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AEC
RESEARCH
and
DEVELOPMENT
REPORT

**QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
FIXATION OF RADIOACTIVE RESIDUES
JANUARY-MARCH, 1966**

A. M. Platt

May, 1966

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QUARTERLY PROGRESS REPORT
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FIXATION OF RADIOACTIVE RESIDUES
JANUARY-MARCH, 1966

By

Members of the Staff
Chemistry Department

Edited by
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QUARTERLY PROGRESS REPORT
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INTRODUCTION

This progress report is the twenty-ninth in a series presenting research and development activities in the field of radioactive wastes.

Experimental work charged to programs other than those of the Division of Reactor Development and Technology is sometimes included for general interest and completeness; such work is identified in the headings.

SUMMARY

A survey of properties of melts and solid products in the system PW-1 waste- Na_2O - P_2O_5 was made. The data obtained aided in defining flowsheets for spray calciner-melter processing of PW-1 waste with and without addition of melting-temperature-lowering constituents to the melter.

A statistical study of the effects of variation in composition of a Purex-type waste has been completed but the data are only partially analyzed at present.

A thermoanalytical system has been acquired and partially tested. It will be used primarily for a study of thermal expansion of various solids.

All major Waste Solidification Engineering Prototype equipment has been installed in the Chemical and Materials Engineering Laboratory. Installation of services is 80% complete and preliminary equipment tests are underway.

The mechanically-wiped film evaporator worked well in tests using simulated Purex wastes with added phosphate.

Experiments to examine heat loss mechanisms in Rack 6A resistance furnace were completed.

The ultrasonic tester for pot wall thickness has been developed and is ready for field tests.

Heat tests with the liquid transfer casks indicate that the cask can tolerate normal Purex wastes without cooling for greater than eight hours.

A new readout system was developed for use with capacitance probes to measure liquid level in waste casks.

Fission product release studies involving simulated high level ceramic wastes were extended to include samples of phosphate ceramic prepared from actual high level waste. Release rates at 1100°C for Cs^{137} were found to be about 1% per hour. Releases of Ru^{106} and Sr^{90} were measured.

Studies on precipitation-scavenging indicate that ion exchange in the diffuse double layer, chemisorption or both are the principle mechanisms whereby ions are sorbed. Furthermore these mechanisms are related directly to the degree of crystallinity of the adsorbent.

A mixture of hydrous ferric oxide, hydrous manganese dioxide and nickel ferricyanide scavenged greater than 98.5% Ru^{106} , Ce^{144} , Cs^{137} , Sr^{85} and Co^{60} from a simulated glass melter condensate.

High temperature (100°C) sodium sulfate crystallization experiments show that about 50% of the strontium from a glass melter condensate remains with the sodium sulfate.

Plugging of the prototype immersion heater-circulator in plant tests resulted in an expedited experimental investigation of the causes, and the development of instrumentation for, detecting flow in the circulator.

An empirical correlation was developed relating maximum temperature in waste storage tanks to thermal conductivities and thicknesses of the salt cake and soil cover.

Scintillation measurements with a prototype detector indicates this system can indicate sludge deposits in waste storage tanks.

Quantitative extraction of strontium and rare earths from a Zirflex-type waste were achieved with D2EHPA solvent in pulse column studies.

Two techniques for measuring ion exchange resin level are being developed.

CALCINATION AND SOLIDIFICATION STUDIES

(R. E. Burns, C. R. Cooley, R. L. Moore)

LABORATORY STUDIES

Waste Melt Composition Studies

Effects of Variation in Concentration of Purex Waste Composition on Melt Properties - G. B. Barton

Since it is known that considerable variation in the concentration of the Purex process cationic constituents - sodium, iron, aluminum, chromium and nickel - occurs, a statistically designed series of experiments was carried out to learn how the variation in individual element concentration affects the properties of the resulting solids.

