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CONCENTRATION OF RADIOACTIVE WASTES

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CONCENTRATION OF RADIOACTIVE WASTES

by

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ABSTRACT

Radioactive wastes from the processing of irradiated fuel elements can be reduced to an immobile concentrate with about 1/3 of its original volume by one or more successive evaporations of the decantable liquid. During these concentrations the ^{137}Cs content increases ~17-fold. The concentrate can be remobilized at rates exceeding 0.1 ft/hr, if necessary, by the addition of water.

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INTRODUCTION

Waste solutions from the processing of radioactive fuel elements in two separate areas at the Savannah River Plant (SRP) are stored in carbon steel underground tanks of 3/4 to 1-1/3 million gallons capacity. The solutions are alkaline, with a dissolved solids content of 30-35 wt %. The wastes are of two general types: "high level waste," which contains sufficient radioactive fission products to produce decay heat at 0.5 to 5 Btu/(hr)(gal); and "low level waste," with fission product content 1/1000 to 1/100,000 that of the high level waste, but still too high to discard to a seepage pond or to streams and rivers. The low level waste contains principally sodium aluminate from the caustic dissolution of the aluminum jacket on the irradiated fuel elements. The high level waste, principally sodium nitrate with some sulfate and carbonate, contains nearly all of the radioactive fission products from the processing of irradiated fuel elements. Both wastes separate into a layer of sludge and a layer of relatively clear supernatant liquid.

Costs are reduced in the long-term storage of radioactive waste solutions at SRP by transferring the waste supernate, after sufficient time for decay of highly active fission products, from storage tanks with cooling coils (Fig. 1) to less expensive uncooled tanks (Fig. 2). The tanks with coils are then reused for fresh waste. Further economy is obtained by evaporative reduction of volume of the aged wastes during the transfer to the uncooled tanks.

A tank farm evaporator, shown in Fig. 3, was installed in both waste storage areas at SRP (1960 in F Area and 1963 in H Area). Each evaporator, central to four large uncooled storage tanks, has operated satisfactorily since installation. The present evaporators are designed to concentrate the supernatant solution from tanks (which contain either aged high activity waste or low level waste) from ~35 to ~70 wt % solids (total solute plus solid phase) and to discharge the concentrated waste by steam lift and gravity drain or a pumped recirculating loop to the storage tanks. These radioactive slurries were transported from one location to another in tests at the Savannah River Laboratory.[1]

To keep storage costs at a minimum and to ensure an operable concentration system, it was necessary to determine the characteristics of waste solutions during concentration and to determine the distribution of radioisotopes between solid and liquid phases as the salts crystallize during cooling. The distribution of radioisotopes, particularly ^{137}Cs, could affect the cooling requirements for the evaporated waste, and require additional shielding around the evaporator during the latter concentrations. Also of interest are changes in the solid residues as the temperature increases because of fission product decay heat.

