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What the DOE Knows it Doesn't Know about Grout:

Serious Doubts Remain About the Durability of Concrete Proposed to Immobilize High-Level Nuclear Waste in the Tank Farms at the Savannah River Site and other DOE Sites

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updated October 18, 2004

The U.S. Congress has come together on a proposal that would allow the Department of Energy (DOE), with the consent of the State of South Carolina, to cover an unspecified fraction of the high-level nuclear waste currently stored in underground tanks at the Savannah River Site (SRS) with grout and leave it onsite permanently.[1] Of particular concern regarding this waste is the nearby Savannah River, which is one of the most important water resources in the South and currently provides food and drinking water to people downstream of the Savannah River Site. It is claimed that grouting the tanks will safely immobilize the remaining high-level nuclear waste and prevent it from posing a danger to either human health or the environment. The reality, however, is that there is no valid scientific basis for such claims of safety and effectiveness of grout, and that even within the DOE complex the current lack of information regarding the long-term durability of the grout and its ability to immobilize radionuclides over hundreds to thousands of years is widely recognized. The current proposal can best be summarized as a continuation of what the National Research Council called the DOE's "out of sight out of mind" philosophy of waste management.[2] Once the tanks are grouted they will be virtually impossible to further remediate and therefore, from what we know the DOE doesn't know about grout, no decision should be made on allowing this effort to proceed without a minimum of several years of additional laboratory and field-scale research.

Before discussing the current concerns regarding the durability of grout, a significant lesson in precaution should be learned from the history of the DOE's science regarding plutonium migration. Despite warnings from the National Research Council in the 1960s that there was no conclusive evidence available that supported the then Atomic Energy Commission's claim that the thick unsaturated zones at Hanford and the Idaho National Engineering and Environmental Laboratory (then called the National Reactor Testing Station) would provide an effective long-term barrier to plutonium migration, the AEC

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[1] The language in the defense authorization bill that would allow high level waste to be left permanently in the tanks at the Savannah River Site and possibly at other areas within the DOE complex such as the Idaho National Engineering and Environmental Laboratory was accepted by a conference committee between the U.S. House of Representatives and the U.S. Senate on October 8, 2004.

[2] J.C.S. Long et al. 2000 p. 29

continued to base its waste management strategies on this assumption.[3] Over the following decades, it was discovered that the real world was far more complicated than the AEC had considered, and that their assumptions had been in considerable error. By the year 2000, low levels of plutonium and other contaminants had been detected in the groundwater near one of the waste management sites at the Idaho complex. Revisions of the transport models have shown that instead of taking tens of thousands of years for the contaminants to reach the groundwater in Idaho, as claimed by the AEC in the mid-1960s, they could reach groundwater in just a few tens of years.[4] The National Research Council concluded that the errors in the earlier analyses from the AEC (and later the DOE) could be attributed to many factors "including incorrect conceptualizations of the hydrogeologic system, improper simplifying assumptions, incorrect transport parameters, and overlooked transport phenomena."[5] The lessons of the past should be carefully considered before again rushing into far reaching and effectively irreversible decisions based on admittedly limited and incomplete information.

Concerns regarding the long term durability of grout as a means of immobilizing radionuclides are not new and have, in fact, been raised within the government for more than a decade. In 1991 the Congressional Office of Technology Assessment (OTA) issued a report on the proposed strategies for managing the radioactive wastes that had accumulated within the DOE complex. At the time grout was being proposed as a potential means for stabilizing the low-activity portion of the waste that could be separated from the high-level waste, as well as being proposed as a means for trying to immobilize transuranic wastes. Key questions that the OTA raised concerning these strategies were that the long term behavior of the grout was not known and thus that it was not well understood how long the grout would last or how long and how well it would retain the radionuclides in the waste.[6] Despite 13 years of additional research and claims to the contrary, these same questions remain unanswered today. In many ways, the answers to these questions are even less well understood in relation to the option of grouting waste into the tank farms given the greater structural and chemical complexity and inhomogeneity of this waste as compared to those considered by the OTA in 1991.

Writing in the journal of the *Minerals, Metals, and Materials Society* in 1997, researchers from Argonne National Laboratory described the long-term durability of the type of grout then being proposed for immobilization of radioactive waste as "suspect at best." The authors also pointed out that past efforts to make use of grout to encapsulate low and intermediate level waste had met with limited success because the typical materials used "do not always meet performance requirements for structural integrity and leach resistance."[7] A great deal of research on new types of cement has occurred since 1997, but many serious questions and uncertainties remain.

