nitric acid fractionator condensate will also be demonstrated in the laboratory on actual condensate generated in WSEP hot runs.

DEGREE OF TREATMENT REQUIRED

Research on glass melter condensate has shown that all of the most promising alternative treatment methods will utilize asphalt incorporation of the final effluent stream. Research results have shown 15 gal/tonne as the minimum asphalt volume which can accomodate 60% solids. The following table (Table I) shows the decontamination factors required for radionuclides in the glass melter condensate with the allowable total dose to the asphalt as 10^8 rads.⁽⁸⁾ Note that the decontamination factors cited are based on the supposition that only one radionuclide will be incorporated in asphalt. In actual fact, mixtures of all the radionuclides in various concentrations will be found in the melter condensate.

The decontamination required for nitric acid fractionator condensate is somewhat more straight forward. The decontamination goal is MPC_w for a 168 hour week. Table II shows the MPC_w (168 hr/week) values for the principal radionuclides which could conceivably be detected in the acid fractionator condensate. A detailed estimate of decontamination required is not possible at this time because of variations in composition.

*TABLE I. Decontamination Factors Required for Glass
Melter Condensate Prior to Asphalt Incorporation*

Fission Product Isotope	Estimated Fission Products in Glass Melter Condensate,* Ci/tonne			Allowable Ci/gal of Asphalt for 10 ⁸ rads	Decontamination Factor Required for Incorporation in 15 gal/tonne Asphalt		
	Low	Med	High		Low	Med	High
¹⁰⁶ Ru	2.1 x 10 ³	4.2 x 10 ⁵	2.1 x 10 ⁴	9.0	15.5	31.1	155
¹³⁴ Cs	11.0	22.0	110	6.9	NR	NR	1.1
¹³⁷ Cs	8.0	16.0	80	0.87	NR	1.2	6.1
⁸⁹ Sr	0.5	1.0	5.0	175	NR	NR	NR
⁹⁰ Sr	6.0	12.0	60	0.45	NR	1.8	8.9
⁹⁰ Y	6.0	12.0	60	2.1 x 10 ³	NR	NR	NR
⁹¹ Sr	1.0	2.0	10	145	NR	NR	NR
¹⁴⁴ Ce	41.0	82.0	410	13.5	NR	NR	2.0
¹⁴⁷ Pm	11.0	22.0	110	84.2	NR	NR	NR
⁹⁵ Zr	3.0	6.0	30	86.7	NR	NR	NR
⁹⁵ Nb	6.0	12.0	60	346	NR	NR	NR

NR No decontamination required

* Based on processing of power reactor wastes

TABLE II. MPC_w (168/hr week) Values for Radionuclides
Which Could Occur in Acid Fractionator
Condensate

<u>Radionuclide</u>	MPC_w (168 hr/week)
	<u>$\mu\text{Ci}/\text{cm}^3$</u>
^{106}Ru	10^{-4}
^{134}Cs	9×10^{-5}
^{137}Cs	2×10^{-4}
^{89}Sr	10^{-4}
^{90}Sr	10^{-6}
^{90}Y	2×10^{-4}
^{91}Y	3×10^{-4}
^{144}Ce	10^{-4}
^{147}Pm	2×10^{-3}
^{95}Zr	6×10^{-4}
^{95}Nb	10^{-3}

SOLIDIFICATION CONDENSATE COMPOSITIONS

ACID FRACTIONATOR CONDENSATE

While initial laboratory experimentation at Brookhaven National Laboratory demonstrated the need for treatment of glass melter condensate, far less information was available on a second type of solidification condensate which could potentially require treatment - nitric acid fractionator condensate. This condensate is common to all three of the solidification processes. Figure 4 shows the location of the acid fractionator in the WSEP process flowsheet.

The approach used in this study was to plan for the contingency that acid fractionator condensate would not be sufficiently decontaminated to discharge to the environment. Initially, it was assumed that the acid fractionator condensate would contain about 0.1 M nitric acid and small concentrations of radionuclides. The goal for radioactivity in this condensate was set at MPC_w , 168 hr/week. Ruthenium-106 and strontium-90 were expected to be the radionuclides most likely to exceed their respective MPC values. Ruthenium would be present in greater concentrations than other radionuclides because of the volatility of ruthenium tetroxide, while strontium-90 has a low MPC value.

Ultimately, however, evidence of any required treatment was to be determined through analysis of the WSEP hot runs. The condensate from the hot runs did, in fact, show that some treatment was necessary. Total ruthenium concentrations in acid fractionator condensate for 8 WSEP hot runs are shown in Table III.⁽⁹⁾ The MPC_w for a 168 hr/week is $10^{-4} \mu\text{Ci}/\text{cm}^3$ for ^{106}Ru . Notice that 7 of the 8 hot runs exceeded this value.

TABLE III. *Total Ruthenium Concentrations in Acid Fractionator Condensate for WSEP Hot Runs*

<u>Run No.</u>	<u>Solidifier</u>	<u>Feed Type</u>	<u>Total Ru, $\mu\text{Ci}/\text{cm}^3$</u>
1	Pot Calcination	PW-2	$<4 \times 10^{-4}$
2	Spray Solidification	PW-1	6.4×10^{-3}
3	Pot Calcination	PW-2	5.2×10^{-2}
4	Pot Calcination	PW-2	2.8×10^{-3}
5	Spray Solidification	PW-1	1.8×10^{-2}
6	Pot Calcination	PW-1	1.0×10^{-2}
7	Pot Calcination	PW-1	4.0×10^{-1}
8	Pot Calcination	PW-2	8.4×10^{-3}

In the initial phases of research, it was convenient to use an acid condensate generated in the Purex process to simulate the expected nitric acid fractionator condensate. A typical composition of this waste is shown in Table IV. Because of the nature of the condensate stream, some variations can be expected. The composition cited, however, is fairly representative.

The major reason for the use of this particular waste at the outset of the research was due to the characteristics of the ruthenium in the waste. The ruthenium species were expected to closely match those in the nitric acid fractionator condensate.

Fortunately, as exploratory research reached the point where detailed experimentation was required, actual acid fractionator condensate from hot runs was available. This detailed research employed condensate from Run 6 (Pot Calcination) using PW-1 waste feed. The condensate contained 0.3 mole/liter of nitric acid, $1 \times 10^{-2} \mu\text{Ci}/\text{ml}$ of ^{106}Ru , and $6 \times 10^{-3} \mu\text{Ci}/\text{ml}$ of ^{144}Ce . The ^{90}Sr concentration was not measured.

TABLE IV. *Typical Composition for
Purex Acid Condensate**

<u>Radionuclide</u>	<u>Activity, $\mu\text{Ci}/\text{cm}^3$</u>
$^{103-106}\text{Ru}$	10^{-2}
$^{144}\text{CePr}$	10^{-3}
$^{95}\text{ZrNb}$	10^{-3}
^{137}Cs	10^{-4}
^{90}Sr	10^{-6}
<u>Chemical</u>	<u>Concentration</u>
HNO_3	10^{-2}M

* Based on processing of power reactor wastes

GLASS MELTER CONDENSATE

At the outset of the research program to investigate potential methods for treating glass melter condensates, certain observations and assumptions were made regarding the waste composition likely to be encountered. Assumptions were necessary because (1) the composition of glass melter condensate will vary according to the composition of the melter feed and operating conditions, and (2) radionuclide concentrations under actual plant conditions vary considerably.

It was recognized that glass melter condensate generated in the processing of Purex I (first cycle wastes) would not constitute a major problem since first cycle wastes do not contain sulfates. Hence, recycling of the nonsulfate-bearing condensate to the phosphate glass process headend would be possible.

On the other hand, Purex II (combined first and second cycle wastes) is sulfate bearing. The sulfate ion results from the use of ferrous sulfamate reductant in the second cycle of the Purex process. Greater than 98% of the sulfate ion is volatilized from the melter in the phosphate glass process and appears as H_2SO_4 in the glass melter condensate. The presence of a significant amount of H_2SO_4 in the condensate prevents recycle to the headend of the process because of a continual buildup of H_2SO_4 in the system. Recycle of H_2SO_4 would also adversely affect the integrity of phosphate glass.

Segregation of first and second cycle wastes or substitution of U^{+4} reductant in place of ferrous sulfamate are two possible methods of eliminating sulfate ion from the combined cycle wastes. The economic incentives for making any change must be evaluated by considering the overall waste management program.

Originally, the basis for the investigation of potential treatment methods was that the wastes, Purex II (PW-2), could be aged for one year for a burnup of 20,000 megawatt days per tonne (MWd/tonne). Table V shows a typical composition of Purex II wastes. ⁽⁶⁾

Based on preliminary research performed at Brookhaven National Laboratory, an expected glass melter composition was assumed. ⁽¹⁰⁾ Evolution of ruthenium was assumed as 2%, while fission product entrainment was assumed to be 0.1%. Chemically, the most significant constituents of the Purex II feed will be water, nitrate ion, nitrite ion, and sulfate ion. These constituents also comprise the bulk of the condensate. On this basis, projected Purex II waste composition contains 330 moles of sulfate and 2440 moles of nitrate-nitrite per 100 gal of waste per tonne of reactor fuel processed. The volume of PW-2 will be reduced by evaporation prior to being fed to the melter. Most of the nitrate and nitrite ions will be removed as HNO_3 during the concentration step.

TABLE V. *Molarity of Waste Compositions
for Purex II Wastes*

	<u>Molarity</u>
Element Cations	
Fe ⁺³	0.445
Cr ⁺²	0.024
Ni ⁺³	0.010
Al ⁺	0.001
Na ⁺⁶	0.930
U ⁺²	0.010
Hg ⁺²	0.001
Anions	
NO ₃ ⁻	6.44
SO ₄ ⁻²	0.870
PO ₄ ⁻³	0.006
SiO ₂	0.010
Fission Products	
Rb ⁺	0.0071
Cs ⁺	0.0345
Sr ⁺²	0.0155
Ba ⁺²	0.0195
Ce ⁺³	0.1185
Zr ⁺⁴	0.065
Mo ⁺⁶	0.065
Ag ⁺	0.0008
Cd ⁺²	0.0008
Te ⁺⁴	0.0064
Ru ⁺³	0.032
Rh ⁺³	0.0074
Pd ⁺²	0.0172
<hr/>	
Volume, gal per tonne U	100
Burnup, (MWd/tonne)	20,000
Heat, watts per liter:	
After 1 year of cooling	12.2
After 6 years of cooling	2.0
Activity, curies per liter	
After 1 year of cooling	2200

Simulated glass melter condensate solutions were formulated on the basis that all of the sulfate ion, 398 moles of nitrate-nitrite ion, and 13 moles of phosphate ion from the initial 100 gal of PW-2 were carried over from the melter and appeared as acids in the condensate. A total of either 20 or 35 gal of condensate per tonne of fuel was assumed. Table VI shows the concentration of acids in the two simulated solutions.

TABLE VI. *Concentrations of Acids in Simulated Glass Melter Condensate Solutions*

Acid	Solution I	Solution II
	<u>35 gal/tonne, moles/liter</u>	<u>20 gal/tonne, moles/liter</u>
H ₂ SO ₄	2.5	4.4
HNO ₃	3.0	5.3
H ₃ PO ₄	0.1	0.18

Appropriate amounts of metal salts contained in PW-2 were also added to Solution II (see Table VII) to simulate 0.1% entrainment and 2% ruthenium evolution. Initial laboratory experiments with Solution I were conducted on the assumption that the total radionuclide concentration of the condensate (1 yr fuel aging) was less than 5 Ci/gal. Estimates of the total radionuclide concentration were later revised upward as more realistic data became available on full-level, power reactor fuel reprocessing wastes (20,000 MWd/tonne).

As the WSEP program progressed further in the demonstration phase, it became evident that several adjustments would have to be made in the simulated condensate composition. First, the burnup originally assumed was raised to 30,000 MWd/tonne to account for subsequent advances in technology. Second, the use of steam injection in the phosphate glass process was reflected in larger condensate volumes and hence, lower concentrations of acid. Third, a volume of 60 gal of condensate per tonne of fuel was based on actual WSEP cold runs.

Thus, during the experimentation reported here, three variations of simulated glass melter condensate were employed. Fortunately, however, as the condensate composition became better defined, there was a corresponding change in the nature of the research--from a scouting study to rigorous research on selected processes.

Table VIII shows the concentrations of acids in the simulated glass melter condensate solution which is presently regarded as the most representative of those likely to be found in future WSEP hot runs of the phosphate glass process, as well as in the full-scale implementation of the process. For the sake of continuity, this solution shall be referred to as Solution III. Note that the appropriate amounts of metal salts were also added to this solution to simulate 0.1% entrainment and 10% ruthenium volatilization. Table VII lists the metal salts used in the various simulated solutions.