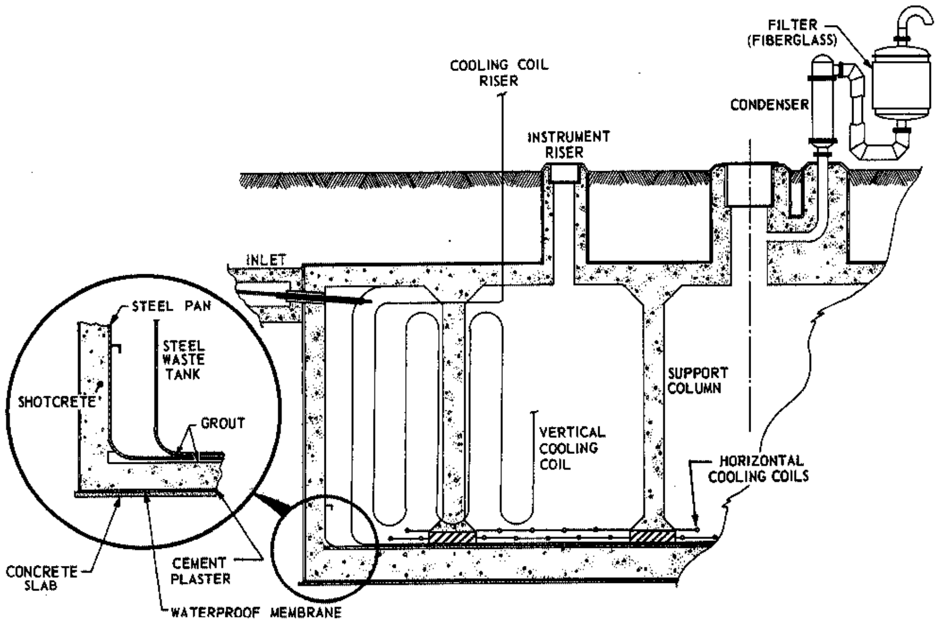

FIG. 1 COOLED STORAGE TANK

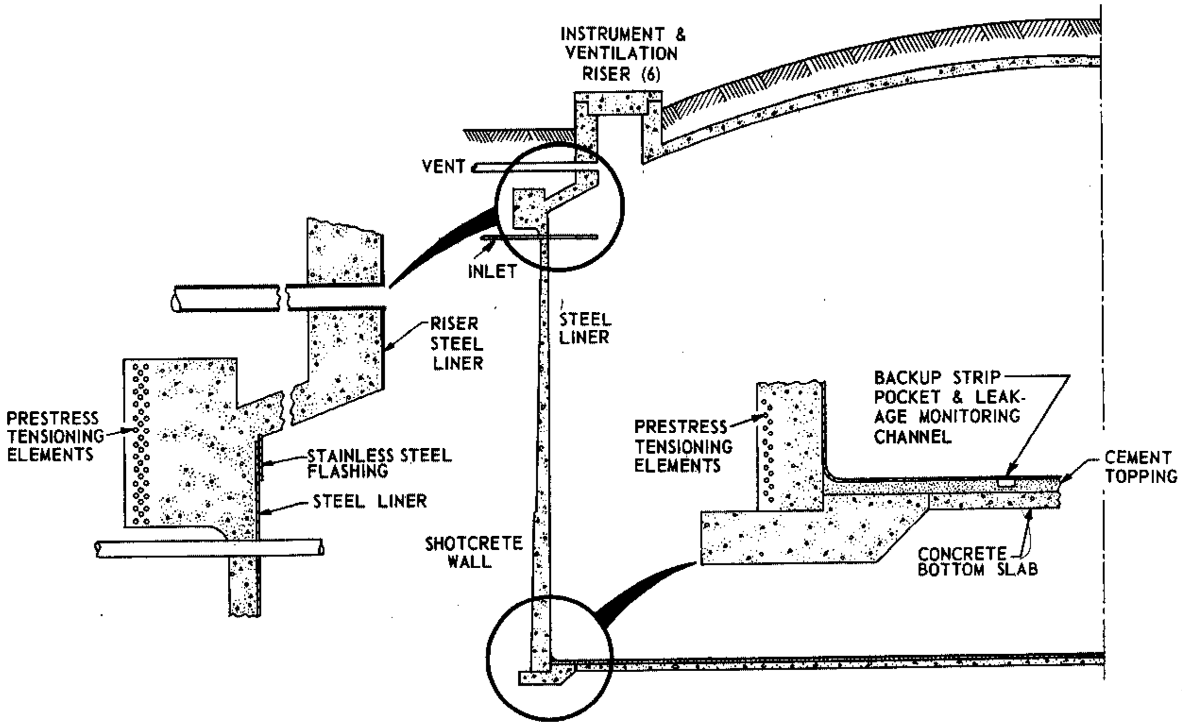

FIG. 2 UNCOOLED STORAGE TANK

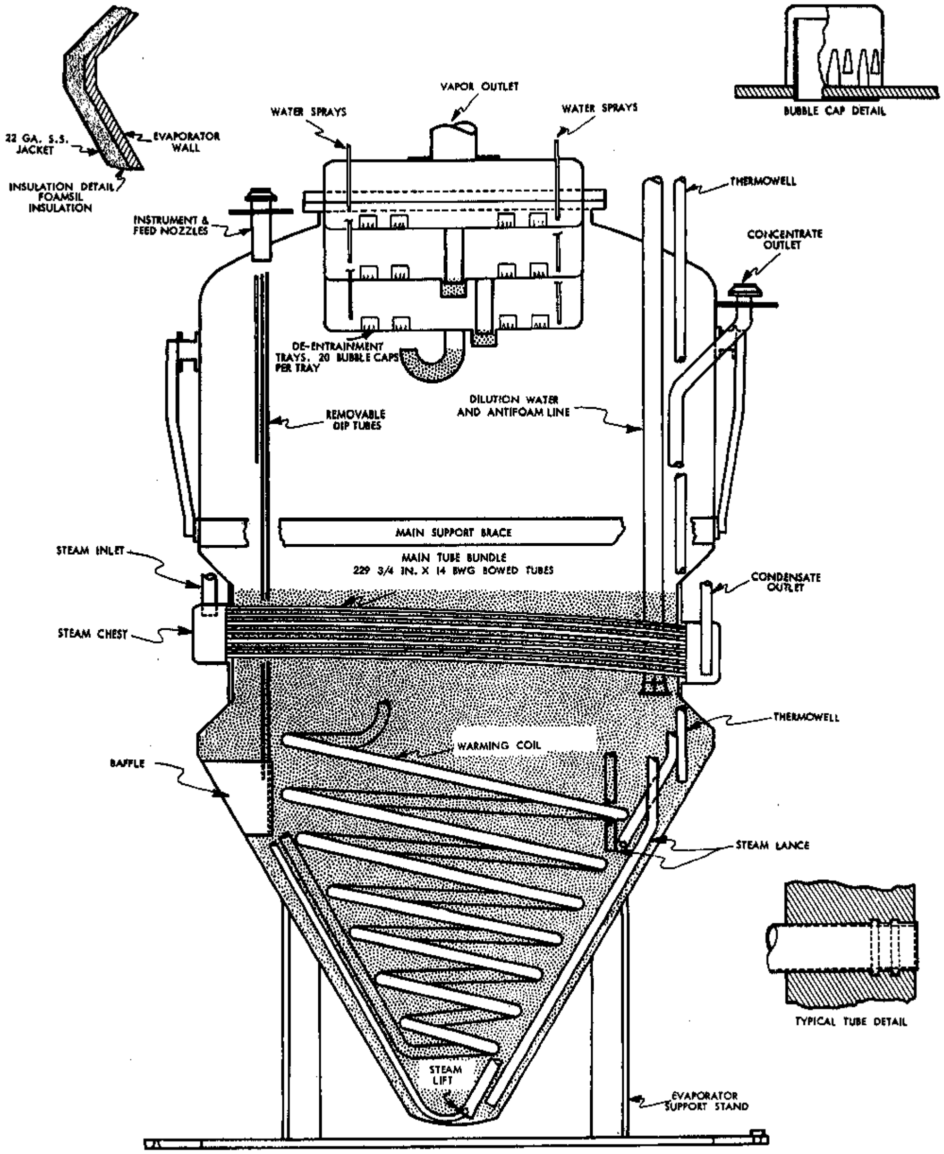

FIG. 3 TANK FARM EVAPORATOR

In some types of waste, large crystalline masses collect on the walls and cooling coils in the waste tanks. Following removal of the liquid phase (predominantly sodium aluminate decanning solution), crystals 8 feet deep on the bottom of the tank, and large deposits of crystals on the walls, thermocouple wells, and dip tubes have been noted. In October 1964, a crystal formation was observed around the center thermowell in Tank 20 that was estimated to be 5-1/2 to 7 feet in diameter and to weigh 30 to 40 tons; a crystal deposit 8 to 12 feet in diameter was on the instrument pipes in this tank (Fig. 4). Without the high-density liquid phase to help support these large crystals, their weight could pull the cooling coils from the tank roof, or collapse the roof. Consequently, the rate of dissolution of synthetic waste crystals was determined to provide basic data for removal of the crystals from the tanks, should this step be necessary.

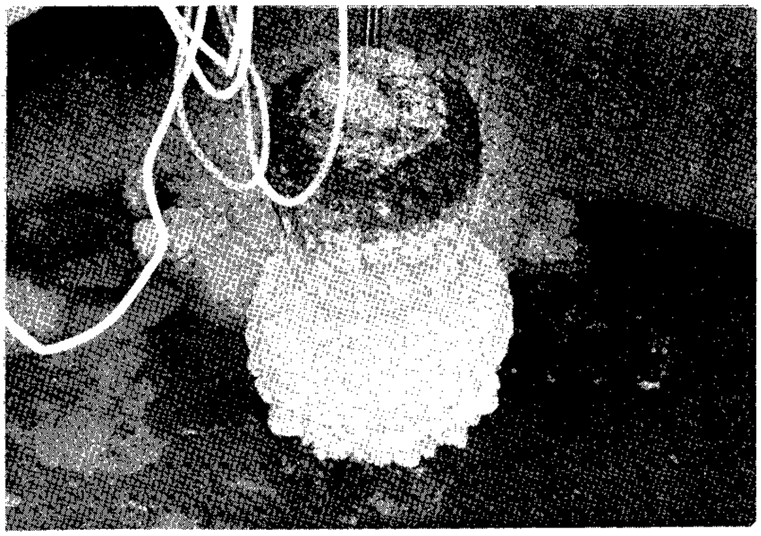

FIG. 4 TWELVE-FOOT-DIAMETER MASS OF CRYSTALS ON 0.8-INCH PIPES

SUMMARY

Tests with both synthetic and actual plant waste showed that all of the radioactive waste stored in the separations areas can be reduced to ~1/3 of its original volume and immobilized by successive evaporation of the decantable liquid. The concentration of ^{137}Cs in the liquid phase of plant waste evaporations increased as much as 17-fold. No vigorous reactions were observed when the solid residues were heated to 700°C.

The measured rates of dissolution for synthetic crystalline wastes indicate that solidified separations wastes from both natural and enriched uranium processing can be dissolved in water in a reasonable time (rates exceeding 0.1 ft/hr).

DISCUSSION

SCOPE OF EXPERIMENTAL WORK

The radioactive wastes stored at SRP are of three general chemical types: coating waste which contains a large amount of sodium aluminate from dissolved aluminum cladding, Purex waste which contains principally sodium nitrate with some sulfate and carbonate, and "HM" waste which is a combination of the previous types and is produced during the co-dissolution of aluminum-uranium alloy. Experiments with synthetic and actual plant waste defined the characteristics of these wastes (physical, chemical, and radiochemical) during evaporation, cooling following evaporation, solidification, and re-dissolution.

PROCEDURE

The waste (synthetic or plant) was concentrated in standard laboratory glassware. The solution volume was normally maintained at 500 ml except during the last stage of the concentration where it was reduced to achieve the desired volume reduction with a reasonable volume of feed. Following the concentration step, the solution was emptied into a weighted graduated cylinder in which total solution volume and solids volume were noted at different temperatures; these measurements were used to calculate specific gravity, volume percent solids, and boildown ratio. (Boildown ratio is the feed volume at 25°C divided by the concentrate volume at the boiling point.) Analytical samples were taken from the liquid phase as needed. Where samples of the solid material were required, the solidified portion was mixed to give a representative sample.

PHYSICAL PROPERTIES OF WASTE

Coating Waste

A synthetic coating waste solution,* concentrated to determine its physical properties, was ideal for further concentration; it contains no solid phase at its boiling point, and a large difference exists between the boiling point of the solution and the temperature at which a solid phase is precipitated. The temperature difference is illustrated in Fig. 5, which shows the measured properties of a simulated supernatant solution after various degrees of concentration. When this solution is concentrated by a factor of 3.4, the hot concentrate is fluid, and a solid phase appears only when the solution is cooled 60°C below the boiling point. Another beneficial characteristic is that the concentrated waste solidifies completely when cooled to room temperature; complete solidification is the ultimate objective of most waste concentration. The viscosity of this solution (Fig. 6) varies between 3 and 70 centipoises over the range of conditions measured.

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* 2.3M $NaAlO_2$, 0.64M $NaNO_2$, 1.4M $NaNO_3$, and 2.3M NaOH.

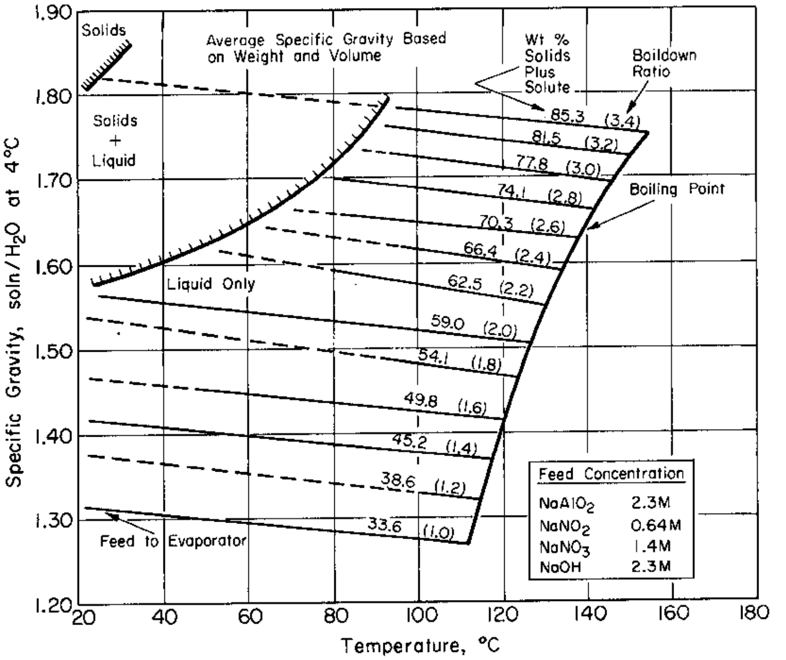

FIG. 5 PHYSICAL PROPERTIES OF SYNTHETIC COATING WASTE

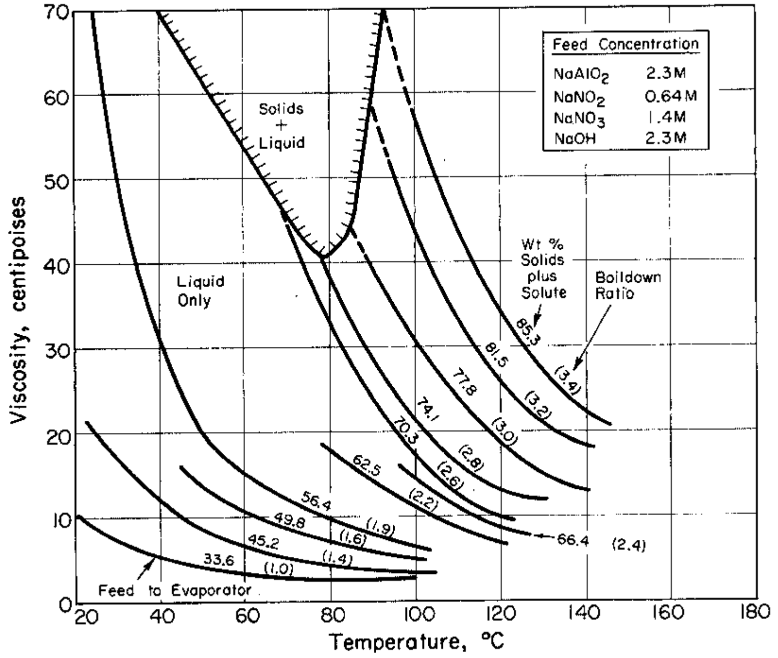

FIG. 6 VISCOSITY OF LIQUID SYNTHETIC COATING WASTE

Purex Synthetic Waste

A synthetic Purex waste* was more difficult to concentrate than coating waste. When concentrated by more than a factor of 2.5, the solution contained a solid phase at the boiling point. The solid phase is initially a sandy, white precipitate of sodium carbonate and sulfate; sodium nitrate is also crystallized as the solution is concentrated further or is cooled. The characteristics measured for a simulated solution of this type during evaporation are shown in Fig. 7 and 8. When concentrated by more than a factor of 3, the solution contains a large amount of solid phase at the boiling point. However, the concentrate does not solidify completely while cooling to 23°C; about one-third remains liquid.