In a 2001 report entitled "State of the Art Report on High-Level Waste Tank Closure," (see select pages attached) the authors point out a number of areas of uncertainty that those within the DOE complex feel need to be addressed before moving ahead with grouting the waste in the tanks. The first area of remaining uncertainty they point out is that despite having already grouted two of the tanks at the Savannah River Site (17F and 20F), the type of grout to be used has only "maybe" been determined while at Hanford there has been no determination of the type of grout that might actually be used.[8] The second major concern is that when discussing the areas of research that still need to be done in order to "more fully develop waste treatment strategies and to improve stabilization of certain contaminants," the authors of the report include as the first item in their list "determining the leachability of the waste itself and of

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[3] J.C.S. Long et al. 2000 p. 30
[4] J.C.S. Long et al. 2000 p. 30
[5] J.C.S. Long et al. 2000 p. 30
[6] OTA 1991 p. 44 and 82
[7] McFarlane et al. 1997
[8] Langton, Spence, & Barton 2001 p. 4

the waste in contact with the fill material."[9] Finally, and perhaps most telling, we find that in a table summarizing available technology and technology needs, the only entry that contains "No" in the "Available Technology" column is that of grout durability. The table cites a 500 to 1000 year time frame for the desired grout stability at Hanford and a 10,000 year time frame for the grout at SRS, and states that the DOE must still "[c]onfirm and justify requirements" for grout durability as well as to "[i]dentify testing and/or protocol for assessing durability."[10] The authors of the report conclude that *"[f]ield measurements should be conducted on all tank fill materials to confirm the design properties prior to full-scale placements."*[11] This document contains a remarkably candid assessment of the current lack, not only of any assurance of the lifetime of the grout waste form, but even of what requirements there should be used for evaluating its long-term durability.

Building on the analysis presented originally by Dr. Arjun Makhijani,[12] I have shown that if even just 1% of the strontium-90 (Sr-90) is left behind in the tanks at the Savannah River Site, that the grout would have to have a leak rate after 100 years of aging that is well below one part in a thousand per year in order to maintain the Savannah River below the safe drinking water standards. This analysis is based on the mean annual flow rate for the Savannah River for the available years between 1930 and 2002.[13] The choice of 1% residual waste is based on the claims that the DOE plans to remove 99% of the waste. However, we note that as of mid-2001 or early 2002 the sludge in the tanks occupied just 7.4% of the waste's volume, but contained two-thirds of the radioactivity.[14] If a larger percentage of the Sr-90 present was eventually chosen to be left behind, the requirements for containment would have to be proportionally tighter. We chose to focus on Sr-90 because it is a particular concern for children because strontium behaves like calcium in the body and children (all the way through puberty) tend to absorb a higher percentage of Sr-90 than adults where it can then be integrated into their developing bones and continue to irradiate them for extended periods. If the additional radionuclides present in the waste tanks and the impact during years with lower than average river flow rates are considered, than an even stricter level of performance over an even longer period of time would be needed.

Importantly, the 2001 report cited above acknowledges that the DOE does not yet have the necessary information on grout durability or contaminant leach rates necessary to determine whether or not the grout could meet such an exacting standard of performance as we have shown would be required, and the current experience with grout does not provide confidence that such a standard could be met after 100 years of grout aging. Experiments in 1982 at Oak Ridge National Laboratory found a minimum release fraction for strontium in grout of 3.9% and a maximum of more than 50% after just 80 days for various types of grout and lengths of curing times.[15] In 1997 additional experiments at Oak Ridge found a minimum release fraction for strontium of more than 1.25% and a maximum of nearly 2.5% after just one week.[16] While these experiments were conducted with samples that had very large surface to volume ratios compared to the tanks, these results raise serious concerns over the ability of the grout to meet a better than 0.1% annual release rate after 100 years of grout aging and deterioration, and highlights the need for more realistic long term studies.

Given the evolving concerns over the long-term performance of grout, the State of Washington entered into an agreement with the Department of Energy in the 1990s that prohibited grout from being used for

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[9] Langton, Spence, & Barton 2001 p. 50
[10] Langton, Spence, & Barton 2001 p. 52-53
[11] Langton, Spence, & Barton 2001 p. 51 (emphasis added)
[12] Makhijani 2004
[13] USGS 2004
[14] Makhijani & Boyd 2004 p. 22
[15] Morgan et al. 1982 p. 7
[16] Spence & Kauschinger 1997 p. 36

the immobilization of the low activity portion of the tank waste that could be separated from the high-level waste.[17] In revisiting the issue of grouting the low activity waste from the tanks at Hanford in 2002, the Tank Waste Committee of the Hanford Advisory Board expressed their continued concern over the long-term durability of grout as well as their concern that the existing laboratory testing programs may not adequately represent the behavior of the grout over an appropriately long timescale, according to the draft meeting summary from August 15.[18]

