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PROPERTIES OF RADIOACTIVE WASTES  
AND WASTE CONTAINERS

PROGRESS REPORT No. 13  
APRIL - JUNE 1979

P. COLOMBO AND R.M. NEILSON, JR.

DATE PUBLISHED - NOVEMBER 1979

NUCLEAR WASTE MANAGEMENT RESEARCH GROUP

DEPARTMENT OF NUCLEAR ENERGY BROOKHAVEN NATIONAL LABORATORY  
UPTON, NEW YORK 11973

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## SUMMARY

An effort aimed at determining a process control parameter envelope within which reasonable assurance can be given that a satisfactory solidification will occur has begun. This purpose of this work and its ultimate utility is described. Initial work has determined the range of waste/binder ratios which can be employed for the solidification of sodium sulfate regenerative wastes (containing up to 50 wt % sodium sulfate) with portland type I, II and III cements.

An experiment was performed to determine the effect of gamma irradiation exposure dose rate on the leachability of urea-formaldehyde waste forms. Cesium and strontium release rates were determined for leaching of urea-formaldehyde-diatomaceous earth filter sludge waste forms at an absorbed dose of  $10^7$  rad for dose rates of  $10^4$ - $10^6$  R/hr. The data indicate that irradiation to  $10^7$  rad increased the rate of cesium and strontium release. While no significant dose rate dependence was observed over this range for cesium release, a positive correlation of the strontium release with dose rate was found. The effect decreases with decreasing dose rate and is small for  $10^4$  R/hr. This dose rate is high relative to those expected for typical actual reactor waste forms and as such, self-irradiation is not expected to produce a significant increase in strontium release. Since an earlier experiment indicated no appreciable affect on the leachability of cesium and strontium for absorbed doses of  $10^6$  rad or less, leaching data obtained with non-irradiated waste forms appear to be representative of at least near-term releases for actual waste forms.

I. PROCESS PARAMETER ENVELOPE ASSURING SATISFACTORY SOLIDIFICATION  
(L.W. Milian, R.M. Neilson, Jr. and P.R. Hayde)

A. Introduction

The Nuclear Regulatory Commission has proposed that solidified waste forms meet certain regulatory requirements. These requirements specify that the waste form shall be a free-standing monolithic solid which is homogeneous and contains no free standing water. Free standing water is defined as water or waste liquids which are not chemically combined or physically held within the solidified waste form matrix. The existence of free standing water is usually made using an operational definition which specifies some type of test such as that suggested in ANSI/ANS-55.1. As a result of the wide variations in the chemical and physical properties of wet solid reactor wastes, a significant potential exists for unsatisfactory solidification. In particular, an unsatisfactory solidification is evidenced by the presence of free standing liquids in the waste form container.

One technique that can be used to meet these requirements is the development of a process control program. In a process control program, process parameter boundary conditions (envelopes) are determined within which reasonable assurance can be given that a satisfactory solidification will occur. These boundary conditions are established considering the ranges of process parameters that exist in a given plant such as, the characteristics of the waste (e.g. chemical composition, pH, physical form), solidification agent (e.g. cement type, catalyst), and the solidification process (e.g. waste/binder ratio, mixing mode). Once these parameter envelopes are determined, procedures require the operation of the solidification system within these limits.

B. Solidification of Sodium Sulfate Waste Using Portland Cement

The primary component of chemical regenerative wastes is sodium sulfate. Experiments were performed to determine the waste/binder weight ratio limits within which aqueous sodium sulfate solutions are solidified acceptably with portland type I, II and III cements. Simulated waste solutions containing 0, 10, 20, 25, 35 and 50 wt % sodium sulfate were employed to consider waste concentrates produced using a variety of concentration techniques and



efficiencies. A minimum and maximum waste/binder ratio was determined for each waste concentrate. The minimum waste/binder ratio represents a lower limit below which insufficient workability exists for mixing. Sufficient workability is dependent upon the mixing method employed. For this reason, the measurement is somewhat subjective and pertains primarily to mixing by means of a mechanical blade stirrer. In any case, most solidification does not take place at or near this minimum waste/binder ratio. A maximum waste/binder weight ratio was also identified for each waste concentration. While this ratio refers to the potential presence of free standing water in a full-scale waste form, it was determined on a more conservative basis because of the small experimental specimen size (300 grams) and the limited number of replications. Any waste/binder ratio which exhibited either drainable liquids or appreciable surface dampness was deemed unacceptable. As a result, the maximum waste/binder ratios are expected to produce full-scale waste forms in which no drainable free liquids exist and a complete solidification is routinely assured.