The solution chosen as nominally representative of the Purex process contained the major process elements at concentrations corresponding to that projected for the original process demonstration in WSEP. Then upper and lower concentration levels were estimated from various flowsheet and analytical data. The final system was:

<u>Variable</u>	<u>Level</u>			
	<u>Lower</u>	<u>Center</u>	<u>Upper</u>	
Na	0.45	0.70	0.95	eq/l
Al	0.09	0.24	0.39	eq/l
Fe	0.18	0.48	0.78	eq/l
Cr + Ni (2:1)	0.048	0.128	0.208	eq/l
FP	10	35	60	wt% of initial oxides
Nominal Fuel Exposure (836)	(4050)	(11,290)	MWd/MT	
M/P	2.5	2.1	1.7	

The design called for 48 "off center" points and six replicates at the center composition making a total of 54. Two heat treatments were used.

The data are currently being analyzed and will be published in a topical report.

Properties of Melts in the PW-1:Na₂O:P₂O₅ System -
J. E. Mendel

A series of 49 melts in the PW-1 waste - Na₂O-P₂O₅ system were prepared to aid in choosing optimum spray calciner-melter flowsheet conditions. Composition and melting point of these are shown in Figure 1. Melts having M/P ratios less than 1.5 were glasses; those with M/P between 1.5 and 2.3 were microcrystalline with some glassy portions if quenched rapidly; those with M/P greater than 2.3 were all microcrystalline.

Two modes of operating the spray calciner-melter system were considered. In the first, no addition of melt-temperature-lowering constituents is made to the melter; stainless steel receiver pots are required for the relatively high melting temperature melts produced. In the second, melt-temperature-lowering constituents are added to the melter; mild steel receiver pots may be used for the relatively low melting temperature melts produced.

For the first mode, the area bounded by the dark line in the upper right hand portion of Figure 1 represents the composition range which can be considered. The P₂O₅- and Na₂O-rich limits are imposed by operating characteristics of the spray calciner; the PW-1-rich limit is imposed by temperature limitations in the melter and receiver pot. To produce melts having the minimum melting point in this composition range (900° C) using PW-1 at 100 gal/tonne U as feed, it is necessary to make the PW-1 1.60M in phosphate and 0.75M in sodium.

Low-melting products which may possibly be collected in mild steel receiver pots can be produced by adding melt-temperature-lowering constituents (such as NaPO_3) directly to the melter. Products having melt points of 750°C or less are required for satisfactory filling of mild steel receiver pots. Corrosion rates for mild steel in some of the candidate melts ranged from 25 to 45 mils/day at 720°C (a temperature at which the melts would just flow). These melts contained 4.6 - 7.5M phosphate and 5.4 - 7.2M sodium (PW-1 at 100 gal/tonne U basis). The solid products from these melts were 5 - 10 times more water soluble than the higher melting temperature products described in the preceding paragraph. Also, they contain much less waste oxide - 20 vs. 45-50 wt.%.

Properties of Melts Containing PW-2 Waste and Additives -
J. E. Mendel

A statistically designed experiment, to define the effects of lithium, calcium, sodium, aluminum and phosphate as additives to PW-2 waste, was completed and the results are being analyzed. The output of the statistical experiment was three equations which express sulfate retention, drip point and solubility as a function of additive concentrations. Contour plots are being prepared to aid in final analysis of the results.

Thermal Analytical System - G. B. Barton

A thermoanalytical system has been acquired to permit measurement of thermal expansion, thermogravimetric changes, and direct calorimetry. It is to be first applied to the thermal expansion of various solids. This is one of the areas of concern since a solid that does not shrink as much as the container will cause stress generation.

FIGURE 1. $\text{Na}_2\text{O}:\text{PW-1}:\text{P}_2\text{O}_5$ Melting Point Isotherms

WASTE SOLIDIFICATION ENGINEERING PROTOTYPES

(J. M. Atwood, C. R. Cooley, J. C. Spanner)

PROTOTYPE STATUS - K. J. Schneider, George Rey, M. O. Rankin
and V. P. Kelly

Installation of WSEP related equipment has continued. Installation of major equipment was completed, and primary emphasis has been on installation of electrical service, electrical and instrument wiring, in-cell piping jumpers, and out-of-cell piping services. Overall completion of the instrument-electrical and piping services is 75 and 95%, respectively. Overall completion of in-cell piping jumpers is 95% complete.

