DEVELOPMENT OF FREE STANDING WATER (FSW) CRITERIA

and

RATIONALE FOR REQUIRING THE SOLIDIFICATION OF

ION EXCHANGE RESINS AND SLUDGES

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DEVELOPMENT OF FREE STANDING WATER (FSW) CRITERIA

Relevant data obtained from the BNL program "Properties of Radioactive Wastes and Waste Containers"

BNL-NUREG 50571	(Apr-June 76)	FSW noted in UF and cement formulations
BNL-NUREG 50617	(Jul-Sept 76)	FSW in UF quantified
BNL-NUREG 50664	(Oct-Dec 76)	FSW in UF and cement quantified, FSW related to UF shrinkage and waste/binder ratio, UF decontamination factors for FSW
BNL-NUREG 50692	(Jan-Mar 77)	FSW in UF formulations
BNL-NUREG 50763	(Apr-June 77)	cement decontamination factors for FSW
BNL-NUREG 50921	(Jan-Mar 78)	mild steel corrosion for contact with UF, cement wastes

BACKGROUND

The objective of solidification is to convert radioactive waste into a stable monolithic form which minimizes the potential for radionuclide release to the environment during interim storage, transportation and disposal. Power reactor wastes in the United States are currently solidified by techniques which employ hydraulic cement and urea-formaldehyde. While hydraulic cement and urea-formaldehyde waste forms have been the primary focus of the work at BNL, other agents which are being actively marketed for reactor waste solidification have been studied. These include bitumen and vinyl ester-styrene.

All solidification agents (with the possible exception of bitumen) can exhibit free standing water (FSW). FSW is water (or waste liquid) which is not combined chemically or held physically within the solidified waste form matrix.

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It is related to parameters including the waste/binder ratio (w/b), waste type, and mixture pH (for UF). While frequently observed at the top of the waste form, FSW also tends to be present in spaces and voids along the side of the waste form and at the bottom of the container.

Hydraulic Cement

Hydraulic cement holds water both chemically and physically. It can chemically combine with approximately 25% water by weight forming hydrated silicate and aluminate compounds. Water is also held physically in cement porosity. A water layer is sometimes observed shortly after mixing due to cement settling. This water (if a proper waste/binder ratio is used) typically is absorbed (and combined physically or chemically with the cement) within twenty-four hours, (although in some cases this may require 2-3 days especially for high w/b ratios). Liquid present after this time is FSW. The amount of FSW is not a function of time; it does not increase or decrease (unless allowed to evaporate). The FSW when present, is normally alkaline (pH ~ 9-12). The concentration of activity in FSW is lower than in the initial waste especially for multivalent nuclides.

Urea-Formaldehyde

Urea-formaldehyde (UF) does not combine chemically with water in the waste; water is held physically within its porosity. UF also produces water since it polymerizes by a condensation mechanism. Because the condensation reaction continues (although at a decreasing rate) for a substantial period of time (at least days), FSW in UF increases with time. Increases in FSW have been noted over at least seven days. The amount of FSW is not a monotonic function of the

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waste/binder ratio but appears to be related to shrink- in the UF. It is also related to the pH of the waste-UF mixture after catalyst addition. UF is polymerized by the addition of an acid catalyst. Sufficient catalyst to give a mixture of pH of 1.5±0.5 appears to minimize FSW. The amount of FSW is also related to the waste type (as in cement) with wastes containing absorbant solids usually producing less FSW. Resultant FSW is acidic with a pH similar to that of the waste-UF mixture after catalyst addition. The concentration of activity in FSW is approximately equal to that in the initial waste.

Bitumen

Bitumen wastes forms should not exhibit FSW since water is almost completely (99.5%) evaporated from the waste during mixing. (This is not true in an emulsified bitumen process, which is not being proposed for commercial reactor use in the US. (Further remarks will be restricted to the screw extrusion process as marketed by Werner and Pfleiderer). It is feasible that the choice of incorrect operating parameters or equipment failure could result in incomplete evaporation of water contained in the waste. In this case, both water droplets and liquid bitumen would be discharged from the extruder. The bitumen will solidify as it cools but the water present would largely not be trapped in the matrix if large quantities of water were discharged. However, the presence of substantial water should be easily noted either as a result of the quantity of water discharged through the last extruder steam dome or steam emanating from the extruder discharge and waste container.