Waste form specimens were prepared in individual polymethylpentene containers with screw cap closures to prevent evaporative water loss. Formulations were developed for a 300 gram specimen mass, producing cylindrical waste forms 6.0 cm in diameter and approximately 6.4 cm in height. Two specimens were initially prepared at each waste/cement weight ratio for a given sodium sulfate concentration in the waste. The waste solutions were heated to approximately 75°C to simulate the output of an evaporative concentrator. Formulations were initially prepared using waste/binder weight ratios which were increased in 0.1 unit increments (0.5 for 35 and 50 wt % Na<sub>2</sub>SO<sub>4</sub> wastes). When the approximate maximum ratio was determined, additional specimens were prepared using waste/binder ratios which spanned the approximate ratio and employed 0.02 unit ratio increments (0.1 for 35 and 50 wt % Na<sub>2</sub>SO<sub>4</sub> wastes). These waste form specimens were examined three days after formulation to determine the maximum waste/binder ratio. At and below this maximum ratio, monolithic free standing solids were formed which had, as discussed earlier, no drainable free liquids or appreciable surface dampness. After mixing the waste and cement, a partial phase separation often occurred in which the cement settles out and an upper water layer results. If an

appropriate waste/binder ratio is employed, this water layer typically is absorbed by the cement and combined either physically or chemically. While this absorption is usually complete within twenty-four hours, it may require two to three days in some cases, especially when high waste/binder ratios are employed.

The maximum and minimum waste/binder weight ratios obtained by this method are shown in Figures 1-3 for portland cement types I, II and III respectively. The boundary indicating the maximum waste/binder weight ratio above which free standing water exists represents a conservative projection for full-scale waste forms since a solid exhibiting either excessive surface dampness or drainable liquids was considered unacceptable. This data is tabulated in Tables 1-3. While little difference in respective limiting waste/binder weight ratios was noted between portland cement types I and II, portland type III cement was able to incorporate significantly higher quantities of waste with sodium sulfate contents of 35 wt % or less without resulting in free standing water. Note that at the maximum limiting waste/binder ratios determined for the 35 and 50 wt % sodium sulfate wastes there is relatively little cement incorporated in the waste form. As such, the resultant waste forms are free standing monolithic solids but may have limited integrity.

When the 35 and 50 wt % sodium sulfate wastes were solidified, a crystal layer was formed above the monolithic cement solid at waste/binder ratios which did not result in free standing water as experimentally defined. This crystal layer did have water associated with it in the form of hydrated forms of sodium sulfate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ ) and, in some cases, absorbed water. This crystalline layer is potentially dispersible since there is no cement to bind it together and it may contain absorbed water. Figures 1-3 indicate the waste/binder ratios above which a crystal layer 0.5 mm or greater in thickness was present. As the waste/binder ratio is further increased, the thickness of the crystal layer increases and its character progresses from a dry hydrated layer to one which contains absorbed water and eventually a layer of unbound water forms above the crystals. The unbound water layer above the crystals was free standing water. The solubility of

sodium sulfate in water increases greatly with temperature (16.3 weight percent at 20°C and 31.8 weight percent at 50°C). As mentioned previously, the waste was heated to approximately 75°C before addition to the cement and a partial phase separation occurs as the cement settles out. While with appropriate waste/binder ratios the water is reabsorbed and participates in cement hydration, sodium sulfate which precipitates out of solution from the upper water layer does not become incorporated into the monolithic cement solid. Since the waste cools appreciably after addition to the cement, sodium sulfate precipitates from the high sodium sulfate wastes (35 and 50 wt %) forming the observed crystal layer. This does not occur to an appreciable extent with lower sodium sulfate content wastes because the waste/binder ratios employed are lower, less phase separation occurs and less sodium sulfate is available for precipitation.