TABLE VII. *Metal Salt Concentrations in Simulated Glass Melter Condensate*

<u>Metal Salt</u>	<u>Solution II,⁻⁵ molarity x 10⁻⁵</u>	<u>Solution III,⁵ molarity x 10⁻⁵</u>
Fe ⁺³	223	74
Cr ⁺³	12	4
Ni ⁺³	5	2
Ru ⁺³	164	275
Zr ⁺⁴	11	4
Cs ⁺	13	4
Sr ⁺²	3	1
Ba ⁺²	3	1.7
La ⁺³	7	2.3
Ce ⁺³	5	1.7
Nd ⁺³	7	2.3
Rb ⁺	1	0.3
Mo ⁺⁶	20	6.7
Y ⁺³	trace	trace

TABLE VIII. *Concentration of Acids in Solution III, Simulated Glass Melter Condensate*

<u>Acid</u>	<u>Moles/Liter</u>
H ₂ SO ₄	1.4
HNO ₃	0.7
H ₃ PO ₄	0.08

In certain cases, ruthenium tracer and a portion of the ruthenium carrier were treated to simulate the complex forms of ruthenium expected to be present in both the acid fractionator and glass melter condensate. Ruthenium-106 tracer was distilled from a solution of 1 + 1 HNO_3 sparged with ozone during boiling. The vaporized ruthenium was condensed in an air cooled condenser and collected in a dilute HNO_3 solution. Stable RuCl_3 was also treated in this manner for use as a carrier in the simulated condensate. About 25% of the ruthenium carrier in Solution III was distilled from HNO_3 solution. The remaining portion of carrier ruthenium was stable RuCl_3 . All Solution III-simulated condensate was of this stable ruthenium composition.

Based on most recent information, a range of fission product concentrations in glass melter condensate was estimated.⁽¹¹⁾ These estimates are reported in Table V. Therefore, Solution III compositions shown in Tables VII and VIII, in conjunction with the radionuclide concentrations in Table IX, represent the best available estimated composition at the time of this report.

Because three variations of simulated glass melter condensate were used throughout the experimentation, it is appropriate to cite which experiments were conducted with a given simulated condensate solution. Therefore, Table X lists the general methods investigated and the simulated solutions used to perform the experiments for each of the methods.

TABLE IX. Fission Product Concentrations in Glass Melter Condensate*
(Full aged one year and 60 gal condensate/tonne fuel)

Fission Product Isotope	Half-Life	Total Curies/ Tonne in Spent Fuel	Estimated DF Melter to Condensate			Estimated Fission Products in Melter Condensate, Ci/tonne			Estimated Fission Product Concentrations in Melter Condensate Ci/gal		
			Low	Med	High	Low	Med	High	Low	Med	High
^{106}Ru	1.0 y	2.1×10^5	10	50	100	2.1×10^3	4.2×10^3	2.1×10^4	35	70	350
^{134}Cs	2.2 y	1.1×10^5	10^3	5×10^3	10^4	11.0	22.0	110	0.19	0.37	1.9
^{137}Cs	30 y	0.8×10^5	10^3	5×10^3	10^4	8.0	16.0	80	0.14	0.27	1.4
^{89}Sr	51 d	0.05×10^5	10^3	5×10^3	10^4	0.5	1.0	5.0	0.009	0.017	0.09
^{90}Sr	28 y	0.6×10^5	10^3	5×10^3	10^4	6.0	12.0	60	0.10	0.20	1.0
^{90}Y	58 d	0.1×10^5	10^3	5×10^3	10^4	1.0	2.0	10	0.017	0.033	0.17
^{144}Ce	258 d	4.1×10^5	10^3	5×10^3	10^4	41.0	82.0	410	0.69	1.37	6.9
^{147}Pm	2.6 y	1.1×10^5	10^3	5×10^3	10^4	11.0	22.0	110	0.19	0.37	1.9
^{95}Zr	65 d	0.3×10^5	10^3	5×10^3	10^4	3.0	6.0	30	0.05	0.10	0.5
^{95}Nb	35 d	0.6×10^5	10^3	5×10^3	10^4	6.0	12.0	60	0.10	0.20	1.0

* Based on processing of power reactor wastes

TABLE X. *Simulated Glass Melter Condensates Used
in Experiments on Various Treatment Methods*

<u>Method</u>	<u>Solution Used</u>
Ion Exchange	I
Sulfate Reduction	II
Sodium Sulfate Crystallization	II
Sulfate Precipitation	I, III
Scavenging	II, III
Ruthenium Volatilization	III
Distillation*	I
Sulfate Melts	II
Plaster and Cement-like Materials	I, II, III
Asphalt Incorporation	II, III

* Research on this method is being performed at
Brookhaven National Laboratory.

EXPERIMENTAL RESULTS

ACID FRACTIONATOR CONDENSATE

Tritium Problems

Quantities

The tritium problem in waste solidification condensate disposal is not clearly defined. Most of the fission product tritium presently is disposed of via the Purex process condensate stream. Only a small portion (2-5%) is retained in the concentrated Purex acid waste⁽¹²⁾. However, if internal recycling of process condensates is practiced, the bulk of the tritium may appear in the Purex acid waste.

Tritium is a low yield fission product produced in the ratio of one tritium atom to $1-2 \times 10^4$ fissions of ^{235}U ,^(13,14) equivalent to about 400 curies of tritium per tonne of fuel at the 30,000 MWd/tonne burnup level. If 5% of the total tritium per tonne of fuel is contained in 100 gallons of Purex acid waste, the tritium concentration will be 0.2 Ci/gal. The tritium will appear in aqueous condensate streams of the waste solidification processes. If, for example, 200 gal of condensate were produced per tonne of fuel in the waste solidification process, the tritium concentration in the condensate would be $30 \mu\text{Ci}/\text{cm}^3$. Since this concentration is 10^3 times greater than MPC_w for tritium, disposal to the environs may be a problem.

Remedial Measures

Tritium removal from aqueous wastes cannot be carried out by conventional chemical or physical means. Although removal by isotopic separation is possible, the cost of these methods would appear to be too high for waste treatment application. Ideally, removal of the tritium from spent fuel elements prior to dissolution in aqueous solutions would permit concentration of the tritium into a small volume possibly by vacuum outgassing

of the spent fuel elements at elevated temperature after dejacketing. The tritium could then be stored in a small volume of solid hydrate. Headend removal of tritium from spent fuels needs further study.

Dilution and dispersal of tritium is currently practiced under controlled conditions at the Nuclear Fuels Services reprocessing plant at West Valley, New York.⁽¹⁵⁾ This approach is usually regarded with disfavor when applied to other radionuclides. However, isotopic dilution of tritium with hydrogen to a concentration below the MPC_w for tritium is readily accomplished if sufficient dilution water is available. There is practically no chance that the tritium can be concentrated by natural processes once it has been isotopically diluted to a safe level. Disposal of the tritium to the atmosphere is a possibility where insufficient ground or surface water is available for dilution. Adequate mixing with air and water vapor must be assured to prevent condensation of water vapor in which the tritium has not been sufficiently diluted. Dispersal of large quantities of tritium to the environs should be thoroughly studied before it is practiced.

Deep well injection of tritium bearing wastes into suitable geologic formations is another possible disposal method. Assurance that the wastes will remain in the formation long enough for decay of the tritium to safe levels is required. This usually requires a thorough study of the geology of a location which includes the drilling of a number of expensive exploratory and monitoring wells.

Treatment Methods

Adsorption

Previous research at this laboratory has shown that several types of adsorbents hold promise for removing radioruthenium from aqueous solution.⁽¹⁶⁾ Two such adsorbents were selected for study to determine possible application in the treatment of acid fractionator condensate. These adsorbents were pyrolusite (MnO_2)

and activated carbon. The pyrolusite was selected because of its demonstrated ability to adsorb cationic ruthenium species, and activated carbon for its ability to remove nonionic species.

Initial experiments were undertaken to determine the optimum range of pH for adsorption. Greatest adsorption was found to occur in the pH range 4.5 to 8.0 for both sorbents. The actual optimum value always fell within this range. The precise value, however, was dependent upon the type of waste and the species found within it.

Two waste solutions employed in these experiments were: (1) purex acid condensate, and (2) a synthetic condensate formed by volatilization of ruthenium into nitric acid. The compositions of both of these waste solutions are described in detail in the section on "Solidification Condensate Compositions."

The results of experiments in which the waste solutions were passed through pyrolusite columns are reported in Figure 5. Note that the removal of ruthenium was much greater for the synthetic waste solution. Greater removals were probably due to the fact that more cationic species were present than in the slightly aged Purex condensate. Although this method appears to be promising for decontaminating acid fractionator condensate where decontamination factors of less than 100 are required, the use of pyrolusite alone may not be sufficient in some cases. Hence, activated carbon adsorption was used subsequent to pyrolusite adsorption. Figure 6 shows the removals attained by this technique. Despite the quite promising outlook for the series use of pyrolusite and activated carbon, experimental data available are insufficient to support firm recommendations. It is suggested, however, that this method be explored further for potential application later in the WSEP program.

FIGURE 5. *Pyrolusite Adsorption of Ruthenium-106*

FIGURE 6. *Activated Carbon Adsorption of Ruthenium-106 (after pyrolusite adsorption)*

Electrodialysis and Electrodeionization

Ion transport through permeable membranes under the influence of an applied electric field is referred to as electrodialysis. This process is used commercially to reduce the salt content of natural waters. Electrodialysis operating efficiency at low electrolyte concentrations falls off rapidly due to high solution resistances and membrane polarization. Strongly ionized ion exchange resins, when placed in the electrodialysis compartments, can overcome the high solution resistance by serving as an ion conduction medium. This technique is referred to as electrodeionization.

The removal of ruthenium from intermediate level wastes by electrodialysis processes has been studied by Coleman and Eliason.⁽¹⁶⁾ Electrodialysis was demonstrated capable of removing ruthenium from dilute nitric acid wastes, but removal of more than 90% of the ruthenium by this method has not been considered economical. Ruthenium DF's* of 20 were reported by electrodeionization, with as high as 50-fold volume reductions. Although greater DF's are attainable by electrodeionization, equipment fabrication and maintenance problems are expected to be greater than those for electrodialysis. Both methods offer the distinct advantage of nitrate ion removal. The nitrate ion can be recycled to the waste solidification process in the concentrate stream along with the ruthenium and other radionuclides. The recommended drinking water limit for nitrate ion is 45 mg/l NO_3^- . A 0.1M HNO_3 solution contains 6200 mg/l NO_3^- .

Laboratory studies were conducted to determine the effectiveness of electrodialysis and ion exchange for removing ruthenium and nitric acid from WSEP fractionator condensate. The condensate

* Decontamination factor (DF) = $\frac{\text{Activity influent}}{\text{Activity effluent}}$.

obtained for these studies contained 0.03 moles/liter nitric acid and 1×10^{-2} $\mu\text{Ci/ml}$ of ^{106}Ru . The condensate was pumped through an electrodialysis stack pack at a flow rate of 1 liter/min. The stack pack contained 20 cell pairs with 220 cm^2 of membrane surface area. The current through the stack pack was 3.5 A and the diluate to concentrate ratio was 10:1. About half of the ruthenium and 93% of the nitric acid was removed from the diluate stream. The diluate was recycled through the stack pack to simulate a second stage. The current was limited to 0.6 A with the recycled diluate because of the low concentration of electrolyte (HNO_3) remaining. The overall nitric acid and ^{106}Ru DF's for the two stages were 128 and 5.5 respectively. Although ruthenium removal by electrodialysis is limited, the removal of most of the nitric acid facilitates final cleanup of the condensate by ion exchange. The treatment of electrodialysis diluate by ion exchange is discussed in the next section.

Ion Exchange

Previous studies on decontamination of radioactive condensate wastes by ion exchange have shown the capacity of anion exchange resins for removing trace ruthenium to be dependent on the concentration of anions such as NO_3^- and Cl^- in solution.^(17,18) Ruthenium breakthrough in the effluent coincides with the breakthrough of NO_3^- or Cl^- . Since the projected nitric acid concentration in acid fractionator condensate is 0.1M, the volume of condensate required to exhaust an anion exchange column is low (10-20 column volumes). Regeneration of the column would create a large waste volume relative to the condensate volume processed. However, laboratory studies show that ion exchange treatment of acid fractionator condensate will be useful if the acid concentration can be reduced either by process alterations or by a method such as electrodialysis.