Vinyl Ester-Styrene

Water in the waste is not chemically combined in the vinyl ester-styrene process marketed by the Dow Chemical Company. Rather, the water is encapsulated as small droplets in the polymer matrix after solidification. The process relies on high shear mixing to form an emulsion between the liquid waste and the monomeric solidification agent. The ability to form this emulsion also depends upon the rate of waste addition, waste type, waste/binder ratio and waste pH. The agent is claimed to form stable emulsions over a wide pH range (2.5 - 11). Since water is not miscible with the vinyl ester-styrene monomer, a two phase liquid will form if a stable emulsion is not produced. The waste will then be largely present as FSW. 'At least one waste (boric acid at concentrations above 8%) requires a simple chemical pretreatment in order to form a stable emulsion. It is possible that some waste types could interact chemically with the promoter-catalyst system used to polymerize the monomer. Such an interaction may require a change in the order of promoter and catalyst addition or an increase in one or both constituents. Since the polymerization reaction is exothermic, interactions which prevent polymerization should be noted because no increase in waste form temperature will result. If polymerization does not occur, a solid product will not be produced and the emulsion will eventually separate.

CONSIDERATIONS IN CRITERIAL DEVELOPMENT

Free standing water has been a particular problem with urea-formaldehyde waste forms. FSW occurs with some frequency in amounts ranging from small to substantial. The FSW tends to occupy all voids in the container and as such, the addition of a bag of cement or straight UF to the top of the waste form may

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solidify visually apparent FSW but does little to free liquids in other parts of the waste container. Also, since the amount of FSW increases with time, such a "fix" may not even be sufficient for FSW at the top of the waste form over long periods of time. Similarly, a waste package drained of free liquids from the bottom on the day after solidification will exhibit additional (although typically smaller) quantities of free liquid after several additional days. This results from hydrostatic pressures in large waste packages and the production of additional quantities of water as the UF polymerization continues. There is concern that the vibration occuring during transportation may be sufficient to remove liquids from the porosity in the UF and result in additional FSW. The FSW from UF will (as a result of its low pH $\sim$ 1.5) contain as high a concentration of activity as the initial waste and also tends to be highly corrosive to its container. FSW releases from pinhole corrosion of mild steel containers holding UF waste forms have been noted.

FSW appears to be less of a problem with cement waste forms. It can usually be eliminated by the selection of proper waste/binder ratios. If it occurs, the concentration of multivalent radionuclides is normally lower than in the initial waste since cement constituents exhibit ion exchange behavior. The pH of such FSW is also alkaline (pH $\sim$ 9-12) and as such is non-corrosive towards the mild steel packaging currently used.

FSW has not been noted at BNL for solidified vinyl ester-styrene products when formulated according to instructions from Dow. If it occurs, the FSW activity concentration and pH are expected to be similar to those of the initial waste stream.

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Note that for the solidification of hot (thermally) evaporator concentrates and for solidification with agents that release significant heat during solidification (cement, vinyl ester-styrene), evaporative water condensing on cold upper surfaces of the solidification container may be a source of FSW. While cement (with a proper waste/binder ratio) will adsorb this water, UF waste forms may not and vinyl ester-styrene waste forms will not. As such, containers are often left open to the atmosphere during solidification to eliminate such condensate as a source of FSW.

Current regulations require a solid monolithic waste form with no free standing water. While "no FSW" is difficult to measure, it has typically been understood to mean less than one percent. On a volume basis, this means FSW is acceptable on the order of 0.5 gallon/55 gallon drum or 7.5 gallons/100 cubic foot liner. The FSW is a concern as it represents a possible mechanism for activity transport and may promote container corrosion leading to a release of FSW and activity from the waste package. If the philosophy which regards the burial site geology as the ultimate barrier and giving no credit to the waste container in burial is accepted, then FSW criteria should be based on transportation considerations. How much activity can be transported by means of FSW? For UF, the effective decontamination factor (DF) for FSW is one, therefore 1% FSW by volume represents something greater than 1% of the activity contained in the waste package. For example, at a packaging efficiency of 0.5, 1% FSW by volume represents 2% of initially contained activity and 2% of the input waste volume. Since the DF should also be one for FSW from vinyl ester-styrene, similar activity limits also apply. Cement however has DF ~ 1 for cesium (+1 valence) but DF ~ 10 for strontium (+2) and DF ~ 200 for cobalt (+2, +3).