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* 3.4M $NaNO_3$, 0.35M Na_2CO_3, 0.08M Na_2SO_4, 0.30M NaOH, and 0.55M $NaAlO_2$

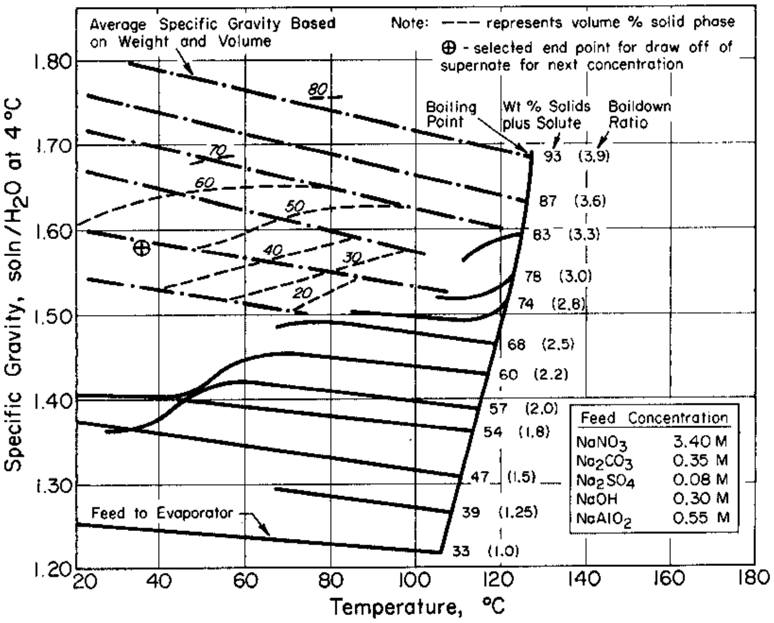


FIG. 7 FIRST CONCENTRATION OF SYNTHETIC PUREX WASTE SUPERNATE PHYSICAL PROPERTIES

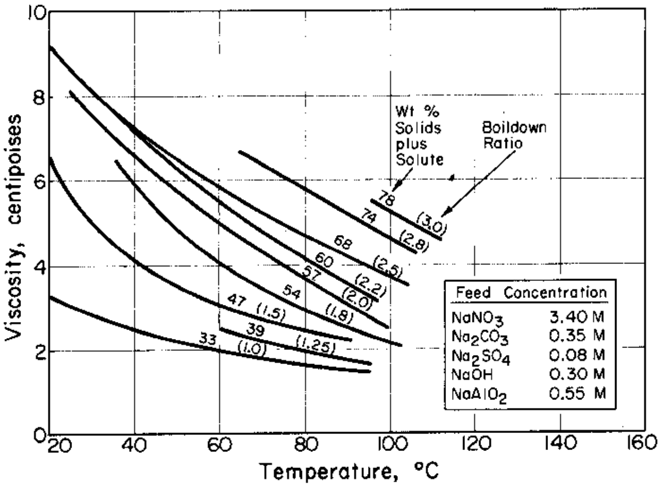


FIG. 8 FIRST CONCENTRATION OF SYNTHETIC PUREX WASTE SUPERNATE
VISCOSITY OF LIQUID

Synthetic Purex waste that simulated cooled supernate from a first waste evaporation in the F-Area tank farm evaporator was concentrated in the laboratory. The characteristics of this supernate during concentration, shown in Fig. 9 and 10, are similar to those of the waste during the first concentration (Fig. 7 and 8). In accordance with concentration that would be applicable to plant operation, the synthetic supernate was concentrated by a factor of 1.6 and the concentrate was allowed to cool to about 50°C; at this temperature the concentrate was about 50 vol % solids. The resulting liquid was collected, and the characteristics of this material were measured during its third concentration (one "plant", two laboratory). These characteristics, shown in Fig. 11 and 12, were quite similar to those of the preceding concentrations. A boildown ratio of about 2 gave a solution which should be readily transferable when hot, but again did not completely solidify when cooled to 23°C (about 75 vol % solids). Cooling to 40°C, which is more representative of plant operation, gave a concentrate of about 70 vol % solids.

Another synthetic waste solution was made, based on analysis of the liquid supernate from the third concentration after cooling to 40°C. This material when concentrated acted similarly to the sodium aluminate-hydroxide solution (coating waste), rather than to the unconcentrated waste. Such behavior and the characteristics shown in Fig. 13 were expected because of the composition of the waste. The concentrate was free flowing when hot, and set up as a solid when cooled to about 30°C.

A representative plan for concentration and complete solidification of aqueous waste from the Purex process is outlined in Fig. 14, and illustrated with the data described above. This plan requires four stages of concentration, and gives an overall volume reduction of about three.