Experiments were performed to evaluate the effectiveness of ion exchange for removing ruthenium from WSEP acid fractionator condensate. The condensate was pumped through a cation exchange column in series with an anion exchange column. The cation column serves to remove cationic radionuclides and other ions such as Fe^{+3} which might foul an anion column. The anion column serves to remove anionic species of ruthenium and NO_3^- . Figure 7 shows ^{106}Ru breakthrough curves for a column of Dowex 50 in the H^+ form, and a column of Dowex 1x 8, OH^- form. The pH curve of the Dowex 1 column effluent is also included to indicate H^+ breakthrough or exhaustion of the anion exchange resin. The ^{106}Ru begins to break through at about the

FIGURE 7. ^{106}Ru and Acid Breakthrough for Dowex 50 and Dowex 1 Resin Columns.

same point that the pH begins to decrease. The ^{106}Ru C/Co* of the Dowex 1 column effluent rises above that of the Dowex 50 column because a part of the ^{106}Ru loaded on the Dowex 1 resin is eluted as the NO_3^- breakthrough front proceeds down the column.

The Dowex 1 resin column was regenerated with 4% NaOH and a second run made with the same acid fractionator condensate. The percent ^{106}Ru eluted, versus the volume of 4% NaOH used, is shown in Figure 8. Forty percent of the ^{106}Ru was not removed by regeneration with the 4% NaOH. Ruthenium breakthrough for the second run is shown in Figure 9. Detection breakthrough of ^{106}Ru occurred at 20-column volumes with the regenerated column, as opposed to 26-column volumes with fresh Dowex 1. This difference may be attributed to low initial ^{106}Ru concentration in the feed (Dowex 50 effluent) to the Dowex 1 column in the first run.

Ruthenium and acid breakthrough for a weak base anion exchange resin (Amberlite IRA-93) is illustrated in Figure 10. The volume of acid fractionator condensate put through the weak base resin column to ^{106}Ru and acid breakthrough is greater than that of the strong base resin due to the greater ion exchange capacity of the former. Weak base resins are regenerated more efficiently than strong base resins. No data, however, are available on elution of ruthenium by regeneration with base.

Removal of ^{106}Ru from the diluate stream of the electrodialysis experiments reported in the previous section are illustrated in Figure 11. A total ^{106}Ru DF of 100 or more was attained through 130-column volumes from a Dowex 1 column. The main advantages of this system are (1) the bulk of the nitrate ion is recycled to the waste solidification process as a nitric acid which is compatible with the influent waste stream, and (2) the amount of caustic regenerent used is significantly reduced below that for ion exchange alone.

* $\text{C/Co} = \frac{\text{Effluent concentration}}{\text{Influent concentration}}$

FIGURE 8. ^{106}Ru Elution Curve for Dowex 1 Resin Column

FIGURE 9. ^{106}Ru Breakthrough for a Regenerated Dowex 1 Column

FIGURE 10. ¹⁰⁶Ru Breakthrough for an Amberlite IRA-93 Resin Column

FIGURE 11. ¹⁰⁶Ru Breakthrough for Dowex 1 Column and Electrodialysis Cell Diluate

Oxidation and Volatilization of Ruthenium

Removal of ruthenium from solutions may be accomplished by oxidizing the ruthenium to its tetroxide and volatilizing it by simultaneous heating and gas sparging. This method was successfully used in the Redox Process for uranium, plutonium, and neptunium product solutions. The ruthenium was removed from these solutions by sparging with air containing ozone. Ruthenium DF's of about 100 were obtained in uranium nitrate solutions during an 8 hr sparge with 1% O_3 in air. A small amount of periodic acid was added to aid the removal of the ruthenium. (19)

Simulated acid fractionator condensate was prepared by volatilizing ^{106}Ru tracer from an acid permanganate solution into 0.1M HNO_3 . The ^{106}Ru concentration in the 0.1M HNO_3 was 4×10^{-3} $\mu Ci/ml$. Oxidation-volatilization experiments were conducted in a heated 1.25 in. diameter glass pipe 3 ft high. Six hundred ml of simulated acid fractionator condensate was placed in the pipe for oxidation by either $KMnO_4$ or O_3 . The permanganate solutions were sparged with air at 90 °C to remove the ^{106}Ru . Ozone was added via the air sparge. An electrical discharge ozone generator was used to produce 1.4% ozone in the sparge air. The off-gas was vented to a caustic scrubber. Material balances for ^{106}Ru to the scrubber were usually very low due to the tendency of the ^{106}Ru to adsorb on the surfaces of the tubing leading to the scrubber.

The effect of $KMnO_4$ concentration on ruthenium removal from simulated acid fractionator condensate is shown in Figure 12. The amount of permanganate required is quite small. Oxidation with permanganate suffers the disadvantage of producing particles of MnO_2 which are contaminated with ^{106}Ru .

The effect of sparging rate with 1.4% O_3 in air is shown in Figure 13. The initial ^{106}Ru removal is low compared to permanganate oxidation. The addition of an oxidant such as periodic

FIGURE 12. Effect of KMnO₄ Concentration on ¹⁰⁶Ruthenium Removal

FIGURE 13. Effect of Sparge Rate on ¹⁰⁶Ruthenium Removal with Ozone

acid should increase this initial removal rate; however, this was not investigated. Reduction of the HNO_3 concentration of the simulated acid fractionator condensate did not appreciably affect the ^{106}Ru removal.

GLASS MELTER CONDENSATE

Separation of Sulfates

Ion Exchange

Although separation of sulfate from glass melter condensate by ion exchange was investigated, laboratory results were not promising. A weak base anion resin, selected for low cost regeneration, showed a preference for nitrate ion over sulfate ion. Twenty-five ml of simulated glass melter condensate (Solution I) was fed to a 45-cm³ column (1 cm diam) of Nalcite WRB exchange resin in the free base form at a flow rate of 270 ml/hr. The feed was followed by 116 ml of water at the same flow rate and direction in order to wash unadsorbed ions from the resin bed. The bed was eluted (reverse-flow) with 90 ml of 10% NaOH followed by 36 ml of water. Figure 14 shows breakthrough curves for SO_4^- and NO_3^- during the loading and elution cycles. Most of the sulfate appeared in the loading effluent, whereas most of the nitrate was retained by the resin. Although anion resins are generally selective for sulfate ion over nitrate ion in dilute solutions, the results indicate a selectivity reversal because of the relatively high concentrations of nitrate and sulfate ions. A large dilution, although apparently necessary to attain the desired sulfate ion selectivity, would introduce a new problem in the large volume of diluted effluent which must then be recycled or disposed of in some manner.

Separation of most of the sulfate ion from the bulk of the nitrate ion was accomplished in the ion exchange experiment, but it should be noted that the cationic fission product activity such as ^{137}Cs and ^{85}Sr will remain with the sulfate in the loading effluent. Additional treatment then would be necessary to separate the sulfate ion from cationic fission products.

FIGURE 14, SO_4^{2-} and NO_3^- Breakthrough Curves During Loading and Elution Cycles

Sulfate Reduction

Several methods are available for reducing sulfuric acid or sulfur trioxide to sulfur dioxide. The main advantage to this reaction is the production of a gas (SO_2) which may be scrubbed and filtered to remove residual radioactivity and vented to the atmosphere. Although the amount of SO_2 produced by processing waste from a 1 tonne/day plant is relatively small (330 moles SO_2), recent trends in reducing atmospheric pollution cast some doubt upon this disposal method. An alternative method might be to adsorb the SO_2 in a caustic scrubber and dispose of the sodium sulfite formed.

A gas phase reaction of SO_3 and CO was initially proposed as a method of reducing SO_3 to SO_2 . However, the safety aspects of this reaction have been questioned. A possible explosion hazard in its use must be thoroughly investigated before implementing this method.

Sulfur and carbon will reduce H_2SO_4 when the acid is concentrated and heated near its boiling point at atmospheric pressure. Reduction by carbon was selected for study because the amount of SO_2 produced is less than that produced by reduction with sulfur. The reactions involved are illustrated below:

Two experiments were conducted to determine the amount of SO_2 produced by the reduction of the H_2SO_4 contained in 300 ml of Solution II. In the first experiment the sulfuric acid was concentrated by boiling off the HNO_3 and H_2O . Then 17 g of powdered charcoal, sufficient carbon for reaction (1), was

added and the mixture refluxed for 1 1/2 hr in an air-cooled condenser which allowed water vapor to pass but condensed H_2SO_4 back to the reaction flask. Vapors from the air-cooled condenser were routed through a water-cooled condenser and trapped to remove water vapor. Finally the stream passed through a caustic scrubber to remove SO_2 . The scrubber solution (3 liters) was composed of 1M NaOH with 2 g/liter sucrose to stabilize the Na_2SO_3 formed. Sulfite ion concentration in the scrubber was determined by adding aliquots to a measured excess of standard iodine solution and the excess iodine titrated with standard thiosulfate. In the first experiment, the scrubber contained 0.75 moles of $\text{SO}_3^{=}$, equivalent to 57% of the total H_2SO_4 used.

In the second sulfate reduction experiment, 20 g of powdered charcoal was added directly to 300 ml of Solution II without prior evaporation of HNO_3 and H_2O . The contents of the flask were heated gently for 4 hr to remove nitric oxides and water. The H_2SO_4 was refluxed as in the first experiment after removal of nitrogen oxides and water. The scrubber in the second experiment contained an amount of $\text{SO}_3^{=}$ equivalent to 45% of the total H_2SO_4 used.

The removal of nitric acid by evaporation at atmospheric pressure prior to reduction of sulfuric acid is expected to result in rather severe corrosion problems. The reduction of nitric acid, as in the preceding second experiment, might overcome the corrosion problem to some extent because of the lower operating temperature. The use of sugar to reduce both the nitric acid and sulfuric acid was considered inasmuch as a sugar solution may be transferred to the reaction vessel more easily than powdered carbon. The use of sugar, however, creates a possible explosion hazard since the high concentration of sulfuric acid along with the nitric acid may lead to the nitration of the sugar.

Although the reduction of sulfuric acid in glass melter condensate by elemental carbon or sulfur may be accomplished

safely, a probable hazard still remains when the residue of the reaction is recycled to the phosphate glass process. Unless the carbon or sulfur has been completely consumed in the sulfate reduction reaction, a violent explosion could occur in the melter when the carbon or sulfur is heated to high temperatures in the presence of nitrates. It is difficult to visualize a method which would absolutely prevent recycle of unreacted carbon or sulfur back to the melter. This problem may be solved by the use of a gaseous reductant (i.e., CO) to react with liquid H_2SO_4 . The use of CO in this manner has not been investigated.

Sodium Sulfate Crystallization

Crystallization of a soluble sulfate salt is an alternate method of precipitation of an insoluble sulfate compound. A possible advantage of crystallization would be formation of readily filterable crystals relatively free of fission products. The process visualized would involve (1) addition of a reagent such as NaOH to the melter condensate, (2) crystallization of the sulfate salt by chilling or evaporation, (3) separation and recycle of the supernatant liquor with most of the fission product activity to the phosphate glass process, and (4) incorporation of the sodium sulfate in asphalt for final disposal.

Low Temperature Crystallization. Initial experiments with Solution I and stoichiometric addition of NaOH to react with the sulfuric acid showed 63 to 71% removal of sulfate as sodium sulfate crystallized at 0°C . Analysis of radioactive tracers in Solution I showed 4, 5, 7, 7, and 9% of the ^{134}Cs , ^{106}Ru , ^{85}Sr , ^{95}Zr , and ^{144}Ce , respectively, associated with vacuum-filtered sodium sulfate crystals. Washing the crystals reduced the ^{134}Cs and ^{85}Sr activity to less than 1.5%. The vacuum filtered crystals had a water content about equal to the heptahydrate of sodium sulfate when either oven dried or when dried by pulling air through the crystals on the filter for 20 min.

Most of the experimental work on sodium sulfate crystallization was carried out with Solution II (with radioactive tracers) which should yield more accurate results than Solution I. The procedure for crystallization and filtration was the same for all experiments. One hundred ml of Solution II in a beaker was placed in a dry ice acetone bath and a 50% NaOH solution was added dropwise from a burette to the desired neutralization level. After the mixture was cooled to the desired temperature, the crystals were separated by vacuum filtration on Whatman #40 filter paper. Washes were pulled through the crystals by vacuum. Aliquots of the dissolved crystals and filtrate plus washes were analyzed for radioactive tracers by gamma counting. Sulfate was determined gravimetrically as BaSO_4 .