The waste form formulation data obtained is also shown in Figures 4-6 in the form of a ternary compositional phase diagram. From these figures, one can determine if a satisfactory solidification will result given the waste form formulation instead of the respective waste/binder ratio and waste stream solids content. While these figures do not consider areas of satisfactory solidification for wastes containing in excess of 50 wt % sodium sulfate, some conclusions can be drawn from them regarding unsatisfactory formulations with higher sodium sulfate content wastes.

Table 1

Waste/Binder Ratio Data for Sodium Sulfate Waste  
Solidification Using Portland Type I Cement

Weight Percent Na <sub>2</sub> SO <sub>4</sub>	Waste/Binder Weight Ratio		
	Workability	Free Standing Water	Crystal Layer
0	0.27	0.64	-
10	0.36	0.80	-
20	0.38	0.80	-
25	0.38	0.80	-
35	0.45	5.0	2.5
50	0.60	8.5	3.8

Table 2

Waste/Binder Ratio Data for Sodium Sulfate Waste  
Solidification Using Portland Type II Cement

Weight Percent Na <sub>2</sub> SO <sub>4</sub>	Waste/Binder Weight Ratio		
	Workability	Free Standing Water	Crystal Layer
0	0.26	0.68	-
10	0.34	0.80	-
20	0.36	0.80	-
25	0.36	0.80	-
35	0.46	4.5	2.6
50	0.60	7.5	3.7

Table 3

Waste/Binder Ratio Data for Sodium Sulfate Waste  
Solidification Using Portland Type III Cement

Weight Percent Na <sub>2</sub> SO <sub>4</sub>	Waste/Binder Weight Ratio		
	Workability	Free Standing Water	Crystal Layer
0	0.32	0.96	-
10	0.40	0.90	-
20	0.40	1.0	-
25	0.40	1.2	-
35	0.50	5.5	2.7
50	0.70	8.0	4.0

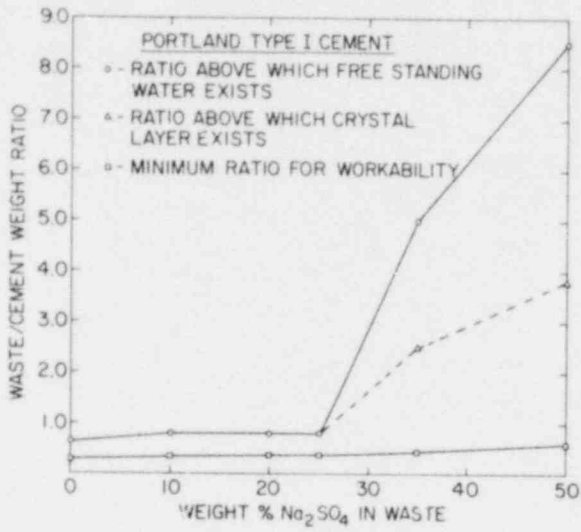


Figure 1. Waste/cement weight ratio versus waste stream sodium sulfate content for solidification with portland type I cement (three day cure).

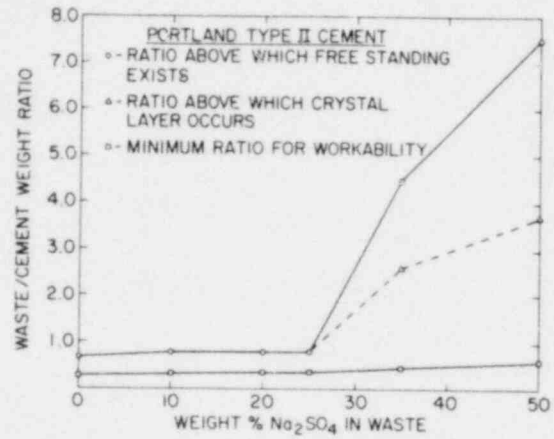


Figure 2. Waste/cement weight ratio versus waste stream sodium sulfate content for solidification with portland type II cement (three day cure).