The resistance-heated annealing furnace (Rack 6A) was checked out operationally. The induction-heated annealing furnace (Rack 5A), and the welding station (Rack 7B) have been installed and are now being checked out operationally. Remotability testing of equipment has been started. The final process off-gas filtration and pumping system has been installed and is now being checked out. The digital computer has been installed and wiring to it is about 90% complete.

The C-MEL building was completely released for occupancy on March 1, with a few final items to be done by the contractor on a call-in basis. Subsequent building efforts by plant forces have been concentrated on detailed check-out of the ventilation system, and final preparations for receiving radioactive waste in the building. The tank vault storage system and load-out station have been installed and are being checked out.

WIPED FILM EVAPORATOR - M. E. Spaeth

The wiped film evaporator is an alternate concentrator for use in the WSEP. The evaporator can be used to concentrate incoming wastes by about a factor of five (5) (PW-1, PW-2, etc.) and then

feed a solidification process. The wiped film evaporator is being tested for capacity, deentrainment factor, operability and denitration using simulated wastes.

An eight-hour shakedown run and a 40 hr run were made using simulated Purex PW-2 type waste ($M^+/P = 0.96$ and $[PO_4^{=}] = 2.77M$). Satisfactory operation was obtained with concentration factors of about 3.5 at a feed rate of 43 liters/hr using a steam pressure of 85 psig. Preliminary analytical results show the deentrainment factor to be about 10^4 and denitration to be about 85% (at concentration factor of 3.5). Following the 40 hr run, visual inspection of the evaporator interior showed it to have a very thin white scale on the deentrainment baffles and bolts on the wiper blades. All other surfaces were quite clean.

THERMAL CONDUCTIVITY AND FURNACE HEAT TESTS - W. V. DeMier

Tests to determine heat loss mechanisms on the six-zone resistance furnace were completed and analysis of the data from the tests is underway. The tests are intended to provide a basis for estimating the pot-cooling performance of the furnace. At steady-state operation, heat losses of 6 kW each were measured from top and bottom zones. Heat loss from remaining zones totalled 19 kW. The maximum temperature observed at the furnace outer shell was $175^{\circ}C$. Inner furnace wall temperature was $800^{\circ}C$.

Cooling characteristics of the furnace were examined by use of a resistance-heated dummy pot to simulate a pot generating heat by radioactive decay. System temperatures were measured at steady-state for various simulated heat generation rates with cooling air rates of 80 scfm per zone. With a pot heat generation rate of 6200 W, no power to the furnace, and 80 scfm cooling air flow rate, the pot wall temperature was $\sim 250^{\circ}C$. Heat balance calculations showed 94% of the input heat was removed by the cooling air. Temperature limitations on the heaters in the resistance-heated pot prevented tests at higher heat generation rates.

POT WALL THICKNESS TESTER - B. E. Dozer

An ultrasonic pot wall thickness tester has been developed to assess corrosion damage caused by solidifying wastes in a pot. The tester measures wall thickness using the pulse-echo method by measuring the time between the front and back surface reflections from the pot wall.

The ultrasonic equipment was installed and tested using a 12 in. diam filled pot. The welding machine successfully rotated the pot while a vertical drive mechanism moved the ultrasonic transducer the length of the vessel. Satisfactory wall thickness results were obtained but transducer alignment problems necessitated redesign of the transducer holder. Further tests have been curtailed pending completion of installation of the welding mechanism in the cell.

WSEP TRANSFER CASK - M. E. Spaeth

Two shipping casks (Figure 2) will be used to ship liquid wastes to and from the WSEP. The casks are spherical in shape (75 in. OD) and have a hollow interior (55.5 in. ID). The inner (3/4 in. thick) and outer (1 in. thick) spheres are made of 304-L stainless steel with eight (8) in. of lead shielding (cast slowly for good bonding). The inner sphere is wrapped with 1/2 in. OD x 0.035 in. wall stainless steel tubing with a spacing of approximately 1-7/8 in. The outer sphere is equipped with lifting ears and a support pallet made of stainless steel.