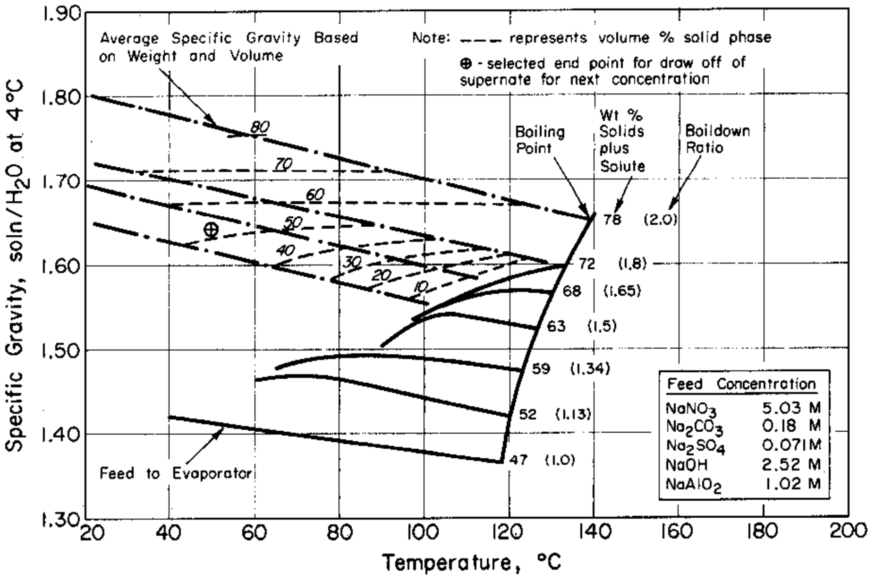


FIG. 9 SECOND CONCENTRATION OF SYNTHETIC PUREX WASTE SUPERNATE
PHYSICAL PROPERTIES

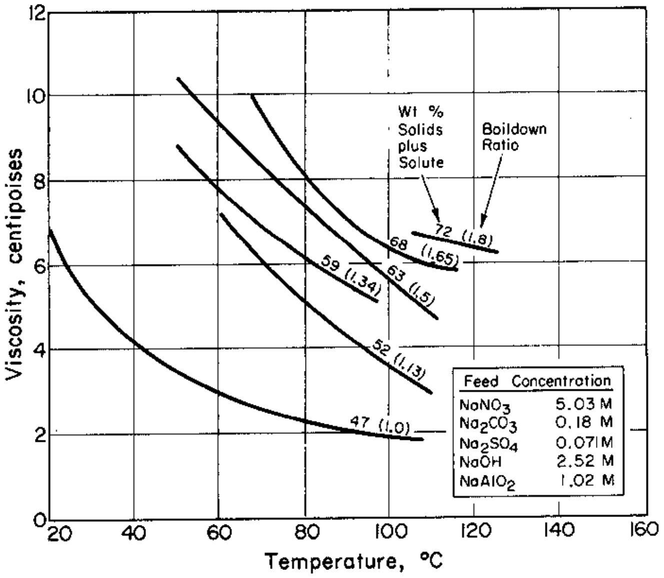


FIG. 10 SECOND CONCENTRATION OF SYNTHETIC PUREX WASTE SUPERNATE
VISCOSITY OF LIQUID

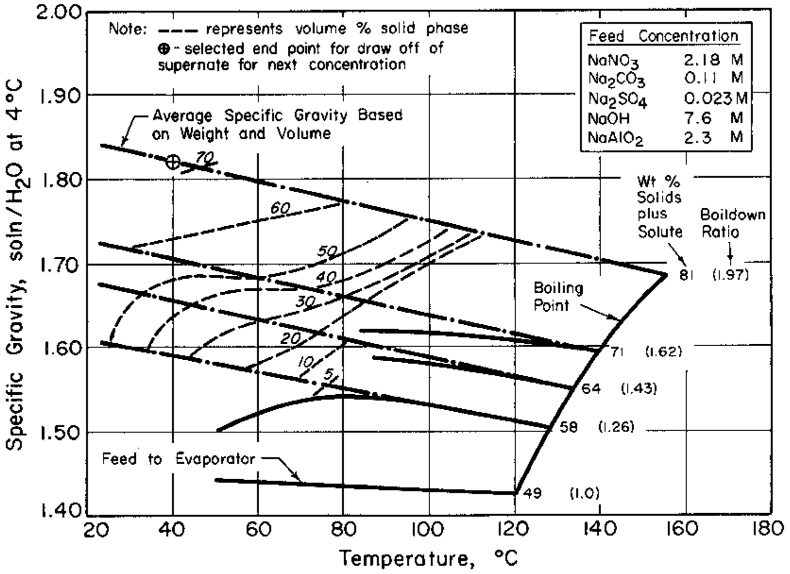


FIG. 11 THIRD CONCENTRATION OF SYNTHETIC PUREX WASTE SUPERNATE PHYSICAL PROPERTIES

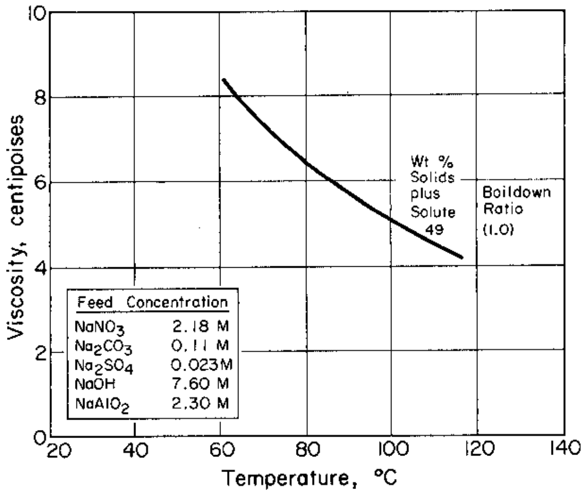


FIG. 12 THIRD CONCENTRATION OF SYNTHETIC PUREX WASTE SUPERNATE VISCOSITY OF LIQUID

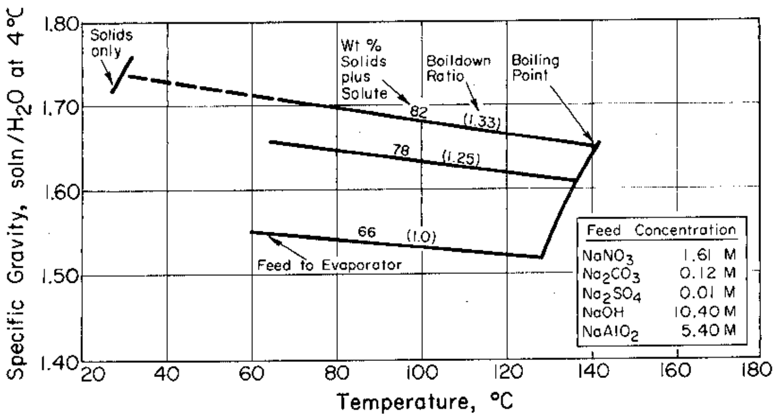
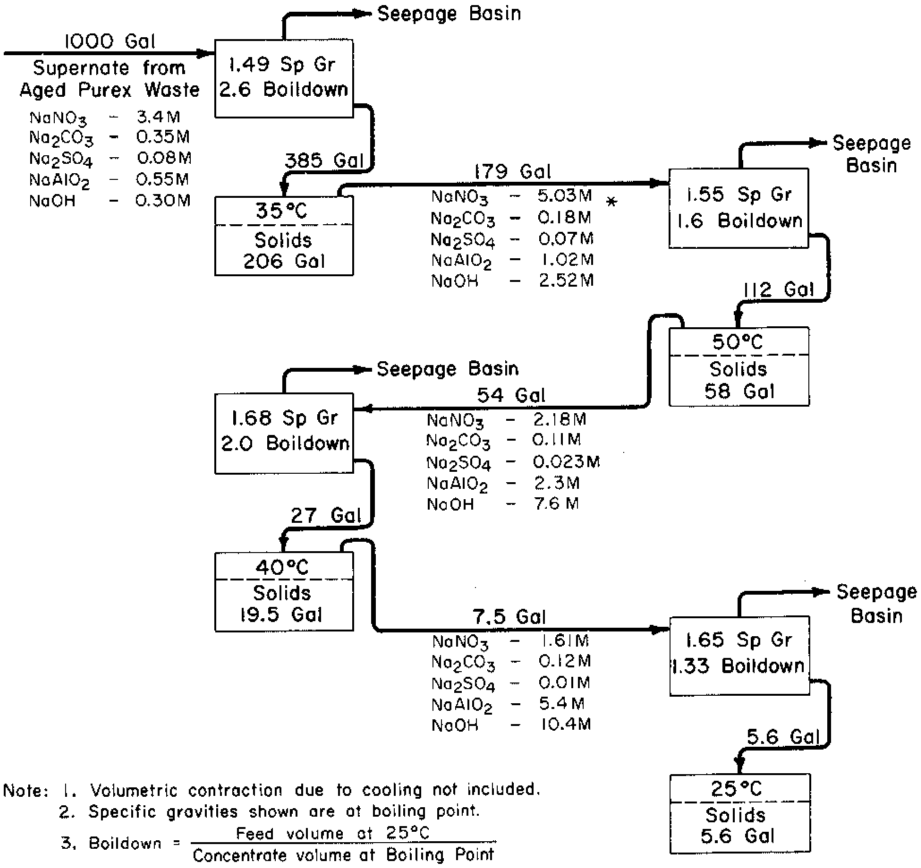


FIG. 13 FOURTH CONCENTRATION OF SYNTHETIC PUREX WASTE SUPERNATE - PHYSICAL PROPERTIES



Note: 1. Volumetric contraction due to cooling not included.
2. Specific gravities shown are at boiling point.
3. Boildown = $\frac{\text{Feed volume at 25°C}}{\text{Concentrate volume at Boiling Point}}$

* Composition based on analysis of waste (Tanks 19F - 1962) which has been concentrated once in the storage area evaporator. (See page 14.)

FIG. 14 SUGGESTED METHOD FOR CONCENTRATION OF SYNTHETIC PUREX WASTE

The procedure is effective because the sodium carbonate-sulfate can be precipitated in the evaporator and carried as a slurry to the waste tank, where it settles. Presumably sodium nitrate could be removed by the same mechanisms, but its large temperature-solubility coefficient allows almost complete removal when the tank contents are cooled.

The effect of cooling on the concentration of chemical components in the waste supernate was determined in the laboratory for the synthetic Purex waste solution (Fig. 7). The synthetic waste feed was concentrated to a boildown ratio of 3.0, and the supernate was analyzed for chemical content at different temperatures. The fractions of the waste components remaining in the supernate at various temperatures are shown in Fig. 15.

Purex Plant Waste

Prior to concentration of actual plant waste, synthetic waste solutions representative of the supernate in Tank 2F (Purex) were evaporated in the laboratory to provide guidelines for concentrating the plant waste. This synthetic waste was evaporated twice (Fig. 16 and 17); the results were similar to, and supplement, the comprehensive data in Fig. 7 through 10.

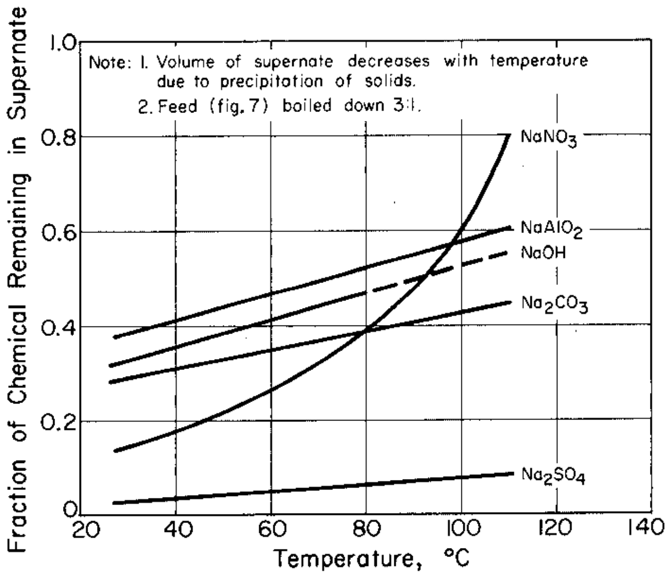


FIG. 15 EFFECT OF TEMPERATURE ON COMPOSITION OF SYNTHETIC PUREX WASTE SUPERNATE

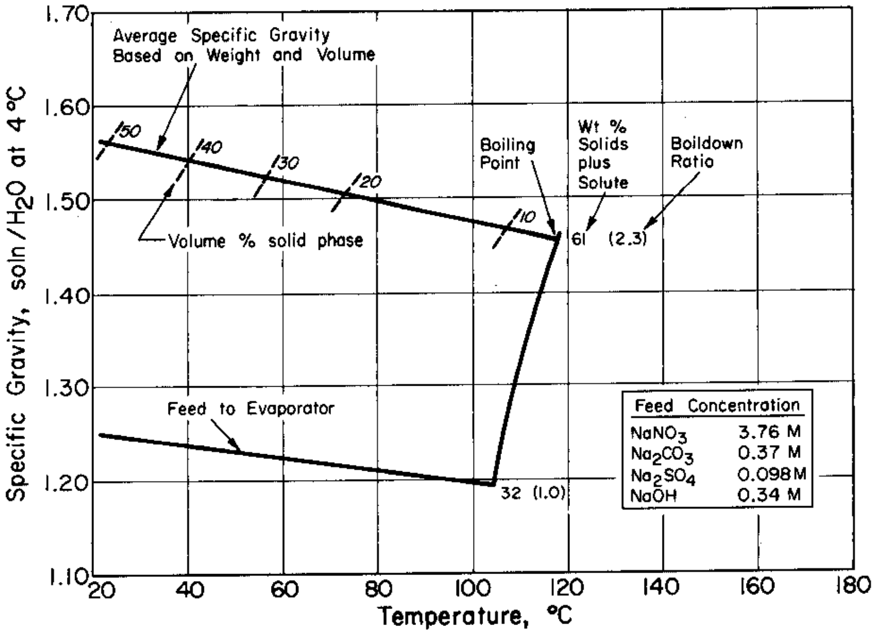


FIG. 16 FIRST CONCENTRATION OF WASTE SUPERNATE (SYNTHETIC PUREX WASTE REPRESENTATIVE OF TANK 2F)

