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PROPERTIES OF RADIOACTIVE WASTES
AND WASTE CONTAINERS

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SUMMARY

Work directed towards determination of process control parameter envelopes within which reasonable assurance can be given that a satisfactory solidification occurs has continued. The purpose of these efforts and their ultimate utility are described. Waste/binder weight ratios within which portland type I, II and III cements can be satisfactorily employed for the solidification of diatomaceous earth filter sludges containing up to 25 weight percent solids were determined.

PROCESS PARAMETER ENVELOPE ASSURING SATISFACTORY SOLIDIFICATION

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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 with 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 Diatomaceous Earth Filter Sludge Waste Using Portland Cement

The primary component of the BWR precoat filter sludge waste is diatomaceous earth. Experiments were performed to determine the waste/binder weight ratio limits within which aqueous diatomaceous earth solutions are solidified acceptably with portland and type I, II and III cements. Simulated waste solutions containing 10 and 25 wt % diatomaceous earth were employed to consider the range of waste

compositions produced. An attempt was made to incorporate 50 wt. % diatomaceous earth filter sludge waste in portland type I and II cement waste forms. This was unsuccessful because the water absorption capacity of diatomaceous earth is such that with a 50 wt. % solids content in the waste, insufficient water is available to permit mixing with cement by reasonable means even at high waste/cement ratios. Portland type III cement was not employed for the solidification of 50 wt. % solids waste since work indicated that for 10 and 25 wt. % solids waste, higher waste/binder ratios are required to achieve workability than with type I and II cements. A minimum and maximum waste/binder ratio was determined for each waste composition. 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 composition. 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 (250 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 polymethylepentene containers with screw cap closures to prevent evaporative water loss. Formulations were developed for a 250 gram specimen mass, producing cylindrical waste forms 6.0 cm in diameter with a height that varied from approximately 5.0 cm to 6.3 cm depending upon the waste/binder ratio employed. The waste solutions were utilized at a temperature of 21°C to simulate typical dewatering operations. Formulations were initially prepared using waste/binder weight ratios which were increased in 0.1 unit increments. When the approximate maximum waste/binder ratio was determined, additional specimens were prepared using waste/binder weight ratios which spanned the approximate ratio and employed 0.05 unit ratio increments. 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 liquids or appreciable surface dampness.

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. A thorough diatomaceous earth-cement mixing procedure is essential to obtain an acceptable homogeneous solidified product. If the proper mixing technique is not employed, inadequate specimen solidification will occur due to the insufficient distribution of waste throughout the total monolithic product. While little difference in respective limiting waste/cement weight ratios were noted between portland cement types I and II, portland type III cement proved to have the capacity to incorporate substantially larger quantities of the waste utilized.

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 25 wt. % diatomaceous earth, some conclusions can be drawn from them regarding unsatisfactory formulations with higher diatomaceous earth content wastes.

TABLE I

WASTE/BINDER RATIO DATA FOR DIATOMACEOUS EARTH WASTE SOLIDIFIED IN
PORTLAND TYPE I CEMENT

Weight Percent Diatomaceous Earth	Waste/Binder Weight Ratio	
	Minimum Workability	Free Standing Water
0	0.27	0.64
10	0.40	0.80
25	0.95	1.20

Table II

WASTE/BINDER RATIO DATA FOR DIATOMACEOUS EARTH WASTE SOLIDIFIED IN
PORTLAND TYPE II CEMENT

Weight Percent Diatomaceous Earth	Waste/Binder Weight Ratio	
	Minimum Workability	Free Standing Water
0	0.26	0.68
10	0.35	0.80
25	0.90	1.20

Table III

WASTE/BINDER RATIO DATA FOR DIATOMACEOUS EARTH WASTE SOLIDIFIED IN
PORTLAND TYPE III CEMENT

Weight Percent Diatomaceous Earth	Waste/Binder Weight Ratio	
	Minimum Workability	Free Standing Water
0	0.32	0.96
10	0.45	1.40
25	1.00	2.40

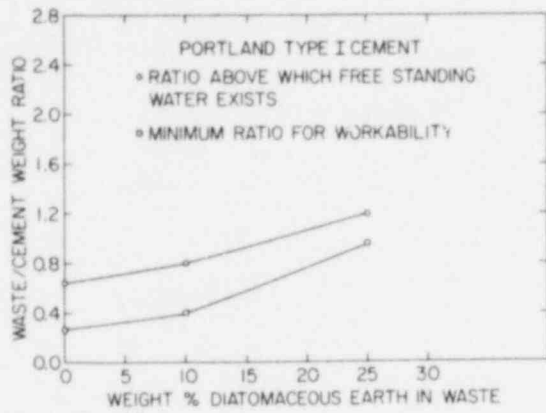


Figure 1. Waste/cement weight ratio versus waste stream diatomaceous earth content for solidification with portland type I cement (three day cure).