The cask is equipped with a series of lines for filling, emptying and venting, etc. All are made of stainless steel pipe which passes through the shielding from the top-wells to the inner sphere. All connections terminate in one of two recessed wells. The smaller well contains only the vent line and the vent valve. The other contains all of the empty and fill connections. It also contains a one-inch vertical opening filter with a capacitance liquid level probe and another normally plugged 1 in.

opening for a spare. The wells are covered by hinged lids which are sealed by O-ring gaskets. For shipment the two lids are covered by an additional stainless steel cap.

FIGURE 2. 30 Ton Liquid Shipping Cask

Other auxiliaries include cooling water and temperature connections on the outside sphere. Two thermocouple probes are provided. One thermocouple measures the inner sphere temperature and the other measures the temperature one inch inside the outer sphere.

Heating tests were made on one of the casks to determine the actual heat transfer characteristics of the casks. The results of the tests are given in Figures 3 and 4.

The results show that without auxiliary cooling, and at a heat input estimated as equivalent to Purex waste, the cask contents require about 16 hr to heat from 125 to 200° F.

FIGURE 3. Initial Heating Rates for Uncooled 400 gal Cask

FIGURE 4. Time Required for Cask Contents to Heat from 125 to 200°F with No Cooling

Calibrations were made of the cask volumes using a capacitance probe and known incremental volumes of water. The results of the tests showed the cask cannot be overfilled under normal filling procedures, and the normal shipping volume of waste should be 320 gal.

WSEP TRANSFER CASK INSTRUMENTATION - O. H. Koski

A new readout system was developed for use with capacitance probes to measure liquid level in waste casks. The integrated system, which uses capacitance to pulse height to DC conversion, was installed and calibrated in the 324 Bldg. This system does not require the careful installation and calibration of a conventional bridge-type capacitance system. The radiation exposed parts consist of the probe and probe head transformer, both of which can be made radiation resistant. External circuitry is all solid state with optional meter or potentiometric readout.

HAZARDS OF SHIPPING SOLIDIFIED HIGH LEVEL WASTE
(A. E. Albrethsen and L. C. Schwendiman)

The maximum quantity of fission products that can be released to the airstream from a shipping accident involving high level radioactive waste and a high temperature fire is an important consideration in the overall evaluation of the accident. Experimental studies directed toward the evaluation of the high temperature fission product release from high level waste were continued. Two mechanisms of release are being studied, volatilization and mechanical entrainment of particles in the airstream.

The experiments are designed to measure the release of important fission products from ceramics simulating the product from high level waste solidification processes. In the experiments to be reported this quarter, portions of an actual high level waste phosphate glass were used as the trace material for the fission isotopes. A sample of this high level waste glass was ground to less than 100 mesh and aliquots of the powder blended with similarly prepared synthetic (non-radioactive) phosphate ceramic. Resulting 15 g samples were gamma-counted for measuring the radioactive constituents present and placed in the metal

crucibles for the release tests. This method of sample preparation is expected to produce a product representative of actual waste material because all of the constituents are in the same chemical form as the actual waste (either a phosphate glass or a micro-crystalline phosphate solid), the radioactive isotopes are in their proper proportions, and there is little chance for segregation of the dry blended constituents.

The fission product release heats are conducted in a controlled atmosphere induction furnace. Sweep gas and the released material are passed through a quartz chimney and any particles present are collected on a fiber glass filter. The filters, washings from the quartz chimney, and washings from other portions of the gas train are analyzed for the released isotopes.

Four release runs were made on one sample of PW-1 type ceramic, having a M^+/P of 2.5. The first run in which the powdered ceramic was fused consisted of slowly heating the sample up to 1100°C and then cooling. During the remaining heats the sample was rapidly heated to the goal temperature which was then maintained for two hours. The analysis of the principal radioactive isotopes is given in Table I; the release data are given in Table II; and the calculated hourly release rates are shown in Table III.