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Therefore 1% FSW by volume in a cement package with a packaging efficiency of 0.5 may represent between 0.01% to 2% of initially contained activity depending upon the radionuclides present.

FSW criteria should be consistant with proposed DOT regulations which limit the loss of activity by leachability to less than 10% per week (actually $0.1A_2$ where A_2 equals the maximum contained activity for a type A package). Since the activity from FSW is mobilized instantaneously in leaching, this implies that the approximate maximum allowable FSW is on the order of 5% of the container volume (for a packaging efficiency ~ 0.5 and DF ~ 1). However, a criterion allowing 5% FSW would require a waste form leach rate of less than 1% per week to meet the DOT standard, since activity release includes both FSW and leachability. Leachability, as observed in the NRC program at BNL, is dependent upon the isotope considered (at least with cement) where the highest leachability is generally found for cesium. Applying estimated scale factors for diffusional cesium releases from 55 gallon drum size UF waste forms, fraction activity release rate estimates of approximately 5% per week are obtained. This represents a probable maximum for solidified waste forms. Thus, FSW below 0.5% by volume would be required to meet the DOT standard. (The activity release from a 300 ft^3 liner would be approximately 1.5% per week allowing $\sim 4\%$ FSW to meet the standard).

A FSW requirement should also consider the minimum FSW detectible. While this quantity is dependent upon the measurement technique employed, it is probably of the order of 0.2-0.5% by volume using reasonable means.

A more satisfying mechanism for developing FSW criteria would consider ultimate dose to man or some relative hazard index. However, while considering

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total activity contained in the waste form, the criteria should not give a large number of limits dependent upon the solidification agent, radionuclide type and total activity. Rather, it should be developed for a type A waste form alone (which does consider radionuclide type and quantity but not solidification agent type). Similarly the proposed DOT standard also considers activity type, activity content and presumably dose to man (or similar index) in setting its leachability limit $(0.1A_2/week)$.

If release of activity into the disposal site is the basis for FSW criteria, the minimum FSW reasonably detectible is still of the order of 0.2-0.5%. The maximum permissible FSW should be related to the ability of the site geology to impede radionuclide movement (by adsorption, etc.). The controlling factor is then dose to man limits at the site boundary which would include total site activity and the ease of activity movement. If radionuclide adsorption is large, as it is usually assumed to be, the allowable FSW would also be large, probably approaching 100%. This would assume instantaneous mobilization of all FSW activity into the burial trench where it is adsorbed by the geologic strata. Evidence suggests however that liquids present in the trenches may impede the adsorption abilities of the surrounding strata, in which case activity transport by FSW can be important. In fact, constituents present in FSW from some waste packages may contribute to this decrease in local sorption. There is also a desire to minimize the quantity of FSW in the burial environment as it can contribute to leaching of other waste packages, container corrosion and other chemical interactions. Some of these problems, such as those resulting from the removal complexing agents or organic liquids from waste packages, are dependent upon leachability as well as FSW and may perhaps be best controlled by segregation of wastes at the burial site.

The presence and characteristics of FSW is a determining factor in waste container lifetimes and as such is important relative to the effectiveness of the container as a barrier.

RECOMMENDATIONS

The proposed DOT leachability standard appears to be met by permitting a maximum of 2.5% free standing water by volume. The minimum FSW feasibly detectible is of the order of 0.2-0.5% by volume. Criteria for FSW based on burial site considerations would probably permit more than 2.5% FSW by volume if adequate site adsorption and slow lateral water movement exists. The effects of FSW during transportation (and interim storage) appears to be controlling in this situation but there are arguments for reducing FSW below the 2.5% that appears to conform with DOT activity removal requirements. These include the effect of FSW constituents on leachability, container corrosion, the sorption ability of the surrounding geologic media, and activity transport if adsorption and water movement characteristics are not optimum in the burial environment. Proposed criteria would be of the form:

1. Efforts should be taken in waste form formulation to reduce the quantity of free standing water to the minimum reasonably achieved through careful selection of waste/binder ratio and other relevant processing parameters.