Sodium sulfate crystallization did not occur in initial experiments with Solution II where a stoichiometric quantity of NaOH was added to react with the H_2SO_4 only, and the resulting solution cooled to 0 °C. Although crystallization occurred under the same conditions with Solution I it is believed that the higher concentration of HNO_3 in Solution II prevented crystallization. Without nitric acid present, the sodium sulfate crystallization was 96% at 0 °C. Figure 15 shows the effect of percent crystallization of sulfate from Solution II at crystallization temperatures of 0 to -10 °C. The crystals were not washed in this set of experiments.

Table XI summarizes the percent of the radioactive tracers associated with sodium sulfate crystallized at low temperature and washed with water.

Good separation of sulfate from fission products with a single crystallization of sodium sulfate at low temperatures can be anticipated for actual glass melter condensate. No attempt was made to determine further separation by repeated crystallizations. Increasing the wash volume to 200 ml of water at 0 °C did not significantly reduce the radioactivity of the crystals.

FIGURE 15. Effect of Percent Neutralization with NaOH on the Percent Sulfate Crystallized at 0° and -10 °C

TABLE XI. *Percent of Radioactive Tracers Associated with Sodium Sulfate Crystallized at Low Temperatures*

Total Acid Neutralized with NaOH, %	Crystallization Temperature, °C	Volume of Water Wash, ml	Temperature of Water Wash, °C	SO ₄ in Crystals, %	Total Radioactive Tracer Associated with Crystals, %			
					<u>⁸⁵Sr</u>	<u>¹⁰⁶Ru</u>	<u>¹³⁷Cs</u>	<u>¹⁴⁴Ce</u>
88	-10	100	12	78	2.4	2.4	2.8	3.6
88	-10	100	0	87	2.2	2.6	1.5	2.1
88	-10	200	0	76	1.8	--	1.6	1.2
88	0	100	0	82	3.3	2.8	0.7	1.8
93	0	100	0	88	2.7	2.3	2.0	3.2
95	-10	100	0	90	4.5	2.9	0.2	2.9
95	0	100	0	88	2.5	2.5	2.9	5.6

However, the amount of sodium sulfate dissolved from the crystals increased from about 3% with 100 ml of water wash to about 14% with 200 ml of water wash (crystallization at -10°C in both cases).

A major drawback to the low temperature crystallization of sodium sulfate is the amount of Na^{+} recycled with the supernatant liquor. Recycled liquor from crystallizations at -10°C will increase the Na^{+} in the phosphate glass feed by more than 100%. The degree of neutralization above the H_2SO_4 stoichiometric requirement does not significantly affect the amount of recycled Na^{+} .

In addition to this problem, the amount of decontamination effected even in the optimum case may not be sufficient to allow incorporation of the sodium sulfate into asphalt.

Consideration was given to the use of alum salts to separate sulfate from the glass melter condensate by crystallization. This method was rejected because cesium alum will crystallize with such other alums as potassium or ammonium alum.

High Temperature Crystallization. Crystallization of sodium sulfate (nonhydrated) by evaporation at boiling ($>100^{\circ}\text{C}$) was investigated but did not appear promising because of poor separation of radiostrontium from the crystals. Two hundred and twenty ml of Solution II was 70% neutralized with 18M NaOH to yield 365 ml of solution which was traced with ^{85}Sr . Fifty milliliter batches of the neutralized solution were evaporated to 25 ml and the sodium sulfate crystals filtered and washed with 50 ml of the neutralized solution. Evaporation to 25 ml yielded a thick slurry largely occupied by Na_2SO_4 crystals. The filtrate and wash were combined with the remaining neutralized solution. Seven crystallizations were completed after which 50 ml of solution remained from the original 365 ml. Forty-six percent of the original ^{85}Sr tracer was found in the remaining solutions. The crystals retained 54% of the ^{85}Sr tracer.

The foregoing procedure was repeated with the following changes: (1) 100 ml of 70% neutralized solution was evaporated to 45 ml; and (2) a 25 ml water wash was substituted for the neutralized solution wash in (1). After 8 crystallizations, 50 ml of solution containing only 30% of the total ^{85}Sr tracer remained. The crystals retained 70% of the tracer.

Since evaporation to a thick slurry is believed to have caused high retention of ^{85}Sr tracer by the sodium sulfate crystals, a further experiment was conducted to measure strontium retention by crystallization of a small fraction of the sodium sulfate with continuous removal of the crystals. In this case, 48 ml of 18M NaOH was added to 100 ml of Solution II (60% neutralization) to facilitate sulfate crystallization. Fifty-eight percent of the nitric acid was removed by evaporation to a thick slurry with water addition to maintain the slurry. The sodium sulfate crystals were then dissolved and the solution re-evaporated until 10 to 15% of the sodium sulfate crystallized. The crystals were removed by filtration and washed with 1 to 2 ml of water. These steps, repeated 5 times, separated 53% of the sulfate. Twenty-one percent of the total ^{85}Sr was found associated with the separated sodium sulfate crystals. The results clearly show that high temperature crystallization of sodium sulfate will not attain a high level of strontium removal.

Sulfate Precipitation

Because the sulfates of barium, calcium, and lead are rather insoluble in acid solutions, each was regarded as a possible precipitate for sulfate removal from glass melter condensate. Table XII shows solubility data for each of these sulfates.

TABLE XII. *Sulfate Precipitate Solubility Data* (20)

<u>Precipitate</u>	<u>Solubility, g/100 ml</u>	<u>Temperature, °C</u>
BaSO ₄	0.000222	18
	0.000336	50
CaSO ₄ (anhydrite)	0.209	30
	0.162	100
CaSO ₄ ·1/2H ₂ O (plaster of paris)	0.3	20
	slightly soluble	hot water
CaSO ₄ ·2H ₂ O (gypsum)	0.24	0
	0.222	100
PbSO ₄	0.00425	25
	0.0056	40
PbSO ₄ ·PbO	0.0044	0
	very slightly soluble	hot water

The precipitation process envisioned would involve precipitation, separation of the precipitate by centrifugation, rinsing of the precipitate to remove additional activity, and drying and packaging of the precipitate in a suitable storage container, or storage in asphalt or cement. Figure 16 shows a potential sulfate precipitation treatment scheme. Nitric acid, phosphoric acid, and a portion of the radionuclides in the supernatant liquid and rinse water would be returned to the headend of the phosphate glass process.

Experimentation showed that the calcium sulfate precipitates formed from Solution I behaved quite differently than the sulfates of barium and lead or any of the sulfate precipitates from Solution III. Hence, Solution I calcium sulfate precipitates will be discussed separately under the subsection dealing with conversion of plaster and cement-like materials to solid forms.

Solution I Sulfates. Stoichiometric amounts of Ba(OH)₂ and PbO were added to the simulated glass melter condensate in order to effect complete reaction with the sulfate present in the waste. The products of these reactions were identified by X-ray diffraction as BaSO₄ and PbSO₄, respectively. Both precipitates were filterable only with extreme difficulty.

FIGURE 16. Sulfate Precipitation Treatment Scheme

However, they were readily separated by centrifugation. Precipitation of BaSO_4 , using Ba(OH)_2 as the reactant, effectively removed 99.4% of the sulfate from solution. When PbO was used as the reactant for precipitation of PbSO_4 , 98.5% of the sulfate was removed from solution.

The volumes and densities of the precipitated sulfates are reported in Table XIII.

TABLE XIII. Volume and Density of Precipitated Sulfates - Solution I

Reactant, Stoichiometric	Volume of Precipitate/100 ml Waste, ml				Density of Pre- cipitate, g/cm ³	
	After Settling 1 hr	After Centri- fugation	Dried 100°C	Dried 1000°C	100°C	1000°C
Ba(OH)_2	31	17	35	40	1.7	1.4
PbO	23	20	10	7	7.3	8.0

Each of these reactions results in a violent release of gas with a concomitant evolution of heat. Thus, care must be exercised in maintaining proper safety conditions. Upon cooling, crystals form in the BaSO_4 solution, but crystallization was not apparent in the PbSO_4 solution.

Experimentation was undertaken to determine the relative distribution of the major radionuclides of concern in these sulfate precipitate systems. The radionuclides used were ^{106}Ru , ^{137}Cs , and ^{85}Sr . Ruthenium was selected because of the rather high concentration of this nuclide in the condensate. Cesium and strontium were chosen because of their contribution to a long-term total integrated dose during ultimate storage. Table XIV shows the relative distributions of each of the radionuclides in the precipitate. Each radionuclide was added separately to simulated condensate prior to precipitation.

TABLE XIV. *Radionuclide Carrying by Sulfate Precipitates - Solution I*

<u>Precipitate</u>	<u>Percent Retained in Solid</u>		
	<u>^{106}Ru</u>	<u>^{137}Cs</u>	<u>^{85}Sr</u>
BaSO_4	31	42	90
PbSO_4	60	31	90

As expected, the ^{85}Sr experiments were quite reproducible. However, ^{106}Ru and ^{137}Cs carrying varied with the rate of reaction, while ^{106}Ru varied the most. The ruthenium results were variable by as much as $\pm 10\%$.

Solution III Sulfates. Experimentation with the 60 gal/tonne condensate proceeded in much the same manner as that outlined for the Solution I case. Barium, calcium, and lead sulfates were produced by reacting stoichiometric quantities of $\text{Ba}(\text{OH})_2$, CaCO_3 , or PbO with the sulfate present in the simulated melter condensate. All of the precipitates exhibited poor settling characteristics but were easily centrifuged. The violent release of gas noted in the Solution I reaction with $\text{Ba}(\text{OH})_2$ and PbO was not evident in this case. However, the CaCO_3 reaction with Solution III was accompanied by a violent evolution of CO_2 . Each precipitation reaction resulted in a large volume of solid material as can be seen from inspection of Table XV. Upon centrifugation, all of the precipitates formed a sticky paste which was extremely difficult to handle in later operations.

TABLE XV. *Volume of Sulfate Precipitates - Solution III*

<u>Precipitate</u>	<u>Volume of Precipitate/100 ml Condensate, ml</u>		
	<u>Settled Volume, 1 hr</u>	<u>Settled Volume, 7 days</u>	<u>Centrifuged Volume</u>
BaSO_4	125	70	38
CaSO_4	125	100	54
PbSO_4	70	70	26

Radionuclide distribution studies were conducted with ^{85}Sr , ^{95}Zr , ^{106}Ru , ^{137}Cs , and ^{144}Ce . Preliminary investigations designed to determine the degree of ruthenium retention by the three precipitates indicated that CaSO_4 retained 7-25% of the initial Ru; BaSO_4 , 10-13% and PbSO_4 , 8-10%. Thereafter, major emphasis was placed on the BaSO_4 precipitate since it had volume advantages, a faster reaction time, and somewhat better handling characteristics than the CaSO_4 precipitate. Lead sulfate was abandoned because of the possibility of some lead finding its way to the platinum melter. It was suggested⁽²¹⁾ that there was a potential for damaging a reaction between the platinum of the melter and the lead.

Subsequent work revealed ruthenium retention by BaSO_4 to be as high as 40%. However, these high values were obtained in experiments using aged (4 months) ruthenium. It is believed that the increased ruthenium levels in the precipitate were due to changes in the ruthenium species in the condensate solution. Data on the retention of radionuclides by the BaSO_4 precipitate is presented in Table XVI.

TABLE XVI. Radionuclide Carrying by BaSO_4 - Solution III

Radionuclide	Percent Retained in Solid		
	Unwashed ppt	Washed ppt*	Double Washed ppt*
^{85}Sr	96	91-95	85-87
^{95}Zr	78	71	67
^{106}Ru	10-40	6-24	5-20
^{137}Cs	82	67-96	60-61
^{144}Ce	78	73	62

* Precipitates washed with distilled water. Ruthenium retention values reported in text for BaSO_4 , CaSO_4 , and PbSO_4 were following one water wash and one 0.1M NaOH wash.

The cost of precipitating agents is shown in Table XVII.

TABLE XVII. *Cost of Precipitating Agents*

<u>Precipitant</u>	<u>Price, \$/ton</u>	<u>Treatment Cost, \$/ton U*</u>
Ba(OH) ₂	280	16
PbO	240	25
CaCO ₃ (calcite)	20	0.7

* On the basis of 330 moles SO₄/ton uranium

Calcite has an economic advantage over the other sulfate precipitates, but CaSO₄ is the most unsatisfactory of the precipitates in all other respects. Processing and materials costs in a sulfate precipitation process employing Ba(OH)₂ or PbO would be rather high. The violent reaction and concomitant release of gasses observed in some instances could lead to safety problems. Ultimate storage of sulfates as dried products is questionable due to the relatively high solubility when compared to fixation in solid media as well as to the possible transport of particles if contacted with an aqueous medium. Incorporation of sulfates in asphalt is unsatisfactory due to relatively high radionuclide concentrations in the precipitate. The total integrated dose to the asphalt would probably be detrimental to the retentive properties of the asphalt product. Storage of sulfates in cement mortar remains a possibility but may present difficulties in handling. This alternative is discussed more fully in the section of this report dealing with plaster and cement-like materials. An attractive feature of the sulfate precipitation scheme is its simplicity from a chemical standpoint.