The cesium releases appear to be a little higher than expected from the previous release studies (BNWL-139, 170, 213). The ruthenium releases are considerably higher than expected from the previous studies. This could possibly be due to residual oxidants in the ceramic or to incomplete reduction of RuO_4 during the solidification process. Residual volatiles were present as judged from the bubbling observed during the initial fusion. The influence of a highly reducing environment on ruthenium retention resulting from stainless steel

TABLE I. Analysis of Principal Radioisotope in Release Sample H-1*

Cs ¹³⁷	3.45 x 10 ⁸ dpm
Ru ¹⁰⁶ -Rh ¹⁰⁶	1.50 x 10 ⁸ dpm
Ce ¹⁴⁴ -Pr ¹⁴⁴	5.54 x 10 ⁸ dpm
Sr ^{90**}	2.63 x 10 ⁸ dpm
Cs ¹³⁴	1.34 x 10 ⁷ dpm

* PW-1 type ceramic waste, M⁺/P = 2.5, nickel crucible.

** Sr⁹⁰ calculated from Cs¹³⁷ activity by using
 $\text{Sr}^{90} / \text{Cs}^{137} = 0.763$

TABLE II. Release of Radioisotopes from Release Sample H-1*

Heat	Temperature (°C)	Time (hr)	Isotope Release in dpm		
			Cs ¹³⁷	Ru ¹⁰⁶	Sr ⁹⁰
H-1a	1100	--	4.0 x 10 ⁵	1.5 x 10 ⁶	2.8 x 10 ³
H-1b	1100	2	4.7 x 10 ⁶	1.2 x 10 ⁵	2.5 x 10 ³
H-1c	1100	2	10.4 x 10 ⁶	1.1 x 10 ⁵	1.5 x 10 ²
H-1d	1200	2	8.4 x 10 ⁶	4.0 x 10 ⁴	2.8 x 10 ³

* PW-1 type ceramic waste, M⁺/P = 2.5, nickel crucible

TABLE III. Fractional Release Rate from Radioisotope from Sample H-1*

Heat	Release Rate for Isotope in Fraction/Hour		
	Cs ¹³⁷	Ru ¹⁰⁶	Sr ⁹⁰
H-1b	.68 x 10 ⁻²	4.0 x 10 ⁻⁴	5 x 10 ⁻⁶
H-1c	1.5 x 10 ⁻²	3.6 x 10 ⁻⁴	3 x 10 ⁻⁷
H-1d	1.2 x 10 ⁻²	1.3 x 10 ⁻⁴	5 x 10 ⁻⁶

*PW-1 type ceramic waste, M⁺/P = 2.5, nickel crucible

crucibles -- used in earlier studies -- is being evaluated. The Sr^{90} releases were consistent with the previous studies where releases of less than 10^{-5} , the lower detection limit, were found.

WASTE SOLIDIFICATION CONDENSATE TREATMENT

(G. J. Alkire)

SCAVENGING MECHANISMS - C. J. Touhill

A study of scavenging mechanisms was undertaken in order to eliminate some of the empiricism usually associated with precipitation reactions of this type. Experimentation was focused on the hydrous oxides and hydroxides since most scavengers fit into this category. A principal aim of the study is to uncover ways in which radioruthenium, which is often difficult to remove from radioactive effluents, can be more efficiently scavenged from solution.

Adsorption mechanisms on hydrous manganese dioxide were studied in the first phase of the investigation. Manganese dioxide was selected for several reasons. Hydrous manganese dioxide has been used as a radiochemical carrier and scavenger since the earliest studies of natural radioactivity, and in certain aspects it is a more versatile carrier than the hydrous oxides of either aluminum or ferric iron. In addition, it can be formed by a number of different chemical reactions and it has extremely low solubility in alkaline, neutral or strongly acidic solutions.

Ions appear to be sorbed by either ion exchange in the diffuse double layer of the colloid or by chemisorption, or by a combination of the two mechanisms. Both of these mechanisms are related to the degree of crystallinity. X-ray diffraction studies revealed that hydrous manganese dioxide formed by the Guyard reaction:

possesses a fairly consistent crystallinity pattern in widely varying hydrogen ion concentrations (pH 1 to 12). These patterns are shown in Figure 5.