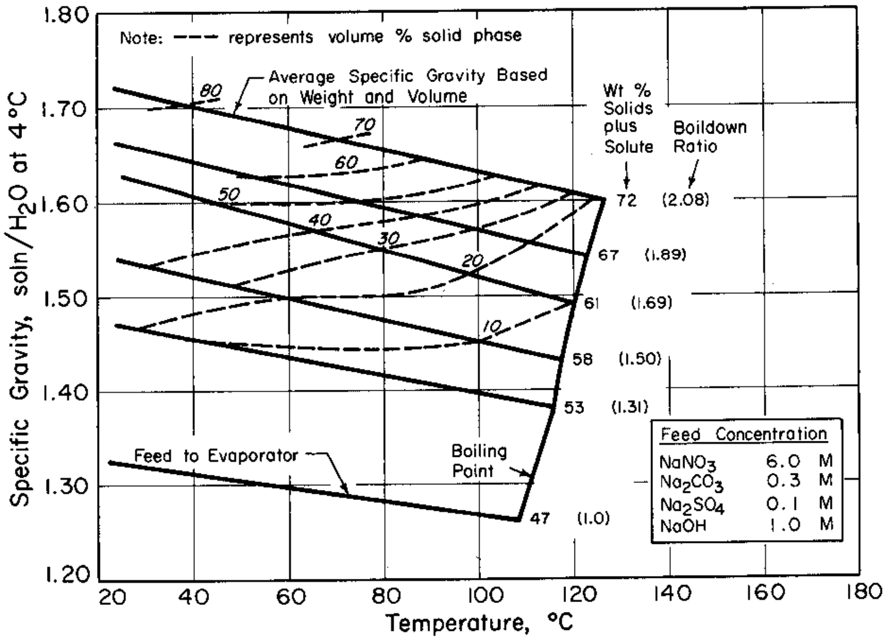


FIG. 17 SECOND CONCENTRATION OF WASTE SUPERNATE (SYNTHETIC PUREX WASTE REPRESENTATIVE OF TANK 2F)

A 17-liter sample of the supernatant solution from Waste Storage Tank 2 in F Area was concentrated in the laboratory High Level Caves. The waste was evaporated sufficiently that 50 vol % of solid material crystallized when the concentrate was cooled to about 25°C. The same process was repeated sequentially in two more evaporations. The supernate from the third evaporation was then evaporated a fourth time so that when the material cooled, it was almost completely solidified. The final waste concentration resulted in 97 vol % solid phase when cooled to 25°C (a small sample of supernate was needed for analysis). The final liquid volume was only 0.06% of the original waste volume; the volume of solid material accumulated during the four concentrations was 33% of the initial volume of waste.

The data obtained during these evaporations are summarized in Table I, and the formation of solid phase during cooling of each concentrate is shown in Fig. 18. The results are similar to those obtained with the synthetic wastes. Analyses for the concentration series are shown in Table II.

TABLE I

EVAPORATION OF PLANT PUREX WASTE

	Concentration			
	First	Second	Third	Fourth
Feed Material	Tank 2 Supernate	Supernate from 1st evap	Supernate from 2nd evap	Supernate from 3rd evap
Boildown ratio	2.13	1.43	1.20	1.48
Vol of feed @ 25°C / Vol of supernate @ 25°C	4.28	3.63	2.41	40 (10 cc supernate)
Boiling point, °C	117	124	125	132
Number of batches in evaporation	16	5	2	1
Vol of solids @ 25°C / Vol of feed @ 25°C	0.208	0.360	0.345	0.591
Average specific gravity based on weight and volume				
30°C	1.58	1.52	1.58	1.71
Boiling Point	1.48	1.62	1.47	1.61
Cumulative volume of solid phase at 25°C/step 1 feed volume	0.208	0.292	0.314	0.33

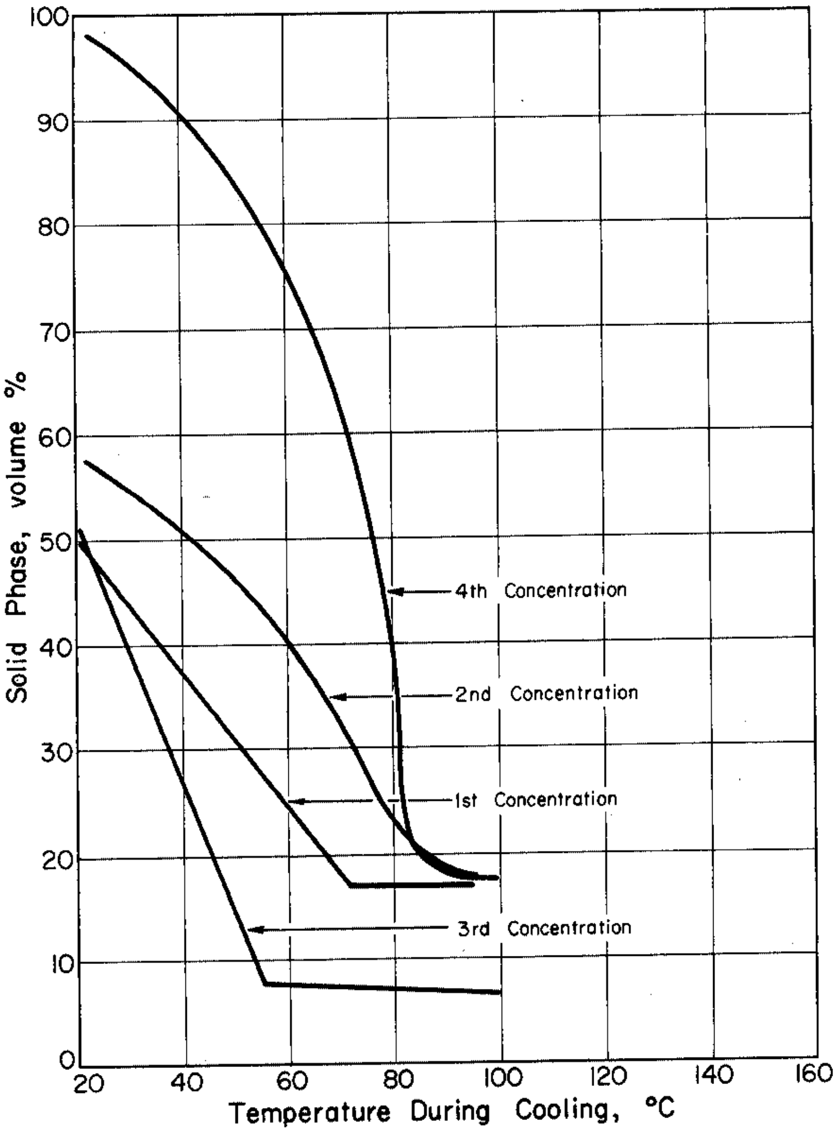


FIG. 18 SOLIDIFICATION OF CONCENTRATED PUREX WASTE

TABLE II

ANALYSIS OF SUPERNATE FROM CONCENTRATION OF TANK 2 PLANT PUREX WASTE

		Supernate from 1st Concentration				
	Plant Feed	90°C*	75°C*	50°C*	25°C*	Composite @ 25°C
Gross α, d/(min)(ml)	5.9×10^4	4.1×10^3	3.1×10^3	3.0×10^3	2.5×10^2	-
Gross β, c/(sec)(ml)	2.4×10^7	7.0×10^7	6.4×10^7	7.0×10^7	5.7×10^7	6.9×10^7
Sr β, c/(min)(ml)	2.9×10^5	3.8×10^4	1.4×10^4	6.6×10^3	5.0×10^3	2.2×10^4
^{137}Cs, d/(min)(ml)	4.6×10^8	1.1×10^9	1.0×10^9	1.0×10^9	8.8×10^8	1.3×10^9
Ce-^{144}Pr, c/(sec)(ml)	17	<60	120	55	<45	156
Total rare earths, c/(min)(ml)	4.7×10^5	5.3×10^4	2.7×10^4	1.8×10^4	7.0×10^3	3.7×10^4
NO_3^-, M	4.2	-	-	-	-	3.23
NO_2^-, M	0.91	-	-	-	-	3.3
OH^-, N	0.033	-	-	-	-	0.59
HCO_3^-, N	0.0037	-	-	-	-	0.22
Al^{3+}, M	0.007	-	-	-	-	0.0099
CO_3^{2-}, N	0.95	-	-	-	-	0.68
Cl^-, ppm	365	-	-	-	-	135
PO_4^{2-}, M	0.0061	-	-	-	-	0.014
Fe, M	$<4\times10^{-5}$	-	-	-	-	-
Na+, M	5.78	-	-	-	-	-
Total solids, %	45.5	-	-	-	-	54.5 (47**)
Sp Gr	1.27	-	-	-	-	1.56 (1.45**)
pH	11	-	-	-	-	11
Pu, d/(min)(ml)	3.2×10^3	-	-	-	-	-
U, g/l	2.2×10^3	-	-	-	-	3×10^{-3}
Reducing normality	0.28	-	-	-	-	1.94

---

* Temperature at which sample was taken.

** Analyses for total solids and specific gravity were made approximately one year later than the other analyses. To compensate for water lost in the intervening period, the samples were re-analyzed for ^{137}Cs, and the total solids and specific gravity were adjusted according to the indicated change in ^{137}Cs concentration. Values shown in parentheses were estimated from work with synthetic waste solutions.

NOTE: Gross γ was all ^{137}Cs.

TABLE II (Continued)

ANALYSIS OF SUPERNATE FROM CONCENTRATION OF TANK 2 PLANT PUREX WASTE

Supernate from 2nd Concentration					Supernate from 3rd Concentration				Supernate from 4th Concentration @ 25°C
100°C*	75°C*	50°C*	23.7°C*	Composite @ 25°C	100°C*	75°C*	50°C*	Composite @ 25°C	
-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	$4.0x10^8$
$1.7x10^3$	$1.1x10^3$	$5.2x10^2$	$5.2x10^2$	$2.4x10^3$	$3.0x10^2$	$3.1x10^2$	$6.0x10^2$	680	830
$1.6x10^9$	$1.9x10^9$	$1.6x10^9$	$1.7x10^9$	$2.3x10^9$	$1.4x10^9$	$4.2x10^9$	$3.8x10^9$	$3.8x10^9$	$8.0x10^9$
52	41	-	-	-	-	-	-	-	-
$6.2x10^3$	$5.7x10^3$	$2.9x10^3$	$3.3x10^3$	-	-	-	-	-	-
-	-	-	-	3.23	-	-	-	2.04	3.17
-	-	-	-	1.23	-	-	-	4.52	3.46
-	-	-	-	0.88	-	-	-	1.92	4.51
-	-	-	-	0.077	-	-	-	0.47	0.66
-	-	-	-	0.015	-	-	-	0.018	0.025
-	-	-	-	0.69	-	-	-	0.75	0.76
-	-	-	-	-	-	-	-	-	
-	-	-	-	0.0117	-	-	-	0.018	0.041
-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-	-
-	-	-	-	60.3 (48**)	-	-	-	69.3 (60**)	63 (66**)
-	-	-	-	1.44 (1.45**)	-	-	-	1.57 (1.53**)	1.63 (1.58**)
-	-	-	-	-	-	-	-	-	-
-	-	-	-	-	-	-	-	$1.3x10^3$	$9.3x10^2$
-	-	-	-	-	-	-	-	-	-
-	-	-	-	0.100	-	-	-	0.78	0.33

"HM" Synthetic Waste

A synthetic "HM" waste,* representative of the material present in Tank 11 in H Area, was concentrated to determine its physical properties prior to evaporation of actual plant waste from this tank. In this initial evaporation (Fig. 19), "HM" waste behaved similar to Purex waste.