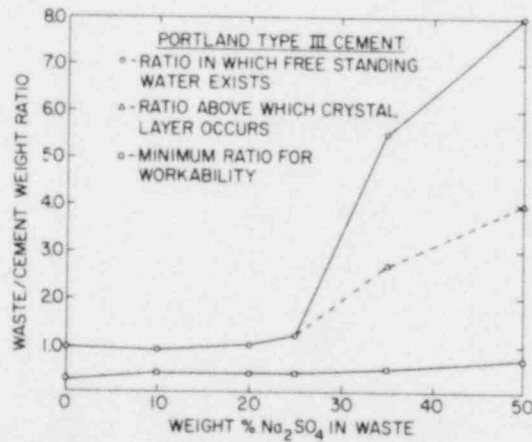


Figure 3. Waste/cement weight ratio versus waste stream sodium sulfate content for solidification with portland type III cement (three day cure).

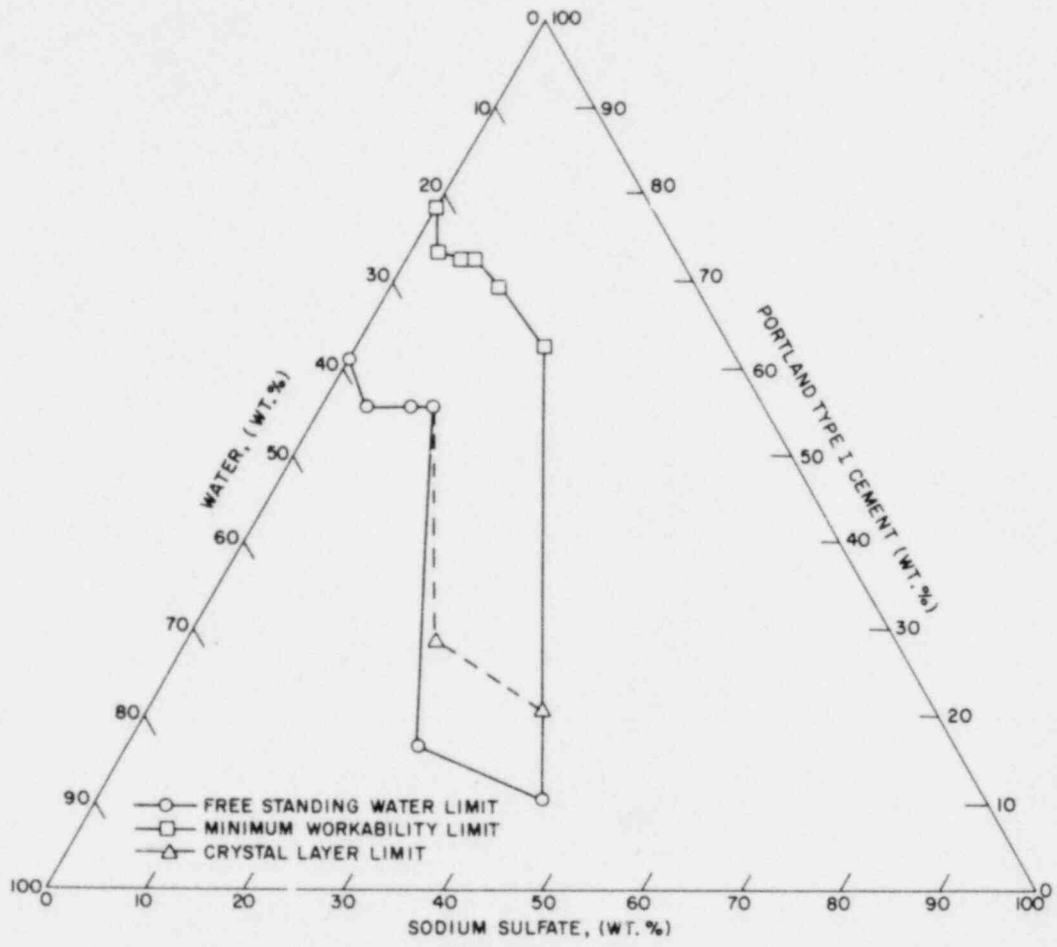


Figure 4. Compositional phase diagram for the solidification of aqueous waste containing 50 wt % or less  $\text{Na}_2\text{SO}_4$  with portland type I cement (three day cure).