Electrokinetic studies showed that the adsorptive behavior of Guyard manganese dioxide is highly predictable. In conjunction with the X-ray diffraction studies, electrokinetic reversibility measurements yield evidence that the mechanism of adsorption is probably ion exchange in the diffuse double layer.

Manganese dioxide formed by the oxidation of a manganous salt by air in an alkaline environment does not exhibit a consistent crystalline structure over the same pH range (Figure 6). From a pH of 7.9 to 12 the colloid is readily identified. Below pH 7.9 the structure deteriorates to amorphousness until pH 6.8 where the pattern is rather diffuse.

This discontinuity drastically affects the scavenging behavior of the hydrous manganese dioxide. When electrokinetic measurements are used to supplement the X-ray diffraction data, it appears that adsorption can be predicted by diffuse double layer model in the pH region from about 7.5 to 12 or slightly beyond. This model does not apply in the lower pH region, i.e. pH about 7.5 to 1. Electrokinetic reversibility measurements indicate that while there is some adsorption of the ion exchange type, chemisorption is probably the predominant mode of scavenging in the lower pH region.

FIGURE 5. Guyard Reaction

FIGURE 6. Oxygenation Reaction

In preliminary experiments an attempt was made to correlate sorption on hydrous manganese dioxide and the mineral pyrolusite, which has a well defined crystalline structure. Pyrolusite column studies showed that radioruthenium in adjusted acid condensate waste (pH = 5.1) is sorbed to less than 10 % breakthrough at 400 column volumes and less than 20 % breakthrough at 1250 column volumes. The results of acid elution studies show that for pyrolusite, radioruthenium removal is controlled by the chemisorption mechanism. Further studies will be undertaken to relate this behavior to that found for the hydrous manganese dioxide.

Additional experiments were designed to determine what factors influence chemisorption. Presumably, for chemisorption ions will be incorporated within the crystal microstructure of the central oxide particle. The two factors which were found to influence this incorporation most markedly were hydrated ion size and ionic charge.

Tracer level experiments were performed on manganese dioxide precipitates using Cs^{137} as the tracer and stable Cs^+ , K^+ , Co^{++} , Sr^{++} , Ce^{+++} , and Al^{+++} as the interfering ions. The degree of interference is shown in Table IV.

TABLE IV. Ion Interference with Cs^{137} Removal - Guyard Reaction at pH = 3.3

Ion	Percent Removal	
	10^{-3} moles/liter	10^{-4} moles/liter
K^+	5.4	10.5
Cs^+	1.5	4.2
Co^{++}	6.0	12.2
Sr^{++}	7.4	11.7
Ce^{+++}	1.4	2.3
Al^{+++}	4.1	4.5

The results showed that, in general, the higher valence ions interfered most, but ions with certain hydrated radii were able to interfere significantly due to radii which allowed migration closest to or within the crystal lattice. These findings were corroborated by reversibility studies which indicated that ions which interfered most were bound by the chemisorption mechanism.

The theory as developed thus far is presently being evaluated for practical cases, most notably for the scavenging alternative in the treatment of sulfate condensate wastes generated in the WSEP program.

SCAVENGING OF FISSION PRODUCTS - C. J. Touhill and J. E. Fager

Experimentation was undertaken to determine the degree of fission product scavenging by hydrous ferric oxide and by a mixture of hydrous ferric oxide and hydrous manganese dioxide from simulated glass melter condensate. The initial iron concentration in the simulated waste was 2×10^{-3} M Fe^{+3} . A comparison of the effectiveness of both methods, i. e. ferric oxide and mixed oxide scavenging, showed that 3×10^{-2} M of Mn^{+2} added to the simulated waste subsequent to precipitation at pH = 10.0 produced a more effective scavenger than an addition of 3×10^{-2} M of Fe^{+3} subsequent to precipitation at pH = 10.0.