Finally, a December 2003 draft report prepared for the DOE on the use of grout to stabilize the contaminants that have leaked into the soil surrounding the Operable Unit 3-14 Tank Farm at the Idaho National Engineering and Environmental Laboratory highlighted many of the continuing shortcomings in the DOE's knowledge about grout durability and performance in real world applications involving nuclear waste. The draft report noted that "parameters such as hydraulic conductivity, chemical buffering, and monolith cracking have proven difficult to measure in field-scale applications" and that therefore only a "limited body" of such data exists.[19] In addition, the report noted that there may not be sufficient data available on the leach rates for plutonium and neptunium from short term laboratory experiments to even support a feasibility study at the Idaho site and that for all radionuclides "[l]onger-term leach tests (multiple years) may also provide useful data."[20] Finally, the report added that during the long-term leaching experiments the durability of the grout should also be tested in order to aid in determining the grout's expected useable lifetime. Such multi-year studies should be conducted in as realistic conditions as possible in order to make them truly applicable to the problem being studied.

There are additional researchers, outside of the DOE complex, working on the uses of grout in managing radioactive waste who have highlighted the need for long-term studies of the properties relating to grout's durability and the leaching of radionuclides. This is particularly important given the complicated chemistry of cement and the many interacting and time dependent effects that occur as grout ages in an underground environment. We will note a number of these needs as we touch on some of the major outstanding issues surrounding the long-term performance of grout that have grown out of this independent research.

In addition to normal aging processes, grout is vulnerable to a number of different types of external attack from chemicals such as sulfates, which are also present in the high-level waste to be left in the tanks. However, even pure water will damage and degrade concrete overtime both as a liquid and when it undergoes freezing and thawing cycles. Despite the importance of these degradation pathways, the actual physical mechanism behind the damage they cause is still not fully understood.[21] Importantly however, it is known, that the mechanism that drives the damage may be different when the grout is exposed to different concentrations of sulfates and other chemicals, and therefore that it is difficult to translate laboratory experiments into the real world without knowing the precise chemistry of the waste in each tank and that of the tank's surroundings. In addition, the temporal evolution of the damage may be different at different concentrations and effects may begin to show up only after a long time. Studies on the expansion of concrete have been carried out for up to 22 years in order to gauge this response to sulfate exposure.[22]

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[17] Garrick et al. 1999 p. 37
[18] Tank Waste Committee 2002 p. 7
[19] U.S. DOE 2003 p. 6-12
[20] U.S. DOE 2003 p. 6-12 to 6-13
[21] Tian & Cohen 2000 p. 117,123, Santhanam, Cohen, & Olek 2002 p. 915, and Zuber & Marchand 2000 p. 1929-1930, 1937
[22] Allan & Kukacka 1997 p. 442-443, Maltais, Samson, & Marchand 2004 p. 1587, and Tian & Cohen 2000 p. 118

Experiments on the laboratory scale have demonstrated some of the features of the complex temporal (i.e. time dependent) evolution of damage in concrete. Damaging effects can be unapparent for long times (sometimes up to a year or more) and then suddenly begin to have a measurable impact on the grout's durability. In addition, it has been shown that the so-called "sulfate resistant" grouts are not immune from damage, but instead often show only slower rates of damage from sulfates while showing more severe damage from pure water.[23] It has even been observed that up to 90 days (the maximum length of time over which most radionuclide leaching tests are conducted) the ability of some grouts to immobilize contaminants actually improve as the pores of the material begin to fill up with reaction products. Beyond 90 days the expansion caused by the further buildup of reaction products begins to crack and damage the grout increasing the leach rates for the contaminants.[24] Thus measurements that follow the standard procedure may underestimate the leaching of the radionuclides in significant ways. All of this highlights the complex nature of grout's behavior over time and the need for long-term realistic field studies.

In addition there are more exotic types of damage that may be important over the timescale that must be considered for radioactive waste. For example, the South-East, where the Savannah River Site is located, is known to be seismically active and an earthquake centered near the site could cause significant cracking in the grouted underground tanks, especially if the grout has been weakened through aging and degradation processes for several decades.

As implied above, the major importance of cracking and the degradation of grout over time is that even very small cracks can have a strong influence on the material's permeability. This effect adds further to the complex behavior of grout as it ages with microcracks forming, growing, and eventually beginning to intersect and creating interconnected networks.[25] Adding even further to the complexity of the situation in real systems, the drying process can introduce different amounts of cracks with different sizes along perpendicular directions, and thus can cause the material to have a higher permeability along one axis. This type of behavior could affect the leaching rate in a system where the radionuclides are predominately oriented along one direction.[26] We will show below that this is the case for the proposed grouting process at the high level waste tanks at SRS, Hanford, and elsewhere which creates a horizontal "sandwich" with a sludge rich layer in the middle.