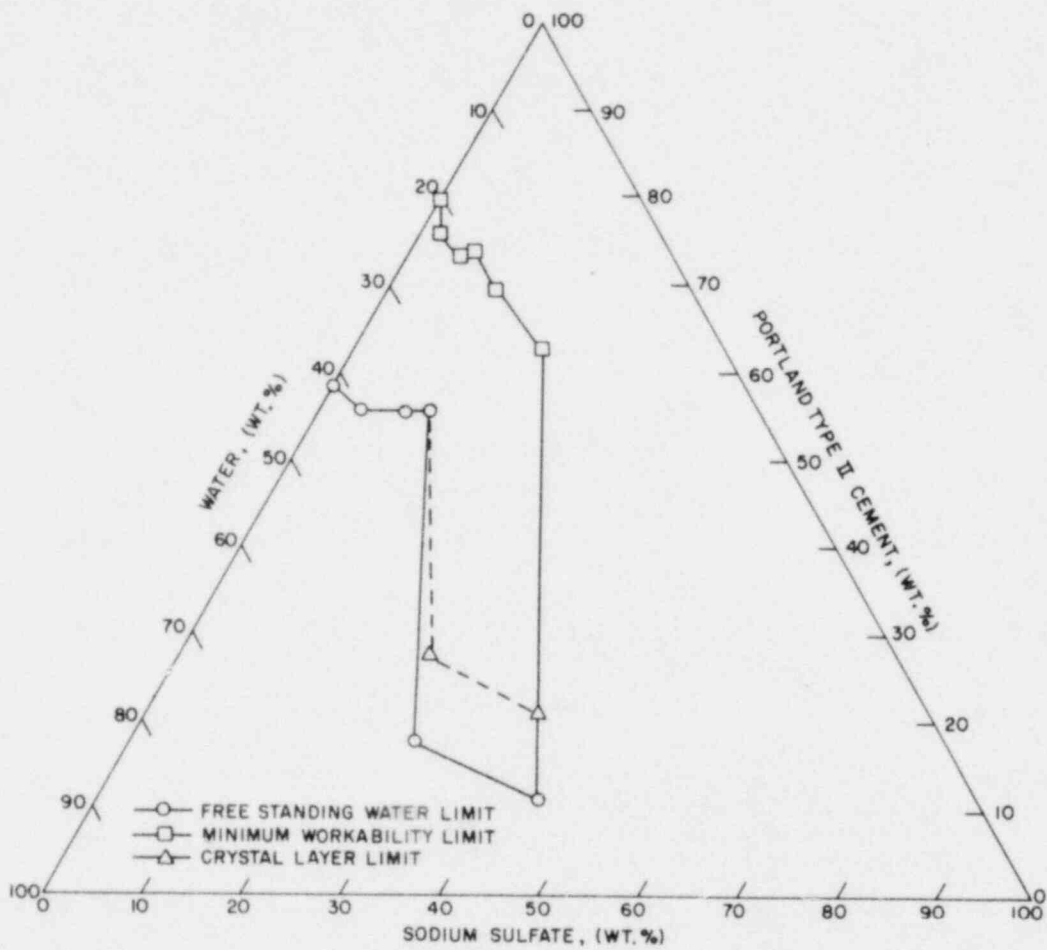


Figure 5. Compositional phase diagram for the solidification of aqueous waste containing 50 wt % or less  $\text{Na}_2\text{SO}_4$  with portland type II cement (three day cure).