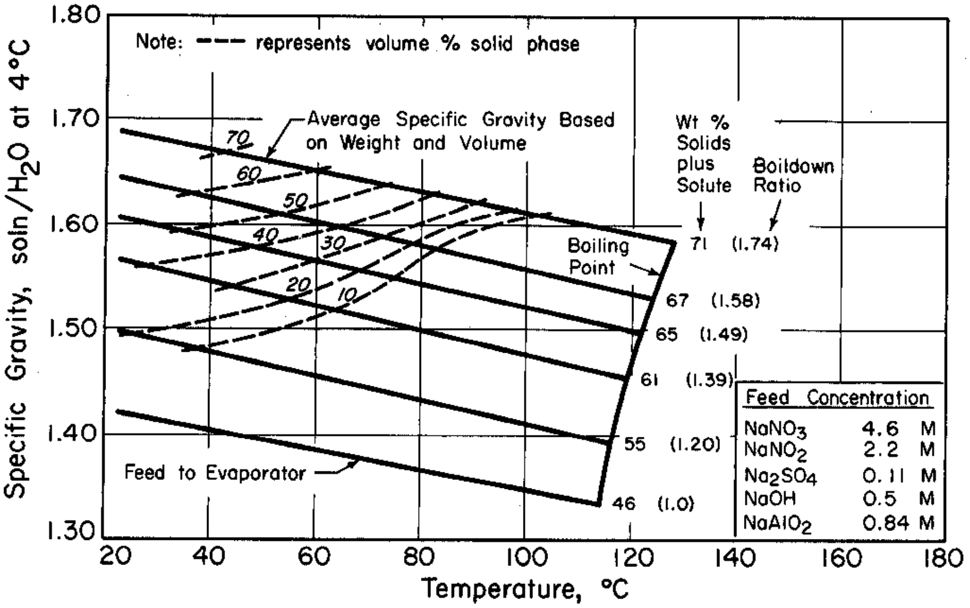


FIG. 19 FIRST CONCENTRATION OF WASTE SUPERNATE - SYNTHETIC "HM" WASTE REPRESENTATIVE OF TANK 11

"HM" Plant Waste

An 8-liter sample of the supernatant solution from Waste Storage Tank 11 in H Area was concentrated in the High Level Caves by the procedures described for the Purex plant waste. The supernate from the second successive evaporation was evaporated a third time so that when the material cooled to 40°C, it was completely solidified. Solutions with high NaOH and $NaAlO_2$ concentrations solidify over a narrow temperature range (Fig. 20). The solid material accumulated during the three evaporations was 40% of the initial volume of waste. The data obtained during these concentrations, summarized in Table III, are similar to those observed with synthetic wastes. Analyses for the concentration series are shown in Table IV.

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* 4.6M $NaNO_3$, 2.2M $NaNO_2$, 0.11M Na_2SO_4, 0.5M NaOH, and 0.84M $NaAlO_2$

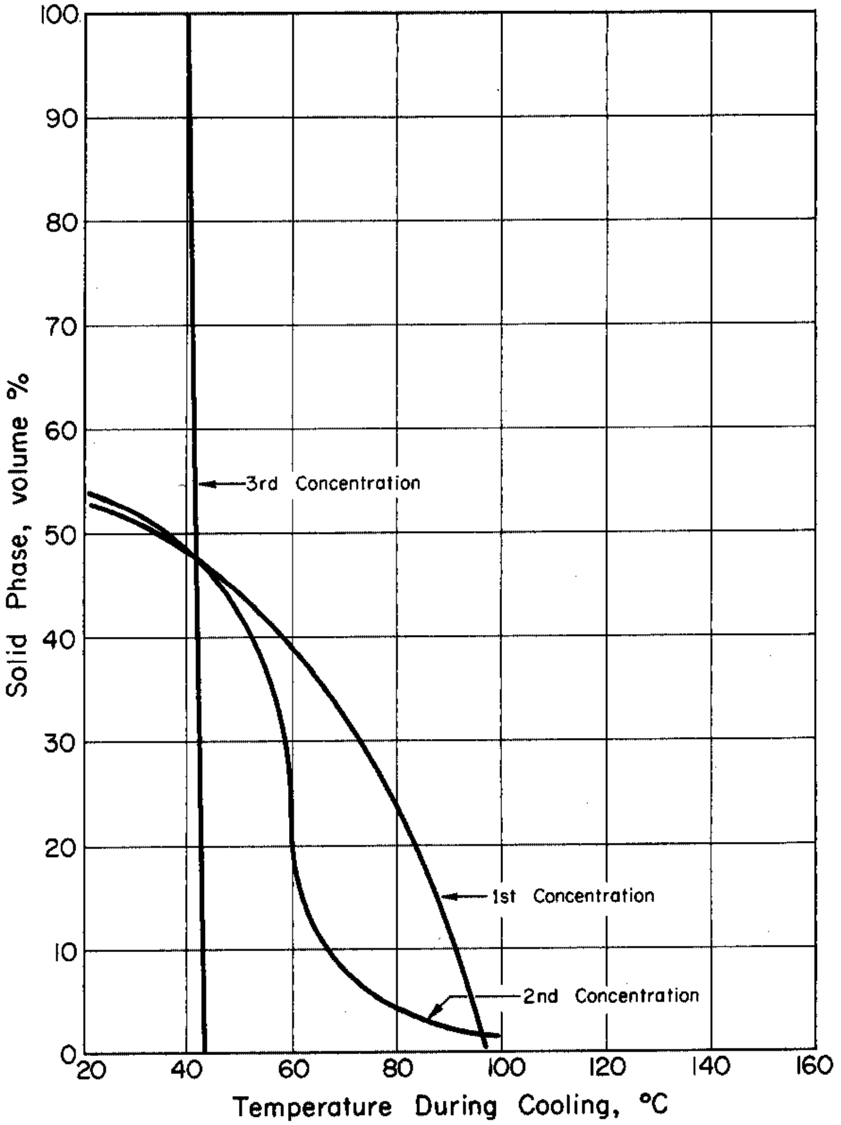

FIG. 20 SOLIDIFICATION OF CONCENTRATED "HM" WASTE

TABLE III

EVAPORATION OF "HM" WASTE

	Concentration		
	First	Second	Third
Feed Material	Tank 11 Supernate	Supernate from 1st evap	Supernate from 2nd evap
Boildown ratio	1.71	1.50	1.45
Vol of feed @ 25°C / Vol of supernate @ 25°C	3.98	3.54	No Supernate
Boiling point, °C	126	135	156
Number of batches in evaporation	8	2	1
Vol of solids @ 25°C / Vol of feed @ 25°C	0.279	0.320	0.616
Average specific gravity based on weight and volume			
30°C	1.60	1.64	1.69
Boiling point	1.50	1.52	1.45
Cumulative volume of solid phase at 25°C/step 1 feed volume	0.279	0.359	0.403

TABLE IV

ANALYSIS OF SUPERNATE FROM CONCENTRATION OF TANK 11 PLANT WASTE ("HM")

		Supernate from 1st Concentration				Supernate from 2nd Concentration			
	Plant Feed	100°C*	75°C*	50°C*	Composite @ 25°C	100°C*	75°C*	50°C*	Composite @ 25°C
Gross β, c/(sec)(ml)	-	$2.8x10^8$	$1.8x10^8$	$2.6x10^8$	$6.6x10^8$	$1.1x10^9$	$5.8x10^9$	$3.6x10^9$	$1.4x10^9$
Sr β, c/(min)(ml)	$2.8x10^8$	-	-	-	-	-	-	-	-
^{137}Cs, d/(min)(ml)	$5.0x10^9$	$5.3x10^9$	$3.42x10^9$	$5.35x10^9$	$1.2x10^{10}$	$8.4x10^9$	$1.10x10^{10}$	$6.8x10^9$	$2.7x10^{10}$
Total rare earths, c/(min)(ml)	-	-	-	-	-	$1.03x10^3$	-	$1.12x10^3$	-
Ru, d/(min)(ml)	$3.9x10^6$	$5.9x10^6$	-	-	$1.2x10^7$	$2.1x10^7$	-	$2.0x10^6$	-
Pm, d/(min)(ml)	$4.9x10^6$	$1.5x10^5$	-	-	$7.0x10^6$	$2.7x10^7$	-	$2.16x10^6$	-
NO_3^-, M	4.4	4.77	-	-	3.18	4.32	-	0.66	-
NO_2^-, M	0.54	0.64	-	-	1.35	2.1	-	0.74	-
OH^-, N	1.25	1.4	-	1.5	2.98	4.2	2.73	1.42	6.6
Al^{3+}, M	0.31	0.39	-	-	0.70	1.1	-	0.396	1.32
CO_3^{2-}, N	1.02	1.0	-	1.3	2.40	4.2	1.9	1.52	4.57
PO_4^{2-}, M	-	$<7x10^{-3}$	-	-	$<5x10^{-3}$	$<6x10^{-3}$	-	$<4x10^{-3}$	-
Fe, M	$<<10^{-3}$	-	-	-	-	-	-	-	-
Na+, M	7.72	-	-	-	-	15.4	5.08	-	-
Total solids, %	50	-	-	-	48	-	-	-	55.3
Sp Gr	1.42	-	-	-	1.48	-	-	-	1.60
pH	>11	>11	>11	>11	>11	>11	>11	>11	>11
Pu, d/(min)(ml)	$1.2x10^4$	-	-	-	-	-	-	-	-
U, g/l	$2.6x10^{-3}$	$4.2x10^{-3}$	-	-	$6.6x10^{-3}$	$1.1x10^{-2}$	-	$4.3x10^{-3}$	-
Reducing normality	0.97	1.7	-	-	3.22	4.2	-	2.04	-

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* Temperature at which sample was taken.