Strontium, cesium, and cobalt removal was about equal for both scavengers. However, the mixed oxide system was 10 to 15% more effective in scavenging ruthenium and cerium. Hence, the mixed oxide system with an addition of 3×10^{-2} M Mn^{+2} was selected for further experimentation. Table V shows the removal of certain radionuclides which was obtained by this system.

TABLE V. Radionuclide Removal Efficiencies Using a Mixed Oxide Scavenger

<u>Radionuclide</u>	<u>pH Range for Optimum Removal</u>	<u>Maximum Removal (%)</u>
Ru ^{106*}	7.7 - 10.5	98.7
Ce ¹⁴⁴	5.0 - 12 ⁺	99.5
Cs ¹³⁷	-	< 10
Sr ⁸⁵	9.5 - 12.0	98.5
Co ⁶⁰	10.5 - 12.0	99.5

*Ru¹⁰⁶ tracer was pretreated to approximate the nitrosylruthenium species.

Since cesium removals were unsatisfactory, various ferricyanide precipitates were used to remove cesium. In these experiments the precipitation of ferricyanide was effected concurrently with the mixed oxide scavenging. The cations used for ferricyanide precipitation were: cerium, cobalt, copper, nickel, and zinc. Table VI shows the results obtained for cesium removal as the ferricyanide. The pH of the final solution was 10, and the $K_3Fe(CN)_6$

TABLE VI. Cesium Removal by Ferricyanide Precipitation

<u>Metallic Ion</u>	<u>Cs Removal (%)</u>
Ce ⁺⁺⁺	95.2
Co ⁺⁺	99.6
Cu ⁺⁺	94.6
Ni ⁺⁺	99.9
Zn ⁺⁺	98.5

and metallic ion concentrations were 0.004 M. The nickel ferricyanide was selected for further experimentation for scavenging optimization.

CRYSTALLIZATION OF SODIUM SULFATE - B. W. Mercer, C. J. Svoboda

Crystallization of sodium sulfate at temperatures near 100° C from partially neutralized, simulated glass melter condensate was investigated. A 50% solution of sodium hydroxide was added to the simulated condensate (4.4 M H_2SO_4 , 5.3 M HNO_3 , and 0.18 M H_3PO_4) in the stoichiometric amount to react with the sulfuric acid. A portion of the partially neutralized condensate was evaporated by boiling to half its original volume. The sodium sulfate crystals were filtered and washed with a portion of the partially neutralized condensate. The filtrate and washes were recycled to the partially neutralized condensate. This crystallization and wash procedure was repeated six times. Analytical results with Sr^{85} tracer indicate that only half of the strontium separated from the sodium sulfate. Substitution of small volume water washes in place of the condensate washes did not improve strontium separation.

WASTE MANAGEMENT

(Not charged to the Division of Reactor Development and Technology)

IN TANK WASTE SOLIDIFICATION - J. Dunn, E. E. Hoar

The prototype immersion heated circulator being tested under plant conditions became plugged with a crystalline deposit, and 10 of the 12 electric heaters failed. Preliminary analysis attributes the malfunction to buildup of sludge in the tank, to a depth sufficient to block circulation during an earlier shut-down to repair the off-gas filters. An investigation of the problem is now underway, emphasizing the development of flow detection instrumentation. In addition to a dip tube flow monitor which will indicate pressure differential due to velocity head, a strain gauge beam deflection flow meter has been designed and fabricated. Also under study is a heated thermistor whose temperature will be a function of ambient flow velocity. A

transparent circulator model has been installed for evaluation of these devices and also for determining conditions for maintaining or re-instituting circulation in the presence of simulated sludge.

Topical Reports Issued

Testing of Immersion Heaters for In-Tank Solidification Circulators, J. Dunn, BNW-101.

Jet Pump Tests for Concentrated Waste Transfer, J. Dunn, BNWL-CC-395.

TEMPERATURE IN UNDERGROUND WASTE STORAGE TANKS - W. E. Willingham

The final report in this series has been completed. It summarizes the previous work on the subject and presents a generalized correlation for the effect of tank size, height and spacing, soil cover depth, water table depth and thermal properties of the system.