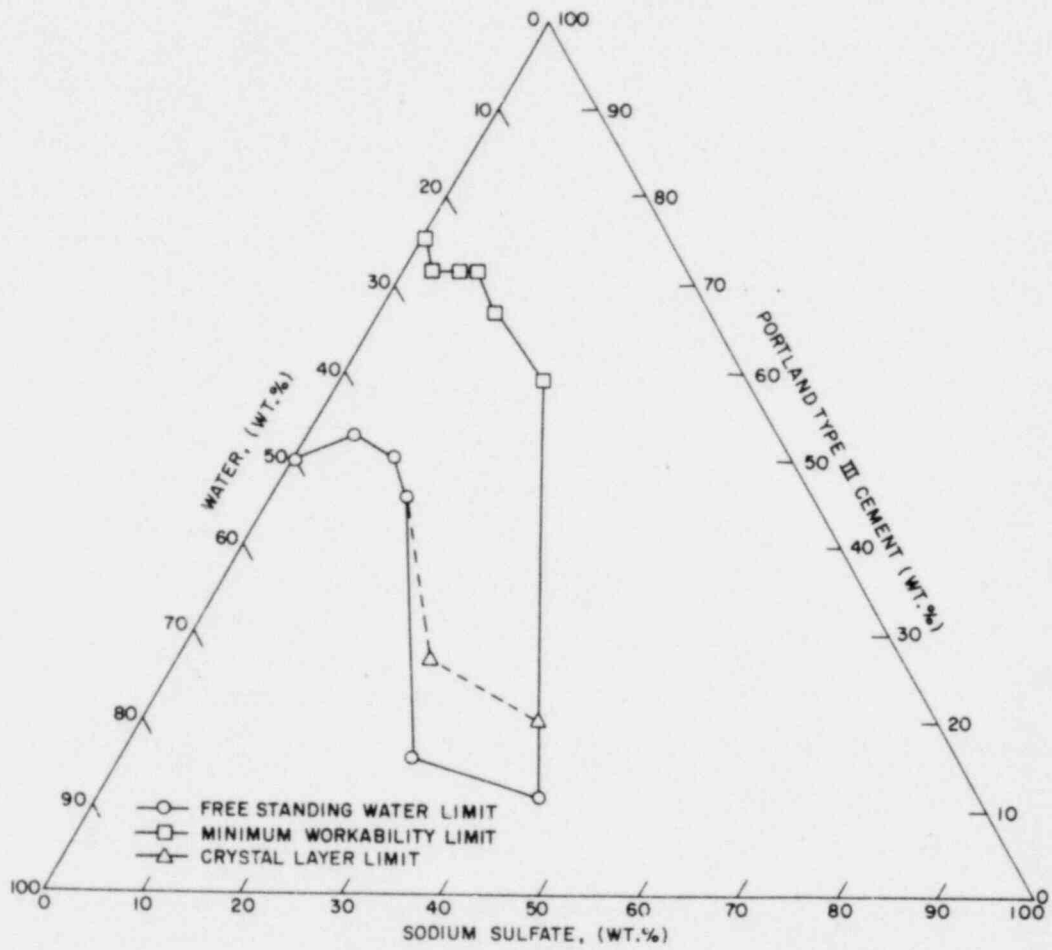


Figure 6. Compositional phase diagram for the solidification of aqueous waste containing 50 wt % or less  $\text{Na}_2\text{SO}_4$  with portland type III cement (three day cure).



## II. THE EFFECT OF COBALT-60 IRRADIATION DOSE RATE ON THE LEACHABILITY OF UREA-FORMALDEHYDE WASTE FORMS

(R.M. Neilson, Jr. and L. Milian)