NOTE: Gross γ was all ^{137}Cs.

HIGH TEMPERATURE PROPERTIES OF CONCENTRATED WASTE

Synthetic Waste

Synthetic waste solutions were heated slowly to 700°C to simulate possible fission product decay heating of the stored immobile waste, and to allow evaluation of (1) the possibility of an explosion hazard in the waste tank, and (2) changes in the characteristics of the waste that might affect adversely its heat transfer properties.

No explosive behavior was observed when the four representative synthetic waste solutions listed in Table V were heated to 700°C in air. The temperature at which changes were observed varied with the type of waste, as shown in Table VI. Of the wastes listed, only concentrates B and C from the first and second supernatant evaporations are relevant to the problem of overheating; the coating waste A has very low fission product content, and the third evaporation D removes only about 3% of the total water. Concentrates B and C lose water between 125 and 160°C, melt at 250 to 350°C, and remain fluid to at least 400°C before decomposition; therefore, no deterioration in heat transfer within the tank is expected until the temperature exceeds 400°C.

TABLE V

EVAPORATOR PREPARATION OF SOLID WASTE RESIDUES FOR TEST

TABLE V

EVAPORATOR PREPARATION OF SOLID WASTE RESIDUES FOR TEST

Evaporator Feed		Composition, M						Volume Reduction,	Volume of Solid at 22°C,
Type	Simulated Waste	$NaNO_3$	$NaNO_2$	$NaAlO_2$	Na_2CO_3	Na_2SO_4	NaOH	feed/conc	% of concentrate
A	Coating waste	1.4	0.64	2.3	-	-	2.3	3.2	100
B	Supernate from Purex waste (1st evaporation)	3.4	-	0.55	0.35	0.08	0.30	2.8	65
C	Supernate from single evaporation of Feed B (2nd evaporation)	5.03	-	1.02	0.18	0.071	2.52	1.7	70
D	Supernate from single evaporation of Feed C (3rd evaporation)	2.18	-	2.3	0.11	0.023	7.6	1.8	70

TABLE VI

PHYSICAL PROPERTIES OF SOLID PORTION OF CONCENTRATE

Concentrate* from Evap Feed	Free Water Evaporated	Solids Melted	Decomposition Started	Temperature at which Color Changes Occurred	Condition of Sample
A	150-175°C	No melting up to 700°C	No indication up to 700°C	475°C, white to light yellow	Powdery after heating to 700°C; severe foaming when free water evaporated
B	125-140°C	250-300°C	450°C	425°C, clear to light green	Crystalline when cooled after heating to 495°C; powdery after heating to 700°C
C	110-160°C	300-340°C	420°C	340°C, clear to light green	Powdery after heating to 700°C; hygroscopic
D	150-190°C	No melting up to 700°C	No indication up to 700°C	275°C, white to brown-green; 325°C, to olive; 510°C, to grey	Powdery after heating to 700°C; hygroscopic

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* See Table V.

Plant Waste

Solidified residues from each stage of evaporation of the plant waste (both Purex and "HM") were heated to 700°C in air; no vigorous reactions were observed. Temperatures at which the physical characteristics of the waste changed are shown in Tables VII and VIII. The plant wastes behave similar to the synthetic waste: the concentrates from the first three evaporations of Purex waste and the first evaporation of "HM" waste melted at 200 to 300°C and remained fluid until about 600°C, at which temperature they began to decompose rapidly.

TABLE VII

HEATING OF SOLID PHASE OF CONCENTRATED PUREX WASTE

	Temperature Ranges, °C			
Solid waste from evaporation*	1	2	3	4
Free water evaporation	100-130	120-130	120-180	130-220
Solid phase melting	230-280	230-275	190	220
Color changes	440[a]	350[b]	220[c]	230[d]
Decomposition starts	630[e]	670[f]	610[g]	635

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* See Fig. 18.

[a] Clear to dark.

[b] White to light brown, followed at 530°C by clear brown liquid.

[c] White to brown, clearing at 325°C.

[d] White to light brown.

[e] Slight preliminary decomposition (perhaps of nitrite) at 240°C.

[f] Some foaming at 280-305°C (perhaps due to nitrite decomposition).

[g] Slight preliminary decomposition at 300°C.

TABLE VIII

HEATING OF SOLID PHASE OF CONCENTRATED "HM" WASTE

	Temperature Ranges, °C		
Solid waste from evaporation*	1	2	3
Free water evaporation	130-140	126-300	160-250
Solid phase melting	260-280	300	350
Color changes	280(a)	300(b)	350(b)
Decomposition	575-625	420-470	-

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* See Fig. 20.

(a) White crystals to brown liquid.

(b) Milky to light grey.

DISTRIBUTION OF ^{137}Cs AND OTHER RADIOISOTOPES DURING EVAPORATION

Purex Waste

The distribution of ^{137}Cs and other radioisotopes was determined for each evaporation step of plant Purex waste. Table IX shows that the ^{137}Cs concentrates in the liquid phase. The ^{137}Cs was ~17 times more concentrated in the final 10 ml of liquid than in the initial 17 liters of plant waste. Other radiochemical analyses for the concentration series are shown in Table II.

TABLE IX

DISTRIBUTION OF ^{137}Cs IN EVAPORATED PUREX WASTE @ 25°C

Evaporation	^{137}Cs in Liquid Phase,(a) d/(min)(ml)	Ratio of Activities,(a) liquid phase/solid phase
Feed	0.46×10^9	- -
First	1.3×10^9	1.49, 1.89
Second	2.3×10^9	1.36, 1.61
Third	3.8×10^9	2.18, 4.54
Fourth	8.0×10^9	1.22, 1.38

(a) Based on zero and 30 vol % void in solid phase, respectively.

"HM" Waste

The distribution of ^{137}Cs and other radioisotopes was determined for each evaporation step of plant "HM" Waste. Similar to behavior in the Purex waste, the ^{137}Cs concentrates in the liquid phase, as shown in Table X. The ^{137}Cs was 8.7 times more concentrated in the solids left from the final evaporation than in the initial 8 liters of plant waste. Other radiochemical analyses for the concentration series are shown in Table IV.

TABLE X

DISTRIBUTION OF ^{137}Cs IN EVAPORATED "HM" WASTE @ 25°C

Evaporation	^{137}Cs in Liquid Phase, d/(min)(ml)	Ratio,(a) liquid phase/solid phase
Feed	0.5×10^{10}	- -
First	1.2×10^{10}	1.71, 2.45
Second	2.67×10^{10}	1.42, 2.32
Third	4.33×10^{10}(b)	- -

(a) Based on zero and 30 vol % void in solid phase, respectively.

(b) No liquid phase present; values shown were calculated by volumetric reduction and uniform distribution.

DISSOLUTION OF SOLIDIFIED WASTE

Preparation of Crystals

During all evaporations the Na_2SO_4, $NaNO_3$, and Na_2CO_3 concentrate predominantly in the solid material, and the supernate is enriched in NaOH and $NaAlO_2$. In the final concentration (completely solid when cooled), the solution is greatly enriched in NaOH and $NaAlO_2$.

Test crystals of the solid waste materials were produced by maintaining concentrated synthetic wastes at ~40°C for 1 week. Photographs of two types of solidified waste, one high in $NaNO_3$ and the other high in $NaAlO_2$, are shown in Fig. 21 and 22. Although both types of waste are crystalline, the $NaNO_3$ type has large brittle crystals, whereas the $NaAlO_2$ type has smaller crystals in a random pattern. When simulated Purex separations waste* was concentrated 2.6-fold by evaporation and allowed to cool slowly, large masses were formed of a light, highly crystalline $NaNO_3$ solid that dissolved rapidly even in cold water.

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* 3.4M $NaNO_3$, 0.35M Na_2CO_3, 0.08M Na_2SO_4, 0.27M NaOH, and 0.55M $NaAlO_2$