The empirical correlation resulted in an equation of the following form:

$$k_s \frac{(T_{MAX} - T_A)}{S \ell_c} = 1.04 \left(\frac{k_s}{k_c} \right)^{-0.22} \left(\frac{\ell_1}{\ell_c} \right)^{+0.88}$$

or rewriting it

$$T_{MAX} - T_A = 1.04 S k_s^{-0.78} k_c^{-0.22} \ell_c^{1.22} \ell_1^{0.88}$$

From this it can be seen that the maximum temperature is a strong function of the soil thermal conductivity and a weak function of the cake thermal conductivity, while cake thickness and soil cover depth have little effect. The standard deviation for a least squares fit of the computer results to the above equation is +8.6% to -7.9%.

Two additional documents on the subject have been completed - BNWL-181 (Feb. 1966) "Buried Radioactive Waste Storage

Tank Temperatures and Soil Temperatures Near Leaks", G. Jansen, W. E. Willingham, and W. V. DeMier; and BNWL-SA-468 (Feb. 1966) "Heat Transfer in Underground Tank Storage of Radioactive Wastes", G. Jansen, W. E. Willingham, and W. V. DeMier, which was presented at the Symposium on the Solidification and Long Term Storage of Highly Radioactive Wastes, Richland, Washington, February 14-18, 1966.

RESIDUAL SLUDGE DETECTOR FOR WASTE STORAGE TANKS - C. E. Huck

A collimated, scintillation gamma photon transducer was developed and tested using a 1/2 g radium sulfide source. Readings were taken with the scintillation head unit assembled to its associated 3/16 ID lead collimator head. Dose rates at the scintillation crystal were varied by mechanically positioning the γ source at different distances from the transducer. Readings varied from 5200 CPM at 7.7 mr/hr to 33,500 CPM at 50 mr/hr. These readings indicate that this prototype system should properly show sludge deposits in waste tanks provided gamma emitter concentrations in the supernate and sludge are the same as the values initially provided to BNW by Isochem. Expected values at the detector head based on calculations are about 10 mr/hr when viewing sludge and 0.1 to 1.0 mr/hr when viewing supernate.

STRONTIUM AND RARE EARTH RECOVERY FROM ZIRFLEX WASTE -
G. L. Richardson

Pulse column studies with D2EHPA solvent in support of Isochem's Waste Management Program demonstrated quantitative extraction of strontium and rare earths from a synthetic Zirflex-type Purex High-level waste. The flowsheet differed from that studied previously⁽¹⁾ in having two- to three-fold more iron and eight-fold more aluminum in the feed. Both tartaric acid and HEDTA at 10 to 20% excess were tested as complexing agents for the iron and aluminum. The HEDTA, as expected, proved to be more effective in preventing the extraction of these

impurities; but even with HEDTA, approximately 0.6 to 1% of the aluminum in the feed was found in the rare earth product. The corresponding contamination from the tartrate feed was about three-fold greater. Although the iron extracted at about the same rate as the aluminum, the contamination in the product streams was generally less than 0.02% with both feeds.

CESIUM ION EXCHANGE RESIN LEVEL MEASUREMENT - O. H. Koski

Two techniques for measuring ion exchange resin level are being developed. One system, identified as the incremental conductivity system, indicates both liquid and resin levels from conductivity measurements performed on an increment of resin column depth. Successive increments of three inches over a fourteen foot span are scanned with a simultaneous recorder readout of both increment location and conductivity.

The other system is based on adaptation of a commercially available ultrasonic testing device. In its operation, a submerged transducer generates an ultrasonic wave which is reflected from the resin surface. The time from the echo to a selected time marker is used as a measure of resin depth. Time corrected gain, material calibration delay adjustments and gain adjustments make possible the rejection of unwanted reflections from supporting hardware and air bubbles on the transducer face.

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- (1) G. L. Richardson, "Solvent Extraction of Strontium, Cerium, and Rare Earths with D2EHPA, Part 2: Pilot Plant Studies", HW-79762, Pt. 2, February, 1964.

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