In addition to the leaching of radionuclides like strontium-90, which are not strongly affected by the chemistry of the grout, other radionuclides of significant concern such as technetium will be strongly affected by the grout chemistry. This chemistry may, of course, change over time adding additional concerns over long-term behavior. The leaching of technetium from grout is controlled in large part by the rate of diffusion of oxygen into the material. The grout proposed to be used in the high-level waste tanks attempts to maintain a chemical environment that retards the mobility of technetium, but oxygen or oxygenated water significantly accelerates its mobility by overcoming this effect. As of 2000, all reported studies on technetium leaching were conducted for less than 3 months.[27] Subsequent studies conducted for the Department of Energy have shown that if the grout is cracked and there is surface water present, than the leach rate would be much higher than for undamaged grout.[28] This type of long-term connection between the durability of the concrete and its ability to chemically retard the release of

[23] Allan & Kukacka 1997 p. 441, Gollop and Taylor 1995 p. 1581, 1589, Tian & Cohen 2000 p. 120, Santhanam, Cohen, & Olek 2002 p. 918, and Maltais, Samson, & Marchand 2004 p. 1585, 1588
[24] Guerrero, Hernandez, & Goni 1997 and U.S. DOE 2003 p. 6-12
[25] Gerard & Marchand 2000 p. 37, 42 and Wang, Jansen, & Shah 1997 p. 381, 388, 391-392
[26] Burlion, Skoczylas, & Dubois 2003 p. 684-685
[27] Shuh et al. 2000 p. 48
[28] Shuh, Lukens, & Burns 2003 p. 45

radionuclides raises serious concerns regarding the performance of the grout and needs to be examined experimentally over a number of years under realistic field conditions.

It is important to realize that virtually all of the laboratory experiments that have attempted to examine the questions of grout's durability and its ability to prevent leaching of radionuclides have been conducted with homogenous samples. For example, the simulated radioactive waste has either been mixed thoroughly with the grout before being allowed to harden, or the grout was mixed without the simulated waste and then the hardened grout was immersed in a uniform bath of water and chemicals. Unfortunately, these experiments deviate quite significantly from the actual conditions that would be experienced in the high-level waste tanks. One of the most serious differences between the laboratory tests and the actual physical situation in the tanks is that the waste sludge will not be uniformly mixed with the grout, but will instead have a complex and inhomogeneous distribution that has strong variations among and within different regions of the final grout-sludge system. This inhomogeneous waste distribution is due primarily to the fact that the grout to be used does not mix with the sludge, but instead pushes it along as the grout is poured into the tank from above. If the grout was poured only from the center of the tank than it would force the waste up along the edge of the tank which would be a very undesirable configuration. To try and address this problem, it was decided by the engineers at the Savannah River Site to make multiple pours from the outside to force the sludge inward and then a final pour from the center of the tank.

To test this strategy, experiments were conducted with a scaled down version of the 85 foot diameter waste tanks at the Savannah River Site in 1997. The results showed that by using the seven openings in the tank cover (six along the outside circumference and one in the center) to pour the grout that approximately 30% of the waste was integrated into this bottom layer. The remaining 70% of the sludge rested on top of the first grout layer forming a center ring with six "spokes" that all together occupied roughly one-third of the total surface area. By adding dry grout to this layer nearly all the sludge was converted into a hardened layer that had noticeably different physical properties than the poured grout. All together 65% of the original sludge was incorporated into this second layer. A final pour of grout from the center of the tank was made, and just 5% of the total amount sludge ended up being integrated into this layer. Importantly, after curing it was found that the sludge rich second layer had weak adhesion to the grout layers above or below it, and that the sludge in this layer formed a "spooked" pattern with a central ring and six "spokes" that were in contact with more than two-fifths of the circumference of the tank wall.[29] The grout touching the tank wall will of course be the first to be exposed to water as the tanks further deteriorate and leak.

While this is a highly undesirable configuration for reasons to be discussed below, this layered behavior was accepted by the Department of Energy for its plans regarding the tanks. In the grouting of the two high level waste tanks at the Savannah River Site (17F and 20F) that have already been completed, the grout and sludge did not mix and the engineers had to add the dry grout layers as was done in the 1997 small scale experiment.[30] In addition, it was acknowledged in March 2004 that this behavior is not unique to SRS, and that the DOE would not expect the waste to mix with the grout at Hanford either.[31] Thus a layered or "sandwich" configuration, and not the uniformly mixed case is the one that must be considered in regards to the high-level waste tanks throughout the DOE complex. This geometry will have a significant impact on the assumptions that can be made concerning dilution of the sludge since only a fairly small volume of grout (i.e. the dry grout layer) contains the majority of the radionuclides. When calculating whether or not the grouted waste in the tanks will exceed the Greater than Class C waste classification (and thus whether or not it should require disposal in a deep geologic repository), the

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[29] Caldwell & Langton 1997 p. 10-11 and 28
[30] Langton, Spence, & Barton 2001 p. 23
[31] Tank Waste Committee 2004 p. 12-13

estimated volume of grout actually containing the radioactive sludge should be used and not the entire volume of the grout poured into the tanks.