2. In no case should the total free standing water present in the waste form after solidification be greater than 0.5-1.0 percent by volume. This quantity could be measured in a manner similar to that suggested in ANSI N198 in which both FSW visually apparent on the upper surface of the waste form and FSW drained from the bottom of the waste container are noted.

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RATIONALE FOR REQUIRING THE SOLIDIFICATION OF
ION EXCHANGE RESINS AND SLUDGES

Relevant Data Obtained in the BNL Program, "Properties of Radioactive Wastes and Waste Containers".

BNL-NUREG 50571 (Apr-June 76) - waste solidification using cement and UF

BNL-NUREG 50617 (Jul-Sept 76) - leachability of bead and powdered ion exchange resins ("cold" Cs and Sr in distilled water), impact strengths

BNL-NUREG 50692 (Jan-Mar 77) - leachability of bead and powdered ion exchange resins (Cs-137, Sr-85 in distilled, tap and salt water)

BNL-NUREG 50763 (Apr-June 77) - compression strengths of waste forms, shielding characteristics, solidification using vinyl ester-styrene)

BNL-NUREG 50927 (Jan-Mar 78) - leachability of bead resin-UF, DE-UF, DE-cement

In Press   (Oct-Dec 78) - dispersibility of bead resin-cement and DE cement waste forms

In Press (Topical Report)   - swelling in cement-ion exchange resins

STATE OF THE ART

All solidification technologies currently available (cement, modified cement, urea-formaldehyde (UF), bitumen and vinyl ester-styrene) are capable of solidifying resins and sludges. Some chemical sensitivities may exist in specific cases that should be considered for solidification. Alkaline sludges may require a pH pretreatment for solidification with UF. Sludge wastes are among the easiest wastes solidified with cement. However, cation exchange resins have been found to produce cement waste forms of relatively low strength, especially when the

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resin is not completely expended. Mixed bed (cation-anion) resins show less of this tendency with cement solidification. Expending resins and a pH adjustment prior to solidification are also helpful. Interactions of sludge wastes with the promoter-catalyst system may cause difficulties with vinyl ester-styrene. This is not meant to imply that any of these solidification agents are unacceptable. Rather, while each of these agents can be used to solidify ion-exchange resins and sludge wastes, some care may be necessary in particular cases.

CONSEQUENCES OF SOLIDIFICATION

Solidification produces benefits during interim storage, transportation and disposal that may be used to justify the need to solidify. The alternative to solidification is packaging of (unsolidified) dewatered resins and sludges.

Unsolidified resins and sludges have large effective surface areas that would be directly in contact with fluids in leaching environments. Solidification generally results in lower leach rates and hence lower fractional activity releases per unit time in leaching due to the decrease in effective surface area. Reduced leachability decreases the consequences of an accident during interim storage and transportation and also serves to minimize long-term environmental impact in burial where, despite past philosophy, the geology may not provide the ultimate barrier to activity transport. For leaching of infinite media by diffusion, an approximate scale factor consisting of the ratio of waste form volume to surface area (V/S) can be used. A 55 gallon drum size waste form has a (V/S) ratio of ~ 11 cm, while (V/S) for bead resin waste is of the order of 3×10^{-3} cm. (Unsolidified resins have a much larger surface area per unit volume than the solidified product). The rate of fractional activity release from a 55 gallon drum is then 0.003/11 (equals 3×10^{-4}) times that for leaching a similar volume of unsolidified bead resin

particles. As a perspective, the amount of activity released from this volume of unsolidified bead resins in one day would require ten years for release from a solidified waste form. Such an analysis is however too simplistic in that it does not consider the total surface area of the solidified waste form (due to porosity, etc.), other release mechanisms, the retention abilities of resins due to ion exchange and the effect of chemical interactions with the solidification agent on those retention abilities. However, on balance solidification is expected to considerably reduce the rate of activity release from resins and sludges in leaching environments.