Scavenging

Scavenging reactions have been quite attractive over the years for treating radioactive wastes because of their effectiveness in processing wastes of highly variable compositions. Moreover, scavenging offers greater economy than many other treatment methods. Based on the work of Touhill,⁽²²⁾ Shuckrow,⁽²³⁾ and McLellon,⁽²⁴⁾ it appeared that the hydrous oxides of iron and manganese might be effective scavengers in the treatment of glass melter condensate. In addition, the hydrous oxide method appears promising since this scavenging is effective even in solutions containing high salt concentrations. Furthermore, the glass melter condensate already contains $2 \times 10^{-3} \text{ M}$ of ferric iron.

Hydrous Oxide Scavenging - Solution II. Laboratory studies were initiated to evaluate the effectiveness of the hydrous oxides of iron and manganese for scavenging fission products from the glass melter condensate. Ruthenium, because of its expected presence in relatively large concentrations in the condensate, was the fission product selected for initial study. Based on previous experience, ruthenium is also one of the more difficult radionuclides to remove by scavenging.

Varying amounts of Fe^{+3} of Mn^{+2} were added to samples of simulated condensate traced with fission product ^{106}Ru . Hydrous oxides were precipitated by adjusting the pH to 10 with NaOH. This pH was selected based upon previous work with hydrous oxides.⁽²²⁻²⁴⁾ In this case, both the stable and radioactive ruthenium were not treated to exactly simulate the complex nitro-, nitrate-, and nitrosyl-ruthenium species which may occur in the actual condensate. Hence, the removals reported in these initial studies are higher than would be expected had these complex species been simulated. However, later experiments were conducted on simulated glass melter condensate with the appropriate complex species, and results reported later in this section will reflect the impact of the complex ruthenium species on scavenging.

Figure 17 shows the amount of ruthenium scavenged as a function of the appropriate added metal cation concentration. The results indicated that the Mn^{+2} addition and formation of a hydrous oxide was superior to pure hydrous ferric oxide up to 0.04M of added cation. Above this point, both the mixed hydrous oxide and the hydrous ferric oxide scavenged equally as well. Experimentation also showed the mixed hydrous oxide to have superior settling and centrifugation characteristics when compared with equivalent amounts of hydrous ferric oxide.

Additional experiments were undertaken to determine the relative effectiveness of the mixed hydrous oxide and hydrous ferric oxide for scavenging other radionuclides. These radionuclides were ^{85}Sr , ^{144}Ce , ^{60}Co , and ^{137}Cs . Figures 18 through 21 show a comparison of the two types of scavenging. In general, the mixed hydrous oxide scavenger performed better than the hydrous ferric oxide scavenger. The results for cesium are quite variable and should be regarded at best as approximations of removal efficiencies. However, other detailed work⁽²³⁾ has shown that the mixed hydrous oxide is probably superior for ^{137}Cs removal as well.

Based on these results, the concentration selected for further study of the mixed hydrous oxide system was 0.03M of added Mn^{+2} . Due to the very high concentration of acid, adjustment to a slightly alkaline pH resulted in appreciable dilution of the simulated waste solution. Initially, a dilution factor of 3.15 was used. However, later experimentation showed that pH adjusted with 9M NaOH would result in a dilution factor of 2.5.

For each of these previous experiments, the pH was adjusted to 10. However, it is well known that the variation in the pH range for optimum scavenging depends upon the

FIGURE 17. Effect of Concentration of Scavenger on Ruthenium Removal

FIGURE 18. Effect of Concentration of Scavenger on Strontium Removal

FIGURE 19. Effect of Concentration of Scavenger on Cerium Removal

FIGURE 20. Effect of Concentration of Scavenger on Cobalt Removal

FIGURE 21. *Effect of Concentration of Scavenger on Cesium Removal*

radionuclide and the particular oxide. Hence, experiments were performed to determine the optimum pH for scavenging the principal radionuclides of concern. The manganese and iron concentrations prior to pH adjustment were 0.03 M and 0.002 M, respectively. Figure 22 shows the results of this experiment. Based on these results, it may be concluded that the optimum pH range for mixed hydrous oxide formation is 10 to 12.

Despite the fact that hydrous oxides are effective scavengers for many of the fission products of principal concern such as strontium, yttrium, cerium, promethium, zirconium, niobium, and ruthenium; cesium is relatively insensitive to removal by hydrous oxide scavenging. Thus two alternative methods for removing cesium were examined for possible process use. These were (1) phosphotungstate, and (2) ferro and ferricyanide precipitation.

FIGURE 22. Effect of pH on Mixed Oxide Scavenging Efficiency

Flow diagrams for the two alternative processes are shown in Figures 23 and 24. Note that the ferro-ferricyanide-mixed hydrous oxide method can be carried out in one reactor due to the stability of the ferro-ferricyanides in weakly basic solution. On the other hand, phosphotungstate dissolves readily in the pH region of hydrous oxide formation. Hence, the reaction must be carried out in two steps.

FIGURE 23. *Phosphotungstate - Mixed Hydrous Oxide Scavenging Scheme*

FIGURE 24. Ferro-Ferricyanide--Mixed Hydrus Oxide Scavenging Scheme

Iron Cyanide Complex Scavenging - Solution II. The ferro and ferricyanide complexes of certain cations are known to form very insoluble precipitates. These precipitates have a marked ability to remove cesium from solution. Experiments were undertaken to determine which of the ferro- and ferricyanides would remove cesium most effectively from the simulated glass melter condensate.

Initial experiments investigated the ^{137}Cs removal efficiencies of several types of ferricyanide complexes. The cations used for ferricyanide precipitation were cerium, cobalt, copper, nickel, and zinc. Table XVIII contains the results obtained for cesium removal by the ferricyanides used. The pH of the final solution was 10, and ferricyanide and added metallic ion concentrations were 0.004M.

TABLE XVIII. *Cesium Removal by Ferricyanide Precipitation*

<u>Metallic Ion</u>	<u>^{137}Cs Removal, %</u>
Cu^{++}	94.6
Ce^{+++}	95.2
Zn^{++}	98.5
Co^{++}	99.6
Ni^{++}	99.9

Previous experiments had shown the optimum concentration of ferricyanide to be approximately 0.004M. Cesium-137 removal was the index upon which the selection of this concentration was based.

As a consequence of these results, nickel ferricyanide precipitation was investigated in greater detail. In addition, experiments were performed to ascertain whether a ferrocyanide species could also be effectively employed. These further experiments were conducted concurrently with hydrous oxide

scavenging since the treatment scheme envisioned would employ such a technique.

A concentration of 0.03M of Mn^{++} was added initially to the simulated condensate. Sufficient Ni^{++} and $\text{K}_3\text{Fe}(\text{CN})_6$ or $\text{K}_4\text{Fe}(\text{CN})_6$ were also added so that the final concentration of each would be 0.004M after pH adjustment (3.15 dilution factor). The condensate in these experiments was spiked with 1 WW and supplemented by trace amounts of ^{137}Cs . The pH was adjusted to 12 and then, in order to determine the effects of pH readjustment, the pH was readjusted by HNO_3 to 2. Radionuclide removals were evaluated at various pH values.

Tables XIX and XX show the results of this study.

TABLE XIX. Radionuclide Scavenging by Mixed Hydrous Oxides and Cesium Nickel Ferricyanide as a Function of pH

<u>Radionuclide Removal, %</u>					
<u>pH</u>	<u>^{144}Ce</u>	<u>^{106}Ru</u>	<u>^{137}Cs</u>	<u>^{95}Zr</u>	<u>Gross</u>
4	97.8	59	99.9	88.7	90.0
6	99.6	94.4	99.9	99.5	96.7
8	99.7	95.4	99.9	99.5	95.3
10	99.8	92.4	99.9	99.9	97.4
12	99.8	87.7	99.9	92.6	96.5
10*	99.7	94.4	99.9	98.9	98.3
8*	99.8	94.8	99.9	99.9	98.1
6*	99.7	94.7	99.9	99.9	97.6
4*	98.7	80	99.9	96.2	94.1
2*	98.1	56	99.9	70.0	90.0

* pH readjusted by HNO_3

TABLE XX. *Radionuclide Scavenging by Mixed Hydrous Oxides and Cesium Nickel Ferrocyanide as a Function of pH*

<u>Radionuclide Removal, %</u>					
<u>pH</u>	<u>^{144}Ce</u>	<u>^{106}Ru</u>	<u>^{137}Cs</u>	<u>^{95}Zr</u>	<u>Gross</u>
4	91.5	40	99.2	85	88
6	97.1	64	99.9	99.2	93.2
8	97.9	67	99.9	99.9	94.2
10	99.5	68	99.9	98.6	94.2
12	91.5	74	99.9	91.3	93.8
10*	98.0	73	99.9	95.8	95.0
8*	97.2	76	99.9	99.1	95.9
6*	94.5	75	99.9	99.2	95.2
4*	87.7	59	99.5	86	91.0
2*	58	44	99.2	54	86.0

* pH readjusted by HNO_3

The results clearly show the ferricyanide precipitate to yield better removals than the ferrocyanide. For purposes of comparison, a similar set of experiments was performed using zinc as the metallic cation. Results of this study are shown in Tables XXI and XXII.

TABLE XXI. *Radionuclide Scavenging by Mixed Hydrous Oxides and Cesium Zinc Ferricyanide as a Function of pH*

<u>Radionuclide Removal, %</u>				
<u>pH</u>	<u>^{144}Ce</u>	<u>^{106}Ru</u>	<u>^{137}Cs</u>	<u>^{95}Zr</u>
4	99.2	74	94	99.8
6	99.8	89	99.0	99.9
8	99.6	91	98.4	99.9
10	99.6	90	97.1	99.9
12	98.9	84	87	99.9
10*	99.6	90	94.5	99.9
8*	99.9	92	98.2	99.9
6*	99.9	92	99.2	99.9
4*	99.4	86	96.9	99.9
2*	97.6	71	86	99.9

* pH readjusted by HNO_3

TABLE XXII. *Radionuclide Scavenging by Mixed Hydrous Oxides and Cesium Zinc Ferrocyanide as a Function of pH*

pH	<u>Radionuclide Removal, %</u>			
	<u>^{144}Ce</u>	<u>^{106}Ru</u>	<u>^{137}Cs</u>	<u>^{95}Zr</u>
4	94.6	30	47.2	99.9
6	95.5	38	57	99.9
8	97.0	46.7	54.9	99.9
10	97.4	45.0	51.3	99.9
12	97.3	36.6	41.8	99.9
10*	96.7	58.2	45.8	99.9
8*	95.5	52.5	48.4	99.9
6*	97.7	57.4	53.4	99.9
4*	97.9	42.6	54.0	99.9
2*	94.2	26.9	51.7	99.9

* pH readjusted by HNO_3

These results serve to confirm the superiority of the nickel iron cyanide complexes. Note, however, in all of these experiments, that the effects of pH readjustment are relatively minor.

The only major radionuclide of concern not investigated in previous experiments was strontium. Therefore, strontium removals were studied separately for the same optimum formation conditions and concentrations, i.e., pH 10, 0.03M added Mn^{++} , and 0.004M Ni^{++} and $\text{K}_3\text{Fe}(\text{CN})_6$ after dilution. ^{85}Sr removal was 93.2% for these conditions.

The solids characteristics were then studied to evaluate the most effective method of disposal. Table XXIII clearly shows the superiority of centrifugation as opposed to gravity settling.

TABLE XXIII. Solids Characteristics of the Hydrous Oxide-Ferricyanide System

<u>Treatment</u>	<u>Time</u>	<u>Solids Volume, %</u>
Settling	2 hr	54
Settling	18 hr	29
Settling	72 hr	24
Centrifugation*	5 min	12
Centrifugation*	30 min	8

* 1500 rpm

For a pilot plant program, the supernate after centrifugation could be incorporated into asphalt for storage by the method described in another section of this report. The solid fraction would be dissolved by successive NaOH dissolution of the cyanide and mixed hydrous oxide dissolution by concentrated nitric acid. The dissolved solids would then be returned to the WSEP feed.