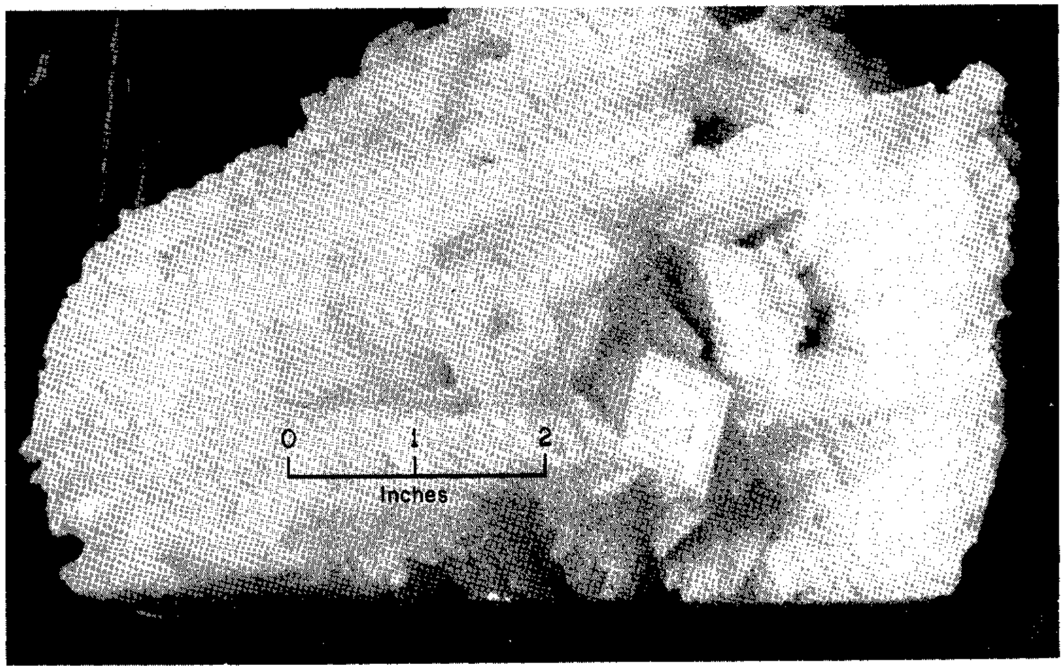

FIG. 21 $NaNO_3$ CRYSTALLINE WASTE

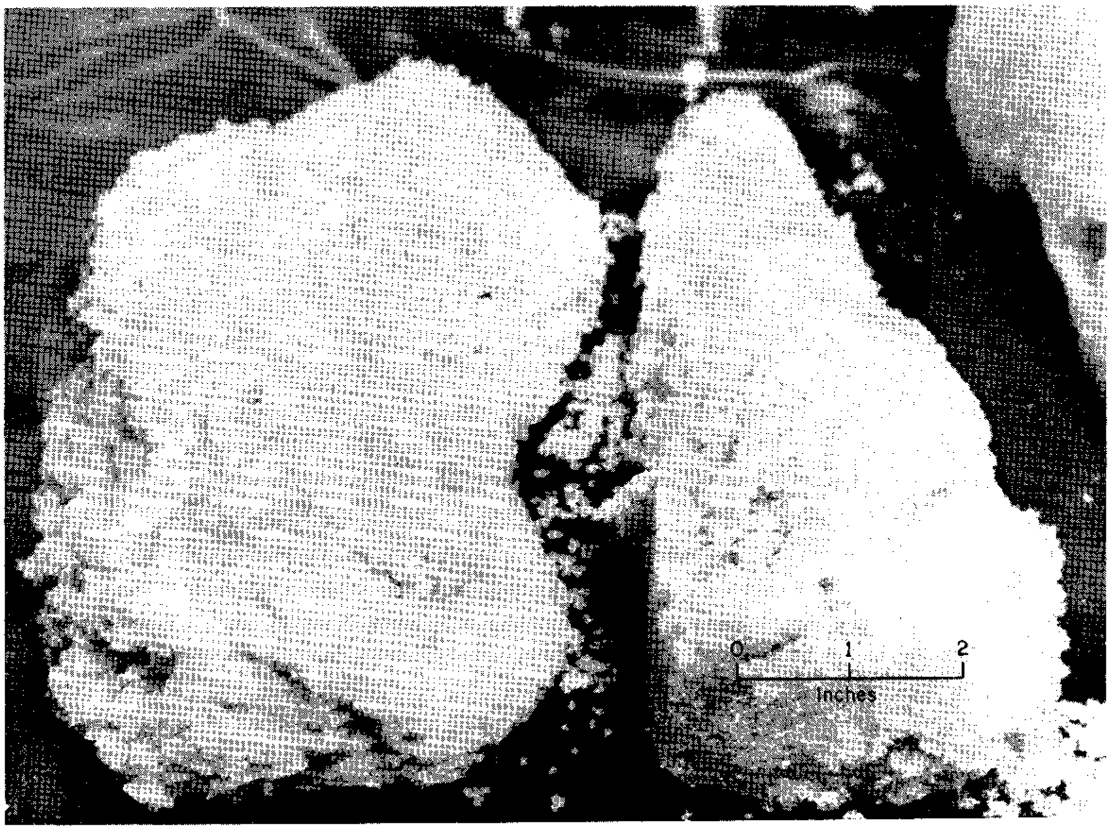

FIG. 22 $NaAlO_2$ CRYSTALLINE WASTE

A dried, granular waste, shown in Fig. 23, was obtained by oven-heating the crystalline $NaNO_3$ wastes (simulation of heat by radioactive decay) at 130-140°C for a week. This heating caused the volume to increase by formation of cavities of varying size in the product, apparently due to removal of water of hydration. One batch of extremely hard, granular material was obtained when the temperature controller failed and the material remained considerably above 140°C for three days. These samples could be sawed only with power tools under considerable pressure.

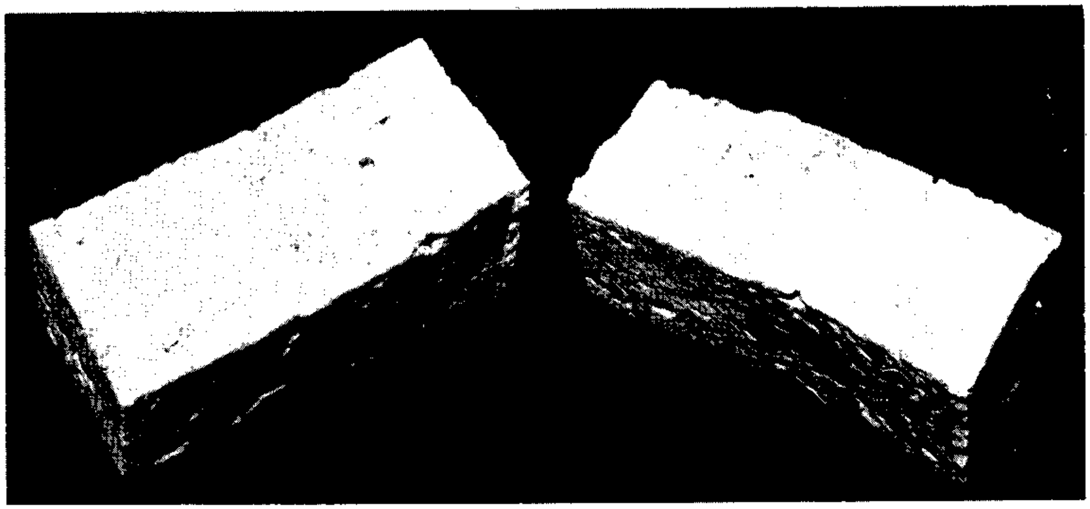

FIG. 23 GRANULAR $NaNO_3$ WASTE
2" x 2" x 5"

Dissolution Tests

Dissolution rates of the crystalline or granular solid synthetic wastes were measured by immersing only the bottom 1/4 inch of 2 by 2 by 5-inch-tall specimens in a water bath. The specimen was supported by a vertical 1/16-inch-diameter rod through an axial hole, and was supported at 1/4-inch immersion by a crossbar at the bottom of the vertical rod. The specimen slid down the rod as the end dissolved, and so maintained a constant area exposed to the solution. The rates of dissolution were obtained by measuring the length of the sample at different times.

Rates of Dissolution

The rates of dissolution did not decrease as the salt content of the solution increased, up to the maximum tested (5.6M Na^+). The data obtained with four types of solid materials under various conditions are shown in Fig. 24. Despite the variability in the data, the dissolution is clearly rapid. A block of crystalline $NaNO_3$ dissolves in 65°C water at 6 ft/hr; crystalline $NaAlO_2$ at ~3 ft/hr.

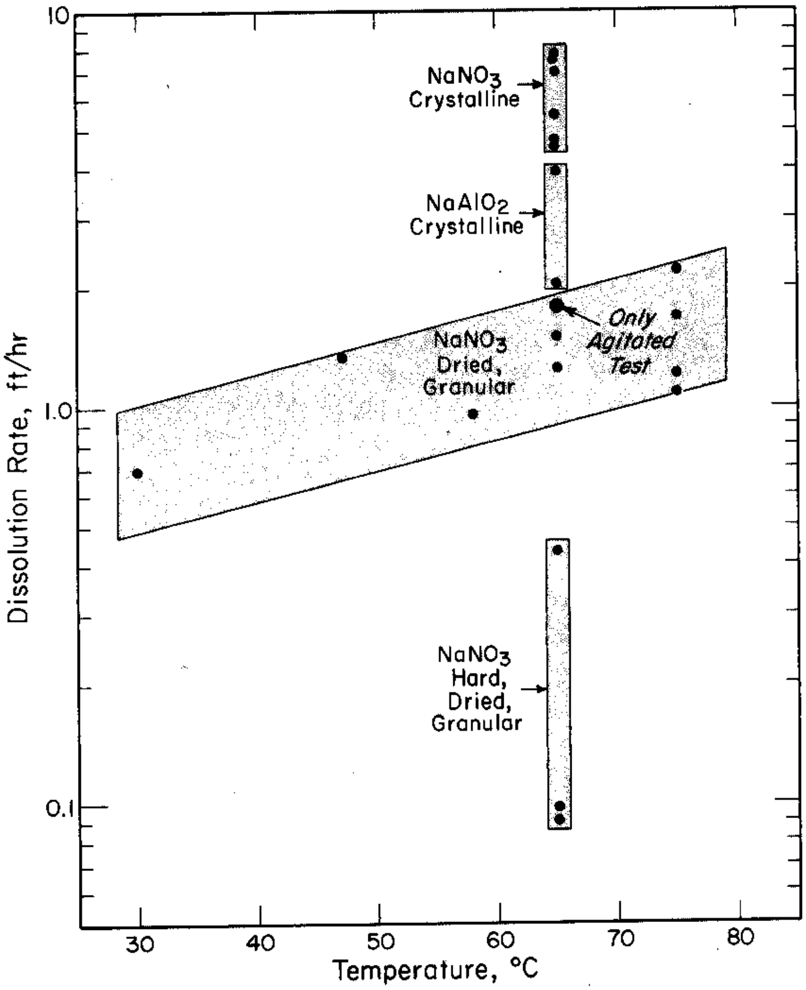

FIG. 24 DISSOLUTION OF SOLIDIFIED SYNTHETIC PUREX WASTE

If a portion of the $NaNO_3$ crystals in a tank are heated under conditions simulating a week in a dry oven at 135°C, the rate of dissolution can be expected to fall to 1-1.5 ft/hr. More severe heating and drying may decrease the rates to the value of 0.1 ft/hr shown for the hard, dried granular $NaNO_3$. As is evident in Fig. 24, an increase from 30 to 75°C only doubles the rate of dissolution. Only slight benefit was obtained in the one test with intense agitation (~5 hp/1000 gal).

The measured rates of dissolution for synthetic waste solution indicate that solidified separations waste from natural uranium processing can be dissolved in water in a reasonable time. The waste from enriched uranium processing should also dissolve at a satisfactory rate, because it has about the same composition as the crystalline $NaAlO_2$ waste.

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