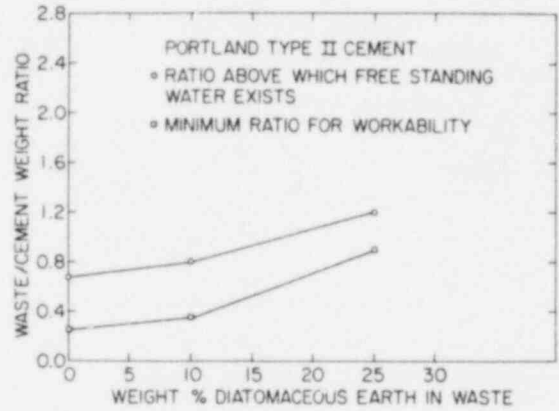


Figure 2. Waste/cement weight ratio versus waste stream diatomaceous earth content for solidification with portland type II cement (three day cure).

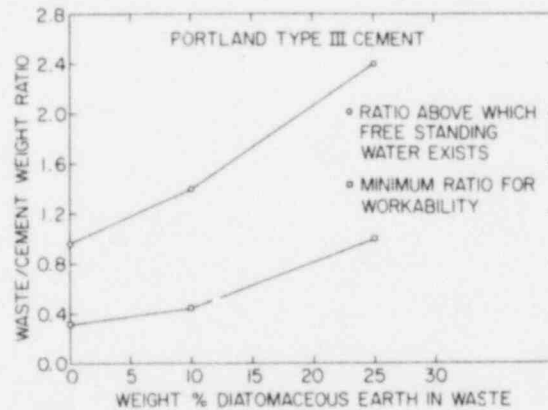


Figure 3. Waste/cement weight ratio versus waste stream diatomaceous earth content for solidification with portland type III cement (three day cure).

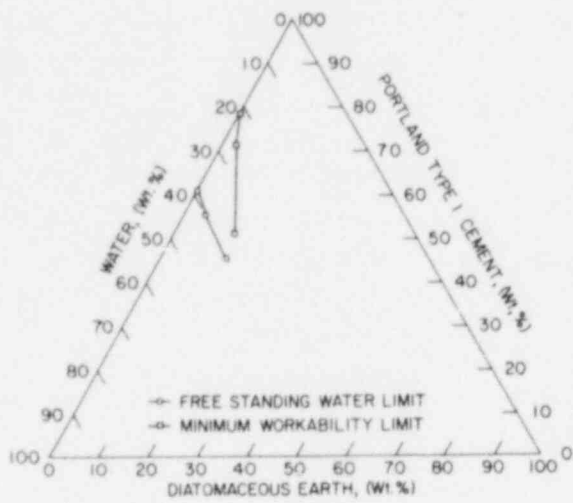


Figure 4. Compositional phase diagram for the solidification of aqueous waste containing 25 wt. % or less diatomaceous earth with portland type I cement (three day cure).

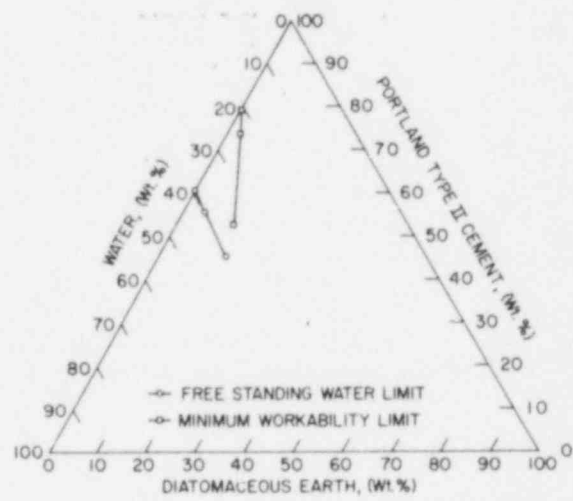


Figure 5. Compositional phase diagram for the solidification of aqueous waste containing 25 wt. % or less diatomaceous earth with portland type II cement (three day cure).



Figure 6. Compositional phase diagram for the solidification of aqueous waste containing 25 wt. % or less diatomaceous earth with portland type III cement (three day cure).

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