In an earlier experiment,<sup>(1)</sup> cobalt-60 gamma irradiation was found to affect the rate of release of cesium and strontium by leaching from urea-formaldehyde waste forms containing diatomaceous earth precoat filter cake waste. While no effect was noted for total absorbed doses of up to  $10^6$  rad with an exposure dose rate of  $1.3 \times 10^6$  R/hr, the rate of cesium and strontium release increased substantially for absorbed doses of  $10^7$  and  $10^8$  rad. The dose rate dependency of leachability is of interest because while total absorbed doses of  $10^7$  and  $10^8$  rad can be attained in reactor waste forms, typically much lower dose rates exist than that utilized in the initial experiment. Self-irradiation exposure doses have been calculated as a function of activity content (Ci/ft<sup>3</sup>) for BWR and PWR waste forms.<sup>(2)</sup> These calculations are comparable to the  $10^7$  rad integrated dose over 100 years estimated by Burns for typical reactor waste forms with an activity content of 2.8 Ci/ft<sup>3</sup>.<sup>(3)</sup> This corresponds to a dose rate of approximately 10 R/hr averaged over 100 years, although the initial dose rate (after 180 days decay) is of the order of  $10^2$  R/hr.

Waste form specimens were prepared using the BWR precoat filter cake with diatomaceous earth (slurry) waste which consists of 75 wt % water, 20 wt % diatomaceous earth and 5 wt % crud. Urea-formaldehyde waste forms were formulated using Borden Casco-Resin 2 UF at a waste/UF ratio of 2.0 by weight. Two volume percent of a 25 wt % sodium bisulfate solution was employed as the UF polymerization catalyst. Specimens were prepared as 2.54 cm diameter by 5.08 cm long cylindrical forms in individual specimen containers which were capped after mixing to prevent evaporative water loss. Activity incorporated in each specimen for leaching purposes consisted of 0.01 mCi cesium-137 and 0.01 mCi strontium-85.

The specimens were irradiated in the BNL cobalt-60 gamma facility while still in their preparation containers. Figure 7 is a photograph of the specimen holder used for the irradiations. The holder has a capacity of four specimens and has a weighted end to facilitate emplacement in the irradiation

tube. The cobalt-60 irradiation facility has approximately twenty irradiation tubes. A circular array of cobalt-60 sources are arranged around the lower end of each irradiation tube such that a uniform gamma flux exists in the bottom one foot length of the tube. Irradiation tubes with exposure dose rates of  $1.3 \times 10^6$ ,  $5.9 \times 10^4$  and  $1.1 \times 10^4$  R/hr were employed. Two specimens were irradiated at each dose rate for sufficient time to achieve a total absorbed dose of  $10^7$  rad. The absorbed dose (rad) was determined from the exposure dose (roentgen) using the method of ASTM D 2568-70, "Standard Recommended Practice for Calculation of Absorbed Dose from Gamma Radiation". This method considers the specimen composition and the mass energy absorption coefficients for the atomic constituents on a weight basis. This calculation included the composition of the UF and the waste as well as the waste/binder ratio employed. The ratio of  $\text{rad}/R$  calculated was 0.96 for the urea-formaldehyde specimens. As a result of the variation in dose rates, a considerable range of exposure times resulted. Since the temperature in the gamma facility pool was approximately  $10^\circ\text{C}$ , all specimens were maintained at this temperature for the duration of the longest specimen exposure. In this manner, each leach specimen had the same thermal and curing history.

The leaching experiment employed the modified IAEA/ISO test procedure. In this method, the leach specimens were placed into distilled water leachant such that essentially all external surface area was exposed. A temperature of  $25^\circ\text{C} \pm 5^\circ\text{C}$  was maintained in individual leaching cells to which sufficient leachant was added to provide a leachant volume to specimen external geometric surface area ratio of 10 cm. Periodically, a ten milliliter aliquot was removed from the leachant for analysis and the remaining leachant was completely replaced. On the first day of leaching, the leachant was sampled at ten minutes, one hundred minutes and six hours. Subsequently, sampling was performed at twenty-four hour intervals from the beginning of the test with the exception of weekends and holidays. Duplicate leach specimens were employed for each dose rate.