A complete discussion of why the layered configuration for the grout and sludge identified in the 1997 SRS experiment is unlikely to be suitable for immobilizing the radionuclides to the required level of performance over hundreds to thousands of years is beyond the scope of this report. However, the major concerns relating to what would occur inside the actual waste tanks are that the multiple pours and multiple grout layers create intrinsic boundaries both within and between regions of varying sludge composition that will be vulnerable to cracking with age and also have naturally higher permeability to begin with. This higher permeability (which will be enhanced by additional cracking as noted above) will allow greater leaching of the contaminants as well as greater ingress of destructive chemicals such as water and sulfates that will act to further weaken the boundary. The process therefore feeds back on itself with the further weakening of the boundaries allowing ever more destructive agents to enter the grout which then leads to an acceleration in the damage. These concerns were raised by the National Research Council in 2000. In its analysis, the NRC concluded that

> Predicting performance in resisting water infiltration can be difficult because of uncertainties that include the degree to which the first layers of grout take up the residue, the water pathway effects of the cold joints between successive pours of grout, and the effects of preferential corrosion of the tank metal and penetrating structures (thereby offering a partial bypass path). Moreover, waste tank residue is likely to be highly radioactive and not taken up in the grout, so there is substantial uncertainty associated with the volumetric classification and average concentration of the waste and prediction of the isolation performance of the system.[32]

The two most important grout boundaries to consider are those between the sludge rich second layer and the grout above and below it. This layer, which is very irregular in shape and thickness, would have different physical properties such as porosity and water content compared to the adjacent grout layers and has been shown to have only weak adhesion to these adjoining regions. The boundaries along this layer's top and bottom would therefore be more permeable and more prone to cracking which is a particular concern given that nearly two thirds of the radioactive waste sludge is locked up in this second layer. In addition, this layer's effective surface area–to-volume ratio would be much larger than that of the tank as a whole. Both of these properties will act to accelerate the total leaching of radionuclides over time. Importantly, none of the homogeneous laboratory experiments can provide directly useful information at this point to predict precisely how this layered configuration will behave. This lack of experimental information is despite the fact that this layering effect has been known since at least 1997.

An additional concern relating to the interactions of these layers is that they will have different thermal properties both because of their differing physical makeup and because of the heat generated by the differing amounts of radionuclides incorporated within them. In the 1997 experiment, the grout in the second layer was found to have an average sludge concentration by weight that was five times larger than that in the grout layer on the bottom and 85 times larger than that in the top-most layer.[33] This means that in the tanks there will be significant internal temperature gradients between regions of the grout with different contaminant concentrations. According to a 1992 study of the durability of double-shell tank waste grouts at Hanford

> The grouts will remain at elevated temperatures for many years. The high temperatures expected during the first few decades after disposal will increase the driving force for water vapor transport away from the grouts; the loss of water may result in cracking, dehydration of hydrated phases, and precipitation of salts from saturated pore solution. As the grout cools, osmotic pressure caused

[32] NRC 2000 p. 40
[33] Caldwell & Langton 1997 p. 12

> by the high salt content may draw moisture back into the grout mass. The uptake of moisture may have detrimental impacts on the behavior of the grout.[34]

These internal gradients will be enhanced by the influence of external temperature changes as well. For example, at the Savannah River Site in 2003, 50% of the days in January and December had low temperatures that dropped below freezing and more than a quarter of the days in July and August had highs that exceeded 90 ^{o}F.[35] While the ground temperature will not change as rapidly as the air temperature, there will be some seasonal variations of temperature at the depths at which some of the tanks are located. Of particular concern is that these overall thermal effects will add additional stress to the boundaries between the sludge rich second layer and those above and below it. This will be due in part to their different temperatures (the heat from the radiation in the second layer will tend to keep it at a more stable higher temperature than the other two layers which will most closely follow the external temperature) and in part due to the fact that the layers will expand and contract by different amounts for the same change in temperature due to their differing physical makeup. This stress will add further to concerns over cracking, increased permeability, and the associated increase in radionuclide leaching.