Ion exchange resins (both bead and powdered forms) have been shown to have low release rates for leaching in distilled water and low dissolved solids water. In high dissolved solids water, the resins release activity rapidly. The liquids to which unsolidified resins might be exposed in burial (and possibly in transportation and storage) would probably also elicit a rapid rate of activity release. High dissolved solids concentrations as well as wide ranges of pH and diverse chemical contents have been observed in burial trench waters.

Similarly, chemical interactions of ion exchange resin with the solidification agent may also result in a loss of retained activity. Of particular interest is the interaction of the low pH (~ 1.5) liquid present in the porosity of UF waste forms. While this undoubtedly affects retention ability, experimental work indicates that some capability to retain activity remains, as evidenced by the larger release rates observed with UF waste forms for leaching in salt water as opposed to ground water. In cement solidification, multivalent cations in solution (Ca^{+2}, Al^{+2}) may also exchange with the resin tending to release lower valence activity, but solidification is expected to result in a net

decrease in leachability. Note that most sludges (with the exception of pow-

dered ion exchange resins) will have little or no ion exchange capabilities and

much of the activity in these wastes will be present in the associated water.

For these materials, solidification should result in a dramatic decrease in the

rate at which activity is released in leaching.

Solidification also reduces the potential for dispersion of activity during

storage, transportation and disposal as a result of an accidental breech of the

waste container. While transportation accidents that could affect the integrity

of the waste container are easily envisioned, the rough handling which occurs

during burial operations frequently results in container failure. In these

instances, unsolidified resins and sludges may contribute to the release of a large

quantity of small discrete particulate matter that may be easily dispersed by wind

or water. Such an occurrence could produce difficult problems associated with

recovery and removal of the waste. Some waste particulate conceivably could be in

the respirable size range. While an accident involving a solidified waste form

could also result in dispersible particulate, the consequences of such an occur-

rence would be considerably lower than for a package containing unsolidified

waste. In addition, the liquid associated with a dewatered waste would be dispers-

ible and is likely to contain activity. Solidification would provide a means for

the chemical combination or physical holding of this liquid within a monolithic

matrix and minimize the importance of this mechanism for activity transport. The

waste liquids that may be released from an unsolidified waste package may also

contribute to the leaching of other waste packages, container corrosion and a

decrease in the sorption ability of the surrounding geologic media in burial.

Impact and compressive strengths of solidified waste forms have been measured.

Experiments have also been performed to quantify the dispersibility of solidified

waste forms.

Solidification provides some degree of radiation shielding for the waste package which may minimize personnel exposure during the handling operations associated with burial and storage as well as during transportation.

The needs met by the solidification of resins and sludges may also be provided by the use of high integrity waste containers. Reuseable high integrity containers are commonly employed in transportation for Type B packages. However, waste packages are normally removed from the high integrity containers before burial where the benefit of these containers as a barrier to activity transport is lost. Thus, if high integrity containers are used as an alternative to solidification, the need to require these containers in burial (rather than reuse) should be considered. Evidence suggests that activity transport in the burial environment may be important due to the effects of trench liquids on the adsorption abilities of the geology and site water movement. Ultimately economic considerations, including the cost of solidification, reduction in the packaging efficiency, and increased transportation costs must be addressed to determine whether solidification and/or improved containers will be used. The volumetric packaging efficiencies (input waste volume/solidified waste volume) that result from the solidification of resin and sludge wastes are high, ranging from 0.7-0.9 for cement and UF. As such, reduction in packaging efficiency resulting from solidification should not be a major concern.

RECOMMENDATIONS

Substantial benefits accrue from the solidification of dewatered resin and sludge wastes. These include decreased leachability of waste packages, particularly in burial environments, reduction in the potential for dispersion resulting from a loss of waste container integrity and the immobilization of liquids associated with the dewatered wastes. While high integrity containers can be used to achieve many of these benefits during transportation, similar considerations should also be applied in disposal (burial). As such, current disposal practices compel a recommendation that dewatered resin and sludge wastes be solidified.