Composite figures showing the (cumulative fraction release)  $\times (V/S)$  versus leach time are found in Figures 8 and 9 for cesium and strontium release respectively.  $(V/S)$  is the ratio of the specimen volume to its external geometric surface area. These curves represent the average of duplicate

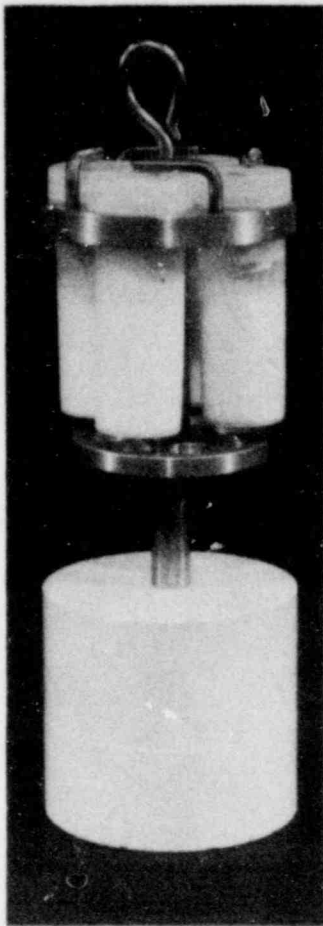


Figure 7. Holder for the irradiation of leach specimens in the cobalt-60 gamma facility.

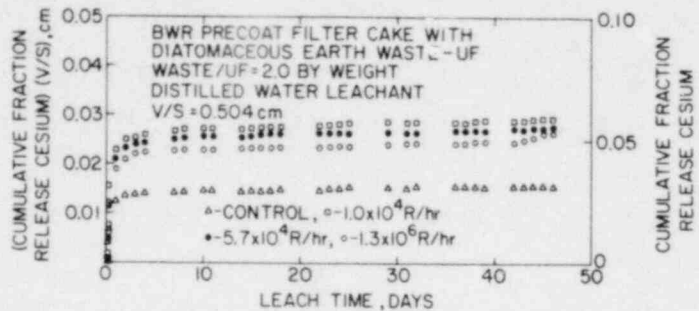


Figure 8. (Cumulative fraction release cesium) x (V/S) versus leach time as a function of dose rate with a total absorbed dose of  $10^7$  rads for urea-formaldehyde waste forms.

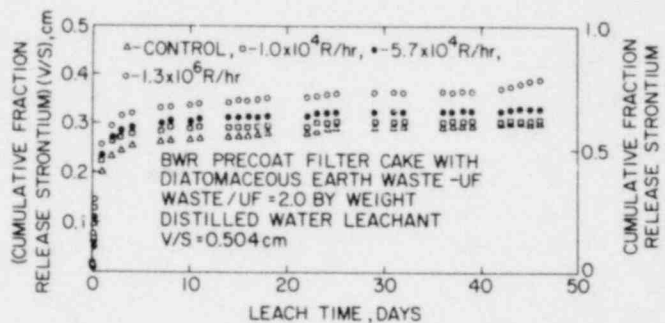


Figure 9. (Cumulative fraction release strontium) x (V/S) versus leach time as a function of dose rate with a total absorbed dose of  $10^7$  rads for urea-formaldehyde waste forms.

specimens tested at each dose rate. The absorbed cobalt-60 dose was found to increase the rate of cesium and strontium release for the range of dose rates employed. The cesium release data suggests that the release rate is independent, or approximately so, of dose rate in the range of  $1.1 \times 10^4$  to  $1.3 \times 10^6$  R/hr. While not indicated in Figure 8, there was an appreciable data spread for the  $1.3 \times 10^6$  R/hr specimens such that the data overlapped the  $1.1 \times 10^4$  and  $5.9 \times 10^4$  R/hr curves. A positive correlation between strontium release and absorbed dose rates was observed. These data suggest however that because of the much lower dose rates typically occurring for reactor waste forms, control specimen leaching data (no exposure dose) is representative of the strontium release which occurs for self-irradiated waste forms. In any case, the previous experiment in which absorbed doses of  $10^5$  and  $10^6$  rad had little or no effect on the rate of release of cesium or strontium indicates that leaching data obtained with non-irradiated waste forms are representative of at least near-term leaching data for actual waste forms.

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