This procedure, however, is not without problems. While the mixed hydrous oxides readily dissolved in concentrated nitric acid, there is a question as to the final product of the NaOH dissolution step. It is apparent that the ferricyanide complex was metathesized to at least a soluble iron form and the cyanide. However, under certain conditions cyanide and nitric acid react explosively. An unanswered question is whether the conditions in this proposed process will lead to such a hazard. This question must be resolved before the process can be pursued further.

Phosphotungstate - Hydrous Oxide Scavenging - Solution II.

As mentioned previously, a phosphotungstate-hydrous oxide process may be used as an alternative to the ferricyanide-hydrous oxide scavenging scheme. In this case, the phosphotungstate is substituted for the ferricyanide to effect cesium removal. Figure 25 shows the effectiveness of three types of phosphotungstates for cesium removal. Note that

FIGURE 25. Effect of Phosphotungstate Concentration on Cesium Removal

there is little advantage to adding K^+ to form potassium phosphotungstate. The phosphotungstate species formed when no accompanying cation is added behaves quite similarly to the potassium phosphotungstate. The addition of NH_4^+ to form ammonium phosphotungstate actually has a slightly detrimental effect. This is presumably due to the competition for exchange sites by the Cs^+ and NH_4^+ ions. Hence, the mixed phosphotungstate was used in further studies.

Since nearly complete sorption of cesium would be unnecessary to meet asphalt incorporation requirements, an added phosphotungstate concentration of $0.0004M$ was used in subsequent experiments.

A study was made to determine the effects of contact time with the phosphotungstate. Ammonium phosphotungstate was employed for this study. Results are reported in Table XXIV. Results show little advantage to great increases in the contact time. Therefore, a contact time of one hour was used in subsequent work.

TABLE XXIV. *Cesium Removal by Ammonium Phosphotungstate ($4 \times 10^{-4}M$) as a Function of Contact Time*

<u>Contact Time, hr</u>	<u>Cesium Removal, %</u>
1	87.6
3	88.3
4.5	88.8
7.4	89.1
9.6	91.0

At this point, the concentrations and conditions of the mixed hydrous oxide scavenging had been defined as well as the type, concentration, and contact time for the phosphotungstate step. Thus, the two-step phosphotungstate-hydrous oxide procedure was performed using 1WW and ^{137}Cs spiked simulated glass melter condensate.

The following experimental procedure was used to determine the effectiveness of this treatment scheme. Sufficient phosphotungstic acid (0.02M) was added to the radioactive simulated glass melter condensate so that a concentration of 0.0004M resulted. The sample was shaken for one hour and centrifuged for 30 min at 1500 rpm. The supernate was decanted (a portion was retained for radionuclide analysis) and an amount of 1.0M $\text{Mn}(\text{NO}_3)_2$ was added so that a concentration of 0.03M Mn^{+2} resulted. Sufficient 9M NaOH was added to increase the pH to 10. The addition was made dropwise into an ice-cooled beaker to avoid excessive heating of the solution. During the addition, the solution was completely mixed. The dilution factor after NaOH addition was 2.5.

After pH adjustment, mixing was continued for 5 min. The samples were then centrifuged for 30 min at 1500 rpm. The two supernates and the raw waste were collected for radionuclide analysis.

The results reported in Table XXV were obtained by two methods. The samples were analyzed by (1) the Radiochemical Analysis Unit, and (2) a gamma analysis employing simultaneous equations. Statistical analyses were performed for all samples. The statistical analysis showed a high degree of reproducibility for all radionuclides except ruthenium. One standard deviation for the ruthenium radiochemical analysis was as great as $\pm 24.7\%$.

TABLE XXV. *Radionuclide Removals for the Phosphotungstate-Hydrous Oxide Treatment Scheme*

Treatment	Radionuclide Removals, %*						
	Total Sr	⁸⁵ Sr	¹⁰³ Ru	¹⁰⁶ Ru	¹³⁷ Cs	⁹⁵ Zr	¹⁴⁴ Ce
Phosphotungstate	6.9	-	9.3	2.1	-	13.3	-
	-	6.6	-	29.7	97.6	0.8	18.1
Mixed Hydrous Oxide	96.8	-	41.0	46.7	-	96.2	-
	-	98.0	-	65.3	68.7	97.1	98.7
(Phosphotungstate-Mixed Hydrous Oxide)	97.0	-	46.5	47.9	98.8	96.7	-
	-	98.2	-	76.5	99.2	97.1	99.0

* The first line for each step is radiochemical analyses, while the second line is gamma analysis using simultaneous equations.

Based on these results, it may be concluded that removals of all radionuclides except ruthenium will be greater than 97%. Ruthenium removals may vary from about 50% to 80%. However, additional experiments are required to more closely define ruthenium removals.

Experiments were conducted to determine the amount of solids accumulated in each step and also to determine the most feasible dissolution techniques. Table XXVI lists the solids volumes for the scavenging steps.

TABLE XXVI. *Solids Volumes in the Phosphotungstate - Hydrous Oxide Treatment Scheme*

<u>Treatment Step</u>	<u>Centrifuged* Volume, %</u>
Phosphotungstate	0.5
Mixed Hydrous Oxides	10.0

* 1500 rpm for 30 min

The phosphotungstate solid formed in 100 ml of solution (0.5 ml) was readily dissolved in 1.0 ml of 9M NaOH. The mixed hydrous oxide solid resulting from scavenging of 100 ml of supernate (10.0 ml) was dissolved in 4.0 ml of concentrated HNO₃ and a very small amount of solid was observed in the dissolved mixed hydrous oxide solution upon standing overnight. This small amount of solid, about 0.1% of the original supernate, was not regarded as significant. However, an additional 2.0 ml of concentrated HNO₃ was effective in preventing the accumulation of even this minor amount of solid.

Hydrous Oxide Scavenging - Solution III. Each of several different methods of forming hydrous manganese oxide results in a somewhat different reaction product. Only one such method was explored throughout the scavenging studies employing Solution II. There was little reason to expect that the mixed oxide of the Solution II studies would behave in a significantly different manner in the more dilute Solution III. Therefore, as the work evolved into its later stages, it was considered more appropriate to study a different hydrous oxide in order to determine whether any advantages could be gained from another formation reaction.

Hydrous manganese oxide, formed using the Guyard reaction, may be represented as follows:

Stoichiometric quantities of reactants were employed in scavenging simulated melter condensate solutions even though the Guyard reaction is known to be non-stoichiometric in some cases. An attractive feature of the Guyard reaction is that it can be carried out in acid solution. Indeed, it has been shown⁽²⁵⁾ that Guyard reaction manganese oxide can be precipitated in 10N HNO₃ and still have marked carrying properties. However, it should be noted that the reaction rate is much slower in acid solution than in basic solution.

No attempt was made to optimize reactant doses. Rather, KMnO_4 and $\text{Mn}(\text{NO}_3)_2$ concentrations in the laboratory experiments were based on the concentration of Mn^{+2} determined in the Solution II case. These concentrations of reactants were probably in excess of the requirements for efficient scavenging in the relatively dilute Solution III. Exact chemical requirements could be determined as actual melter condensate becomes available. Some change in the concentration of the hydrous oxide scavenger should have little effect on the general behavior of the system.

The experimental procedure entailed the addition of KMnO_4 to the simulated melter condensate until the solution was 0.012M in KMnO_4 . Manganous nitrate sufficient to yield a concentration of 0.018M $\text{Mn}(\text{NO}_3)_2$ was then introduced and the pH was adjusted to the desired value with 50% NaOH. It was determined experimentally that pH adjustment, prior to the addition of the manganese compounds, produced results which were indistinguishable from those obtained using the normal reagent addition order. A volume increase of approximately 10% resulted from neutralization to pH 10 with 50% NaOH.

Initial experiments were concerned with the effectiveness of this hydrous oxide as a ruthenium scavenger. Both simulated glass melter condensate and evaporator bottoms from the ruthenium volatilization process (see subsection on ruthenium volatilization) were scavenged by the manganese oxide at several pH values. Data obtained in these experiments are contained in Table XXVII.

TABLE XXVII. Ruthenium Decontamination by Scavenging

<u>pH</u>	<u>Ruthenium Decontamination Factors</u>	
	<u>Simulated Melter Condensate</u>	<u>Evaporator Bottoms from Ru Volatilization</u>
<0 (no pH adjustment)	1.8	-
3.2	3.7	-
6.9	2.8	-
9.0	8.1	7.3
10.0	18-25	12-15
11.0	18	7-15
12.0	12-24	11

Consistently lower DF's noted for the evaporator bottoms result from the much lower initial ruthenium levels in these pre-treated solutions. Since a DF of 23-28 is obtained in the ruthenium volatilization process, the overall DF for the combined volatilization and scavenging at pH 10 would be 276-420. In all subsequent work with this hydrous oxide, the scavenging process was carried out in the pH range 10-12.

System performance with respect to removal of ^{85}Sr , ^{95}Zr , and ^{144}Ce from the effluent of the ruthenium volatilization process was also investigated. The experimentally determined decontamination factors were 91-99, 13-16, and 6.8-7.6 for ^{85}Sr , ^{95}Zr , and ^{144}Ce , respectively. Overall DF's for the combination of the two treatment methods were found to be 91-99, 61-74, and 20-22 in the same order.

Hydrous manganese oxide formed by the Guyard reaction was a more highly oxidized compound than the mixed oxide of Solution II studies. In the latter case, the precipitate was light in color and dissolved readily in HNO_3 . On the other hand, the Guyard oxide was a dark brown highly acid-resistant solid more closely resembling MnO_2 . Dissolution of the precipitate could be accomplished by a reducing agent

in acid solution. The precipitate from 100 ml of glass melter condensate could be readily dissolved in 5 ml of 1 + 5 HNO_3 to which 2 ml of 30% H_2O_2 had been added. Comparable quantities of the precipitate formed in the ruthenium volatilization process could be dissolved in this same manner.

Phosphotungstate - Hydrous Oxide Scavenging -

Solution III. Phosphotungstate precipitation was much the same as in the Solution II studies. At concentrations of 0.004M and with no pH adjustment made, ^{137}Cs DF's of greater than 32 were observed. Any attempt at neutralization caused a drastic reduction in the ^{137}Cs DF. It seemed to matter little whether the phosphotungstate treatment was carried out before or after the ruthenium volatilization process.

A treatment scheme involving ruthenium volatilization coupled with phosphotungstate-hydrous oxide scavenging was conceived. Any one of the components not required for conditioning of the glass melter condensate for ultimate storage could be omitted. The sulfate-bearing liquids could be stored in asphalt while the solids would be redissolved and recycled to the phosphate glass process.

Ruthenium Volatilization

Volatilization of ruthenium from glass melter condensate was investigated as a pre-treatment step prior to further decontamination by some other method. The treatment scheme envisioned involved the production of highly volatile ruthenium tetroxide from lower oxidation state forms of ruthenium by heating the glass melter condensate in the presence of a strong oxidizing agent. Ruthenium tetroxide thus produced could be separated from the bulk of the sulfate condensate by fractional distillation and the condensed ruthenium recycled to the phosphate glass process.

A subsequent treatment step could then be carried out to condition the remaining glass melter condensate for ultimate storage.

Potassium permanganate was selected as the oxidizing agent in the ruthenium volatilization studies since any carryover of KMnO_4 in the glass melter condensate would be compatible with a later hydrous oxide scavenging step. Moreover, ruthenium volatilization from permanganate-treated solutions was carried out successfully in the Redox process for a number of years.

Although the form of ruthenium present in glass melter condensate is not well defined, the principle of RuO_4 production can be illustrated by the reaction between potassium ruthenate and potassium permanganate⁽²⁶⁾:

Since divalent manganese is produced from the reduction of MnO_4^- , a second and simultaneous oxidation-reduction reaction may occur as follows:

Thus, a hydrous manganese oxide precipitate may be formed when RuO_4 is produced from the oxidation of ruthenium compounds by KMnO_4 .

Experimentation involved heating permanganate-treated simulated glass melter condensate in a 500-ml distilling flask contained in a heating mantle. Vapors evolved from the still-pot were passed through a water-cooled condenser and the condensate collected in a receiving flask. Uncondensed gasses were passed through two caustic scrubbers to prevent any release of ruthenium. A slight vacuum was maintained in the system by connecting the effluent end of the second scrubber to a water aspirator. Subsequent experiments indicated the effect of this vacuum on the ruthenium volatilization process to be negligible.