Finally, in addition to the two boundaries along the top and bottom of the sludge rich second layer, there are additional boundaries formed within the first layer where the grout from adjacent pours intersected. It was noted in the experiment that much of the 30% of the total waste sludge that was incorporated into this first layer was either bound to the top or trapped in the boundaries between adjacent grout pours.[36] These intersections, while far stronger than the boundary between the first and second layers, will still be areas that are potentially more prone to shrinkage cracking (the formation of cracks in the concrete as it shrinks during the drying and curing process) as well as other effects such as thermal gradients in areas that have significant quantities of trapped sludge. This is all also ignoring the questions of what will occur in the cooled high-level waste tanks that contain numerous obstructions such as the cooling coils and vertical columns that will further alter the grout and sludge distributions and would provide additional boundary regions.[37] Along with the other effects discussed, these additional boundaries could undergo other types of deterioration such as interactions between corroding metal and concrete which is known to be a serious threat from experience with reinforced concrete structures. All of these weakened boundaries within the tank are a concern for the further enhancement of radionuclide leaching.

Even if the long-term behavior of the homogeneous grout-waste systems studied in laboratory experiments were well understood and could be accurately predicted, which we have shown that it cannot, the serious questions relating to the behavior of the actual configuration that would occur in the grouted tanks would require careful long-term examination under real world conditions before any decision should even be considered. Experiments with a full size system with realistic conditions for both the external environment and the sludge's internal heat should be conducted over the course of several years to provide some level of assurance that the important mechanisms that will control contaminant leaching are understood. The level of containment necessary to prevent the contamination of the Savannah River above the drinking water standard is significant. Recall that our calculations show that leaching must be kept to well below one part in a thousand per year even after 100 years if the DOE succeeded in removing 99% of the Sr-90 in the waste. If the DOE decided instead to leave a larger percentage of the radioactivity in the waste behind, even stricter standards for the grout would need to be met. The inclusion of other radionuclides and the consideration of low flow years would still further tighten the required containment. The experience of plutonium migration highlights the need to make sure that realistic tests are conducted to avoid again making potentially serious and far reaching mistakes based on incomplete understanding and flawed conceptual models.

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[34] Lokken, Martin, & Shade 1992 p. 2
[35] Hunter 2004 from Table 1(a)
[36] Caldwell & Langton 1997 p. 10
[37] Makhijani, Alvarez, & Blackwelder 1986

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WSRC-TR-2001-00359, REVISION 0

Key Words:
Grout
Flowable Fill
High-Level Waste Tank Closure

Retention:
Permanent

STATE OF THE ART REPORT ON HIGH-LEVEL WASTE TANK CLOSURE (U)

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REPORT DATE: JULY 31, 2001

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Prepared for the U.S. Department of Energy Under
Contract Number DE-AC09-96SR18500

Table 2-2. Summary of the grout needs for closure of large tanks in the DOE complex.

Grout Properties	INEEL	WVDP	Hanford	SRS	ORNL
Fresh properties					
Pumpable	Yes	Yes	Yes	Yes	Yes
Flowable	Yes	Yes	Yes	Yes	Yes
Self-leveling	Yes	Yes	Yes	Yes	Yes
Bleed water	Minimum	Minimum	Minimum	Minimum	None
Set time		?	Weeks-months		<72 h
Resist solids settling	N/A	Yes	Yes	Yes	No
Heat of hydration		Yes	Maybe	Yes	Yes
Cured properties					
Strength	>500 psi	Low	Low	Low	>50 psi
Excavatable		Yes	Yes	Maybe	No
Hydraulic conductivity		?		Maybe	
Stabilization/solidification properties					
Radionuclides	No	Am, Cs, Np, Pu, Sr, Tc, U	Tc, I, C, Se, Pu, Am, U, Ni, Nb, Cm, Sr, Cs, Sn, TRU	Yes esp. Tc, Pu, Se	No
RCRA metals	No	Hg, Cr, As, Ba, Cd, Se, Ag, Pb	Cr	Yes esp. Hg	No
Others	No	NaOH, nitrate, nitrite (wash out, not stabilize)?	Nitrate, nitrite		No
Durability	500 years (PA)	Until excavated? 50-100 years	500-1000 years 30 y (RCRA)	10,000 years	None (no credit in PA)
Implementation	Displace and remove heel, pump/tremie	Batch grout & place in tank	Mix heel and grout; Pump/tremie	Mix heel and grout; pump/ tremie	Pump and dump or tremie
Grout Identified	Yes	Yes	No	Maybe	Yes
Other issues	Requires grout to first displace heel for removal, then fill tank; heel will interact with fill	Physical handling properties already evaluated; heat of hydration, and stabilization TBD	Interested in apatitic stabilization	Cost of grout is a concern; likely for other sites as well	Needs already met & currently closing tanks