Initial work was aimed at determining the KMnO_4 concentrations and boiling times necessary to achieve significant ruthenium decontamination of the melter condensate. Following the addition of a predetermined amount of KMnO_4 to the simulated glass melter condensate, the solution was brought to a boil and maintained in this condition for the desired period of time. Data presented in Table XXVIII summarize the results of these experiments. It is evident from the data that both permanganate concentration and boiling time are significant factors and that an optimum value of each exists. Evaporator bottoms of simulated condensate solutions which were initially 0.024 M in KMnO_4 evidenced a slight permanganate color. Increasing the initial KMnO_4 concentration beyond this value resulted in correspondingly higher concentrations of residual permanganate in the evaporator bottoms and no noticeable improvement in ruthenium decontamination. Subsequent to these findings, a concentration of 0.024 M KMnO_4 was used in all of the volatilization studies.

TABLE XXVIII. Ruthenium Volatilization Data

<u>Initial Concentration of KMnO_4, molar</u>	<u>Boiling Time, min</u>	<u>Ruthenium Decontamination Factor</u>	<u>Volume Remaining, %</u>
0	10	1.04	65-70
0	20	1.04	65
0.019	3	4	94
0.024	2	10	90
0.024	6	27	82
0.024	8	22	71
0.024	10	23-28	76
0.024	30	47	28
0.028	3	9.4	96
0.028	7	24	84

A dark brown, almost black, precipitate was observed to form in the permanganate-treated solution during boiling. This hydrous MnO_2 precipitate presumably results from an oxidation-reduction reaction between MnO_4^- ion and Mn^{+2} ion.

In addition to the ruthenium studies, the behavior of Sr, Zr, Cs, and Ce in the volatilization process was also examined. Data on the fate of the several radionuclides can be found in Table XXIX. As can be seen from inspection of this table, significant quantities of activity are to be found in all three phases.

TABLE XXIX. *Distribution of Radionuclides in Ruthenium Volatilization Process**

<u>Radionuclide</u>	<u>Activity Evaporator Bottoms, %</u>	<u>Activity Manganese Oxide Precipitate, %</u>	<u>Activity Vaporized, %</u>
^{85}Sr	~100	nil	nil
^{95}Zr	21	79	nil
^{106}Ru	~ 4	nil	96
^{137}Cs	~100	nil	nil
^{144}Ce	33	67	nil

* KMnO_4 initially 0.024M, boiling time 10 min.

This technique was found to be a relatively simple and straightforward approach to the removal of ruthenium from glass melter condensate. Moreover, it was found to be a highly reliable method compatible with other treatment methods such as hydrous oxide scavenging and phosphotungstate precipitation discussed elsewhere in this report.

Distillation

Distillation was recognized during the planning stages of this program as one of the possible methods that should be considered in treating glass melter condensate. The responsibility for this segment of the research has been assumed by Brookhaven National Laboratory. Preliminary studies at Brookhaven indicate that fractional distillation at reduced pressure appears to be a feasible method for decontaminating glass melter condensate to the levels required for incorporation of the sulfate-bearing stream in asphalt. Results of the distillation studies will be presented in a separate report. However, the implications of Brookhaven results will be considered in the conclusions of this report.

Conversion to Solid Forms

Sulfate Melts

The preparation of relatively insoluble sulfate melts from glass melter condensate was investigated to evaluate the feasibility of using existing phosphate glass equipment for this purpose, i.e., glass melter. A continuous sulfate melt process was envisioned with process steps similar to the phosphate glass process as follows: (1) melt forming chemicals are mixed with glass melter condensate; (2) the mixture is fed to the melter where evaporation and melt formation take place; and (3) the melt flows into a final receiver where it is solidified and sealed for final storage. The glass melter condensate is stored during phosphate glass processing then processed on a campaign basis.

The number of metal sulfates that melt below their decomposition temperature is limited. Alkali metal sulfates are the most stable when melted but are also quite soluble in water.

The dissolution rate of a sodium sulfate melt in water was determined in the flowing system and found to be $30 \text{ g/cm}^2/\text{day}$. Although the radionuclide content of a sodium sulfate melt may be only 0.1% of a phosphate glass, the radionuclide release rate may be several orders of magnitude greater. Attempts to prepare a low solubility melt containing sodium sulfate and sodium silicate were not successful.

Melts containing lead sulfate or calcium sulfate appeared to have the greatest potential for process application. Although the respective decomposition and melting temperatures for PbSO_4 are 803° and 1170°C , and for CaSO_4 1150°C and 1450°C , melts with these compounds can be prepared with the aid of fluxing agents.

Melts composed of PbSO_4 and PbO or PbSO_4 , PbO , and SiO_2 were the least soluble in water. Two-phase melts were prepared with CaSO_4 and PbSO_4 and with borax as a fluxing agent.

Melts with varying compositions of PbSO_4 or CaSO_4 and fluxing agents were prepared in the laboratory. The components were dry mixed and heated for 1 to 2 hr in a muffle furnace. Melting points were estimated by raising the furnace temperature in increments of 50°C . Uniform melts with low melting points and low concentrations of fluxing agents were tested for solubility in water. Samples of these melts were ground and sieved to obtain the 45-60 mesh fraction. One gram of this fraction was placed in a 100-mesh stainless steel bag and immersed in 150 ml of distilled water held at 100°C in a steam bath. The samples were removed, dried, and weighed at 24-hr intervals to determine weight loss per day.

Two melt compositions, (A) $2\text{PbSO}_4 \cdot \text{PbO}$, and (B) $10 \text{ PbSO}_4 \cdot 6\text{PbO} \cdot 1\text{SiO}_2$ were selected for further study in continuous melter experiments to evaluate melt formation and sulfate retention in the presence of water and nitric acid. Predetermined

amounts of either PbO or PbO and SiO₂ were mixed with simulated glass melter condensate to form slurries. These slurries were pumped at a rate of 100 ml/hr to a porcelain crucible sealed in a pot furnace. The off-gas was vented through a condenser for nitric acid removal and a caustic scrubber for sulfur dioxide removal. Pertinent data from the continuous melter experiments is given in Table XXX.

TABLE XXX. Data From Continuous Melter Runs

	(A) 2PbSO ₄ · PbO	(B) 10PbSO ₄ · 5PbO · SiO ₂
Drip Temperature*	960°C	895°C
Density	5.6 g/cm ³	5.8 g/cm ³
Volume Reduction Factor**	3.1	3.0
SO ₄ ⁼ Retention	86%	81%
Solubility***	0.52%/day	0.55%/day

* Determined by placing 1.0 g of powdered melt in a platinum crucible and measuring the temperature when the first drop falls from the crucible.

** Based on 20 gal of condensate per tonne of fuel processed (Solution II).

*** Determined by suspending a 100-mesh SS bag containing 1.0 g of 45 to 60-mesh granules of melt in 150 ml of 100°C water for a 24 hr period and then measuring melt weight loss.

Melts containing PbSO₄ or CaSO₄ were prepared with varying amounts of borax as a fluxing agent. These melts consisted of two phases, one of which was predominately borax glass and the other predominantly PbSO₄ or CaSO₄. The PbSO₄ · Na₂B₄O₇ mixtures melted at lower temperatures than the CaSO₄ · Na₂B₄O₇ mixtures. A minimum of one part of Na₂B₄O₇ to two parts of PbSO₄ or CaSO₄ was found necessary to produce a free flowing melt. The solubility of borax fluxed melts is relatively high as shown in Table XXXI. Attempts to prepare free flowing borax-fluxed BaSO₄ melts, or boric oxide fluxed PbSO₄ melts were unsuccessful.

TABLE XXXI. *Solubility of Borax Fluxed Melts in First 24 hr Period*

<u>Melt</u>	<u>Melt Temperature, °C</u>	<u>Borax Phase Solubility*, %/24 hr</u>	<u>Metal Sulfate Phase Solubility, %/24 hr</u>
$2\text{PbSO}_4 \cdot \text{Na}_2\text{B}_4\text{O}_7$	900	31	17
$2\text{CaSO}_4 \cdot \text{Na}_2\text{B}_4\text{O}_7$	1000	62	58

* Determined by suspending a 100-mesh SS bag containing 1.0 g of 45-60 mesh granules of melt in 150 ml of 100 °C water for a 24-hr period and then measuring melt weight loss

Although sulfate melts, particularly those containing PbSO_4 , may be satisfactory as storage media, the processing of melts in phosphate glass equipment was concluded to be infeasible due to the following:

- The addition of melt-forming chemicals such as lead or calcium compounds to glass melter condensate forms rather thick slurries which may be difficult to transfer to the melter.
- Twenty to 30 gal of condensate slurry per tonne of ruthenium would be processed through the melter. This volume is nearly the same as that for the concentrated feed to the phosphate glass process. Thus, fixation of a small fraction of the fission products in the melter condensate would require about as much processing time as fixation of the bulk of the fission products in the phosphate glass.
- The presence of lead compounds in the platinum melter is undesirable because of possible reduction of the lead to metal which would damage the melter.
- Lead compounds are relatively costly.

As mentioned previously, an advantage of this method would be the utilization of phosphate glass equipment for glass melter condensate processing.

Plaster and Cement-like Materials (Solution I)

As mentioned in the section on sulfate precipitation, calcium sulfate precipitates behave quite differently than the sulfates of barium and lead. When lime $[\text{Ca}(\text{OH})_2]$, pebble phosphate $[\text{Ca}_5(\text{PO}_4)_3\text{F}]$, and calcite (CaCO_3) were added to the simulated condensate, the calcium sulfate hydrates formed a semi-solid mass containing plaster of paris $(\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O})$ and gypsum $(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$. None of the calcium sulfate masses could be centrifuged or filtered. The lime and pebble phosphate reactions were highly effervescent, but effervescence during calcite reaction was not severe at room temperature. An X-ray diffraction analysis showed that the calcite reaction product was $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or gypsum, which formed as a porous deposit on calcite granules.

Table XXXII shows the volumes and densities of the dried calcium sulfate precipitates. Note that each of these precipitates includes the entire volume of both waste and the simulated condensate solution.

TABLE XXXII. *Volume and Density of Precipitated Calcium Sulfate*

Reactant, Stoichiometric	Volume of Precipitate per 100 ml waste, ml		Density of Precipitate g/cm ³	
	Dried 100°C	Dried 1000°C	Dried 100°C	Dried 1000°C
$\text{Ca}(\text{OH})_2$	85	60	0.4	0.5
$\text{Ca}_5(\text{PO}_4)_3\text{F}$	67	57	0.6	0.5
CaCO_3	40	--	0.8	---

The process scheme envisioned for this treatment involves reactant mixing, drying and packaging. Figure 26 shows a flowsheet for this treatment scheme.

FIGURE 26. Calcium Sulfate Treatment Scheme.

Portland cement added to the simulated condensate also formed a solid mass incorporating the entire volume of the waste. The cement mortar was prepared by mixing 540 grams of Portland cement with 11 g of bentonite clay and 83 ml of simulated glass melter condensate diluted to 300 ml with water. This ratio of ingredients is based on the work of White and Lahaie at Chalk River.⁽²⁷⁾ The simulated glass melter condensate contained ^{137}Cs tracer for the static leach tests. After preparation, the batch of mortar was divided into 2 equal portions, and 5 g of synthetic mordenite powder (cesium selective zeolite) was blended into one of the portions. Each was allowed to set and was then subjected to static leach tests by contacting the mortar with 500 ml of distilled water which was changed at weekly intervals.

Initial ^{137}Cs leach rates* were 0.47 and $0.0086 \text{ g.cm}^{-2}\text{d}^{-1}$ for untreated and mordenite-treated mortar, respectively. These leach rates had decreased to 0.030 and $0.0023 \text{ g.cm}^{-2}\text{d}^{-1}$ at the end of 36 days. For comparison, the cesium leach rate of asphalt-waste mixtures is an order of magnitude less than that of the zeolite-treated mortar. About 6 gal of cement mortar is produced per gallon of glass melter condensate.

Most methods which form plaster- or cement-like materials suffer from the same detrimental aspects. The primary defect is the high leach rates due to the solubility of these materials. Cesium-137, in particular, is quite leachable. In addition, almost the entire volume of waste and the reactant must be packaged and stored. Aside from the safety considerations, this method of treatment is the least costly of all methods investigated. Table XXXIII shows treatment costs for this method.

TABLE XXXIII. *Cost of Plaster and Cement-like Materials Treatment*

<u>Reactant</u>	<u>Price, \$/ton</u>	<u>Treatment Cost, \$/ton U*</u>
Pebble Phosphate	10	0.3
Lime	14	0.4
Calcite	20	0.7
Cement	22	0.8

* On the basis of 330 moles SO_4^{2-} /ton U

Also note that, depending upon the drying temperature, the drying process may evolve radioruthenium.

Plaster and Cement-like Materials (Solution III)

The possibility of storing sulfate precipitates in cement mortar was another line of investigation. Barium

$$* \text{ leach rate} = \frac{\text{Activity leached/cm}^2 \cdot \text{d}}{\text{Activity/g of mortar}} = \text{g} \cdot \text{cm}^{-2}\text{d}^{-1}$$

sulfate precipitated from simulated glass melter condensate was employed in this phase of the study. Several possible mortar compositions were examined. It was desired to minimize the quantities of cement and water in relation to the barium sulfate in the mix. Criteria for selection of a ratio of ingredients also included the production of a mortar which would not readily crumble or disintegrate in water after 48 hr of setting. The empirically determined recipe was 75 g of Portland cement, 35 g (dry weight) of barium sulfate, and 50 ml of water. This mix produced about 0.5 gal of cement mortar per gal of glass melter condensate.

Static leach tests involving five different radionuclides were conducted on the cement product. A cesium sorbent, powdered zeolon (synthetic zeolite), was added to one batch of cement mortar in order to study its effect on the cesium leach rate. Results of the leach tests are summarized in Table XXXIV.

TABLE XXXIV. *Leach Rates From Cement Mortar
Containing Barium Sulfate Precipitate*

<u>Radionuclide</u>	<u>Leach Rate ($\text{g} \cdot \text{cm}^{-2} \text{d}^{-1}$)</u>		
	<u>1 day</u>	<u>15 days</u>	<u>29 days</u>
^{137}Cs	0.097	0.004	0.002
^{137}Cs + zeolon	0.0014	0.0001	0.00009
^{85}Sr	0.0065	0.0009	0.0007
^{95}Zr	0.00001	0.000001	0.0000007
^{106}Ru	0.00004	0.000003	0.0000016
^{144}Ce	0.0002	0.00001	0.000004

Sulfates precipitated from simulated melter condensate solutions were evenly distributed throughout cement mortar only with extreme difficulty. Mixing was a severe problem in all cases except when the precipitate was thoroughly dried before attempting to make the mortar.

Storage of contaminated sulfates in this manner appears to be feasible in cases where radiation levels prohibit storage in asphalt and where the somewhat higher leach rates can be tolerated.

Incorporation in Asphalt

A method for incorporating glass melter condensate in asphalt was studied. The method appears to be simple, safe, and inexpensive for storage of wastes where radioactivity levels are low enough to avoid excessive heat generation or radiation damage. Asphalt has good adhesive and coating properties and is relatively insoluble in water. The leach rate of cesium from asphalt-waste mixes is intermediate between cement-waste and glass-waste mixes.

High radiation levels are considered to be the primary problem with incorporation of glass melter condensate in asphalt. Radiation dosages up to 10^8 rads are considered safe. However, studies at ORNL indicate that higher dosages may be allowable.⁽²⁸⁾ Treatment techniques capable of reducing radiation levels of the melter condensate before asphalt incorporation would be needed.

The ORNL asphalt incorporation process⁽²⁸⁾ was considered for disposal of glass melter condensate. This process utilizes emulsified asphalt* into which liquid wastes are mixed and evaporated. Either a batch or a continuous process may be employed. Up to 60% solids have been incorporated in asphalt. An additional advantage of asphalt incorporation is the fixation of chemical pollutants such as nitrates and phosphates.

* Type RS-2 Federal requirements as set forth in United States Government Federal Specifications SS-A-00674C (August 20, 1962).

Estimated radionuclide concentrations in asphalt products prepared with simulated neutralized melter condensate are shown in Table XXXV. Since it may be desirable to remove the HNO_3 or nitrates from the waste, radionuclide concentrations with or without NaNO_3 are listed. A final asphalt product density of 1.5 g/cm^3 and a 60% solids - 40% asphalt weight ratio is assumed in all cases. The weights of anhydrous Na_2SO_4 , NaNO_3 , and Na_3PO_4 used in the computations (per tonne of fuel processed) were 46.9 kg, 33.7 kg, and 2.15 kg, respectively.

TABLE XXXV. *Estimated Radionuclide Concentrations in Asphalt Mixes With Neutralized Glass Melter Condensate*

Radionuclides	Sodium Nitrate Included, 24 gal of Asphalt Mix per tonne Fuel		Sodium Nitrate Excluded, 14 gal of Asphalt Mix per tonne of Fuel	
	Ci/gal at 1 yr Fuel Aging	Ci/gal at 6 yr Fuel Aging	Ci/gal at 1 yr Fuel Aging	Ci/gal at 6 yr Fuel Aging
Ruthenium	100	3.0	171	5.3
Cesium	5.0	2.8	8.6	4.8
Strontium	2.1	1.7	3.6	2.9
Yttrium	2.3	1.7	3.9	3.0
Cerium	9.6	0.1	16.4	0.2
Promethium	3.9	1.0	6.8	1.8
Zirconium	0.6	---	1.0	---
Niobium	1.2	---	2.0	---
Totals	125	10.3	213	18.0

A significant reduction in the radionuclide concentrations listed in Table XXXV by scavenging, a suitable de-entrainment device on the melter off-gas, or some other technique will facilitate processing and storage of the asphalt product. Disposal by burial to eliminate the need for special storage facilities then might be possible.

Laboratory experiments were conducted to evaluate the effectiveness of incorporating simulated melter condensate in asphalt by the ORNL method. Asphalt products containing

60 wt% waste solids and a density of 1.52 g/cm^3 were prepared. Neutralized condensate was mixed with emulsified asphalt (Type RS-2, 63 wt% asphalt, 35 wt% water, and 2 wt% emulsifying agent) at 65°C and the water evaporated by heating to 160°C . The mixtures were stirred continuously at 150 rpm by a four-bladed paddle that scraped the walls of an electrically heated stainless steel vessel. Free flowing asphalt products were prepared from both neutralized condensate and from condensate previously scavenged with phosphotungstic acid ($\text{pH} < 1$) and hydrous manganese oxide ($\text{pH} = 12$) to reduce fission product activity. Sufficient ^{137}Cs was added to the scavenged condensate to permit static leach tests on the asphalt product. The static leach tests were conducted by placing 500 ml of distilled water in a quart polyethylene bottle containing about 150 g of asphalt product spread uniformly on the bottom of the bottle. The water was sampled and changed each week. The leach rate* was $7 \times 10^{-5} \text{ g cm}^{-2} \text{ d}^{-1}$ at the end of 4 weeks.

Another portion of the research involved a study of the feasibility of incorporating sulfate precipitates in asphalt. The previously described experimental apparatus and emulsified asphalt was employed in this phase of the investigation.

Reagent grade plaster of paris ($\text{CaSO}_4 \cdot 1/2 \text{ H}_2\text{O}$) was slurried with water and fed to the evaporator containing emulsified asphalt at 70°C . This temperature and a stirring rate of 130 rpm was maintained throughout the period of slurry addition. The temperature was then increased to 160°C .

* $\frac{\text{Activity leached/cm}^2 \cdot \text{d}}{\text{Activity/g of product}} = \text{g cm}^{-2} \text{ d}^{-1} = \text{leach rate.}$

No major difficulties were encountered with the final asphalt product below 50% solids. Mixtures containing greater than this amount of solids were difficult to make. Mixing problems developed at high solids concentrations and, although a product containing 60% solids was found to be attainable, a period of 2-3 hr was required to achieve this mix. Stiffening of the asphalt during slurry addition appeared to be the source of the mixing problems.

In addition to the plaster of paris slurries, $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ slurries produced from the reaction of CaCO_3 with glass melter condensate were also incorporated in asphalt. Products containing up to 50% solids were produced from this material.

Leach tests were not conducted on these asphalt products since it was felt that leaching should, if anything, be less severe than from asphalt products produced from soluble salts.

A major difficulty identified with the incorporation of sulfate precipitates in asphalt would seem to be the possible presence of prohibitive quantities of radioactive materials in the sulfates. Significant quantities of ruthenium and strontium are contained in the sulfates precipitated from glass melter condensate, as previously reported in this section.

SUMMARY AND CONCLUSIONS

The Waste Solidification Engineering Prototypes (WSEP) program is a comprehensive research and development plan undertaken to provide the nuclear industry with methods for long-term storage of highly radioactive wastes. Three processes - spray solidification, pot solidification, and phosphate glass solidification - will be demonstrated as methods for the fixation of radioactive fission products in stable, solid media. Some low and intermediate level radioactive wastes will be encountered in each of the three processes as minor effluent streams. In all cases, these effluent streams appear as condensates. The research reported herein was undertaken to provide effective treatment methods for these low and intermediate level condensates and thus to prevent their release to the environment.

Two condensate streams, nitric acid fractionator condensate and glass melter condensate, were identified as requiring treatment. The composition of these condensates, based on the best available estimates, was defined at the outset. More detailed compositions were used during the progress of the research as results from companion studies became available.

The initial phases of the research were devoted to a preliminary evaluation of alternative treatment methods. For the nitric acid fractionator condensate, the alternative methods were adsorption, electrodialysis and electrodeionization, ion exchange, and oxidation and volatilization.

The two types of alternatives evaluated for the treatment of glass melter condensate were (1) separation of the sulfates from the condensate with recycle of the fission products to the solidification process headend, and

(2) conversion to solid forms. Sulfate separation methods investigated were ion exchange, sulfate reduction, sodium sulfate crystallization, scavenging, ruthenium volatilization, and distillation. Solid conversion methods were sulfate melts, plaster and cement-like materials, and asphalt incorporation.

The method recommended for treatment of nitric acid fractionator condensate is two-stage electrodialysis followed by anion exchange. A flowsheet for this treatment method is shown in Figure 27. Electrodeionization could also provide adequate treatment of this condensate. However, additional research is required before either a pilot or a full scale method can be implemented.

Three alternative methods recommended for treating glass melter condensate are (1) vacuum distillation (developed at Brookhaven National Laboratory), (2) a volatilization-scavenging scheme with incorporation of the final product in asphalt, and (3) a sulfate precipitation-cement storage method. The latter method is of lower priority than are the first two. Figure 28 illustrates the flowsheet proposed for the vacuum distillation method. In this scheme, the bottoms containing the bulk of the fission products will be recycled to the phosphate glass process. Condensed nitric acid will also be recycled. Sulfuric acid containing fission products will be neutralized and incorporated in asphalt for final storage.

The volatilization-scavenging flowsheet is shown in Figure 29. The first step in this scheme is volatilization, condensation and recycling of ruthenium to the phosphate glass process. This step is followed by phosphotungstate precipitation for cesium removal. Solids generated in this step will be dissolved and recycled to the phosphate glass process. This is followed by hydrous manganese oxide scavenging

FIGURE 27. Flowsheet for Electrodialysis-Ion Exchange Treatment of Fractionator Condensate

Typical Operating Parameters and DF Data:

1. Nominal Pressure, 20mm Hg
2. Nominal Liquid Temperature Range, 25 to 250°C
3. Non-volatile Fission Product, DF = 10⁴
4. Volatile Fission Product, DF = 10⁴

FIGURE 28. Distillation Schematic Diagram (Phosphate Glass Process Melter Condensate Treatment)

FIGURE 29. Ruthenium Volatilization - Phosphotungstate - Scavenging Flowsheet

for removal of the other fission products. Again, the solid phase is dissolved and recycled to the glass process. The final liquid effluent is incorporated in asphalt, as in the vacuum distillation method.

Figure 30 is the flowsheet for the sulfate precipitation-cement storage scheme. Barium sulfate is precipitated in the first step. After centrifugation, the supernate is recycled to the glass process while the barium sulfate precipitate is mixed with cement for ultimate storage.

An engineering evaluation of these various schemes for condensate treatment has led to the following proposed course of action:

- Laboratory research will continue on the electro-dialysis-ion exchange method for treating nitric acid fractionator condensate. When the method is fully demonstrated on the bench scale, research will terminate. Larger scale demonstration is not contemplated.
- The vacuum distillation method will be demonstrated on an engineering scale at the Battelle-Northwest C-MEL facility in conjunction with the WSEP program.
- The volatilization-scavenging method will be demonstrated on a small scale in a WSEP hot cell. This method, considered a strong alternative to the distillation method, will require hot cell demonstration in the event that mechanical difficulties limit the usefulness of the distillation method.
- Although work will be terminated on the sulfate precipitation-cement storage method, this scheme will continue to be regarded as a second-order alternative.

FIGURE 30. Sulfate Precipitation - Cement Storage

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