5.0 COMPARISON OF TANK FILL TECHNOLOGY AND SITE NEEDS

Flowable fill was identified by all of the DOE sites as the material of choice for closing (physically stabilizing) the HLW tanks. (Difficulties associated with consolidating and compacting non-flowable soil, sand or gravel backfills were acknowledged by all of the sites.) American Concrete Institute Standard Practices [ACI 229-R] for designing, preparing and placing flowable fills are applicable for tank closure materials. However, several requirements related to tank fill materials are not addressed in the standard practices because they are not relevant to construction fills. The most obvious exceptions to construction practices for flowable fills are:

1. Minimizing or eliminating bleed water for placements in structures where the excess mixing water can not drain away or evaporate.
2. Including ingredients in the mix that can chemically treat incidental waste to reduce contaminant leachability.
3. Controlling set time to provide flexibility with respect to lift heights requirements.
4. Controlling heat of hydration for mass pour applications.

The DOE Site requirements for placing and curing HLW tank fill materials are tabulated in Table 5-1 along with a list of available technology and a list of technology needs. The requirements for treating contaminants in the waste heel are tabulated in Table 5-2 along with treatment reagents and technology needs.

Additional research is not required to develop new methods for controlling set time and heat of hydration. Set time is not applicable to low-strength flowable fills. If it is an issue for modified higher strength fills, the set time can be adjusted with set accelerating or retarding commercially available admixtures. Heat of hydration is dependent on the amount of cement and hydraulic material used in the mix. Guidelines for mass pour mix designs can be interpreted with respect to flowable fills and are provided in ACI 211.1-91.

Additional effort to identify cost effective zero bleed admixtures is warranted. For example, the admixture system used in the SRS zero bleed CLSM bulk fill and the zero bleed 2000 psi intruder barrier grout added about $15 to the materials cost for a cubic yard of fill. The admixture cost for the fill used in two SRS tanks (12,000 cubic yards) was about $180,000. Consequently identifying less expensive zero-bleed admixtures can lower the materials cost significantly. Both laboratory and field-testing are required.

Research is required to more fully develop waste treatment strategies and to improve stabilization of certain contaminants. This includes:
1. determining the leachability of the waste itself and of the waste in contact with the fill material,
2. determining the effectiveness of repeated washing and removal of the wash water as an effective approach for treating the soluble contaminants of concern (i.e., removal of nitrate, nitrite, soluble C-14, I-129, Tc-99, Np-237 from the tanks),

3. evaluating reagent mixtures and proportions for effectiveness in fill materials (mixtures of portland cement, fly ash and hydraulic slag),
4. specifying reagents, reagent mixtures and proportions for use in fill materials for simultaneously treating a large number of radionuclides such as those identified by Hanford,
5. identifying and testing alternative stabilization reagents, such as phosphate precipitation or absorption for selected contaminants and non-sulfide technetium stabilizaiton.

Field measurements should be conducted on all tank fill materials to confirm the design properties prior to full-scale placements. In addition, compatibility of the admixtures and the reactive stabilizing ingredients should be confirmed.

Table 5-1. Tank fill physical properties versus available technology and technology needs.

Grout Property	Site Response	Available Technology	Technology Needs
Fresh Properties			
Pumpable	Yes	Yes (demonstrated at SRS)	Alternative less expensive admixtures
Flowable	Yes		
Self-leveling	Yes		
Bleed water	Minimum to None		
Set time	<72 hr months ?	Yes	Justify and confirm requirements
Resist solids settling	N/A Yes No	Yes	Justify and confirm requirements
Heat of hydration	Yes Maybe	Yes	Identify method and test protocol for evaluating heat of hydration
Cured Properties			
Strength	Low >50 psi, >500 psi	Yes Yes Yes	None
Excavatable	Yes No Maybe	Yes	None
Hydraulic conductivity	Maybe ?	Yes	Identify requirements
Durability	None (ORR) 50 –100 years (WV) 500 years (INEEL) 500 –1000 years (Hanford) 10,000 years (SRS)	No	1. Confirm and justify requirements. 2. Identify testing and/or protocol for assessing durability
Implementation	1. Use grout to displace heel so it can be removed by pumping (INEEL) 2. Mix heel w/grout (Hanford and SRS) 3. Displace heel so it can be encapsulated with a single "lift" of grout (SRS)	Possibly (depends on specific waste and grout and tank features)	1-3. Conduct pilot-scale testing of the waste retrieval and waste mixing concepts for proof of principle.
Fill Materials Identified	Yes (most sites) No (Hanford)	Yes (SRS closed two tanks)	Specify and validate fill material properties, tank closure plans, and waste treatment strategies for DOE

Table 5-2. Tank fill leaching properties versus available technologies and technology needs.

Grout Property	Site Response	Available Technology	Technology Needs
Stabilization/Solidification Properties			
Radionuclides	Am	Hydroxide/Portland cement	Confirm effectiveness
	C	Portland cement, $CaCO_3$	Confirm effectiveness Identify improved treatment
	Cm	Hydroxide/Portland cement	Confirm effectiveness
	Cs	Clay (Illite) Zeolite (clinoptilolite)	Confirm effectiveness
	I	Silica fume for low porosity	Confirm effectiveness Identify improved treatment
	Nb	Hydroxide/Portland cement	Confirm effectiveness
	Ni	Hydroxide/Portland cement	Confirm effectiveness
	Np	Sulfide/Slag Engineered porous apatite	Confirm effectiveness Same as for Tc
	Pu	Hydroxide/Portland cement	Confirm effectiveness
	Se	Sulfide/Slag	Confirm effectiveness
	Sn	Hydroxide/Portland cement Sulfide/Slag	Confirm effectiveness
	Sr	Cement, Cement-Pozzolan Zeolite Synthetic ion exchange resins CST (Crystalline silico titanate) Phosphate (acidic system) Engineered porous apatite	Test in fills/grouts Identify preferred stabilization agent. Evaluate engineered apatite in cement waste forms and tank fills
	Tc	Sulfide/Slag Engineered porous apatite (irreversible sorption)	Identify and test sulfide/slag alternatives for stabilizing Tc in the grout such as, ion exchange resins. Evaluate engineered apatite in cement waste forms & tank fills
	U	Hydroxide/Portland cement	Confirm effectiveness
	TRU	Hydroxide/Portland cement	Confirm effectiveness
	None	NA	
RCRA metals	As	Sulfide/Slag	Test in fills/grouts. Determine maximum total concentrations and maximum TCLP leachate concentrations. Determine acceptable upper limits for each contaminant and for mixtures of all contaminants.
	Ag	Soluble Cl	
	Ba	Hydroxide/Portland cement	
	Cd	Hydroxide/Portland cement	
	Cr	Sulfide/Slag	
	Hg	Sulfide/Slag	
	Pb	Hydroxide/Portland cement Phosphate	
	Se	Sulfide/Slag Portland cement	
	None	NA	
Others	NaOH	Blast Furnace Slag, Pozzolans	Review and confirm requirements and effectiveness
	Nitrate	None identified	
	Nitrite	None identified	

6.0 SUMMARY

In-situ closure of large empty tanks contaminated with radioactive and hazardous waste is unique to the United States and possibly to Russia. Other countries with nuclear waste plan to clean the contaminated storage tanks and to dispose of them in designated repositories or landfills.

Several DOE sites are currently developing plans for in-situ tank closures. The site specific plans are driven by the:

- applicable regulatory requirements,
- extent of environmental contamination associated with the tanks,
- construction restrictions and integrity of the tanks,
- success of the waste retrieval activities,
- treatment strategy selected for the tank heel and/or incidental waste,
- tank void stabilization strategy,
- intruder barrier methodology, and
- surface cover system (landfill capping technology).

All of the sites identified low-strength flowable fill materials, i.e. controlled low strength material (CLSM), for physically stabilizing the void spaces inside of the large HLW tanks. Enhancements to a generic flowable fill formulation [ACI 229-R94] depended on site-specific needs for contaminant stabilization and on the emphasis placed on certain physical properties.

Flowable fill suitable for routine construction applications was used at ORNL for the OHF tank closure. Fill materials designed for closing tanks at the INEEL are also similar in concept to the ORNL fill except that higher strengths are desired, consequently the formulations contain more cement. Also fly ash was substituted for sand in the INEEL pipe grout to enhance the flow through small openings. Waste treatment was unnecessary and generation and management of bleed water was not an issue at these sites.

Management of bleed water was undesirable at the SRS. Consequently zero-bleed formulations were developed. In addition, a waste treatment strategy was developed and tested that required a chemically reducing environment. This was accomplished by including blast furnace slag and sodium thiosufate in the fill that was placed in contact with the waste.

Stabilization of potential contaminants is a need at WV. Proprietary formulations containing ion exchange resins and/or other reactive ingredients were developed. The tank fill materials for closure of the WV tanks must also be excavatable so the material can be retrieved if necessary at a later time.

In summary, work is in progress in the DOE complex to permanently remove HLW tanks from service and to close/dispose of the tanks in-place. Cement-based grouts are currently being used to fill the tanks and to stabilize the incidental waste remaining in the empty tanks.