Why Grout Failed at Hanford

Chronology of the Failed Grout Program

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Introduction

Hanford Challenge believes that the focus of Hanford tank waste cleanup should remain on vitrifying Hanford's tank waste, even in the face of technical issues, quality assurance problems, and cost/schedule overruns. Unfortunately, grout—or the encasing/burying of waste in cement—is once again being discussed as an option to treat and dispose up to 80% or more of Hanford's tank waste. In these discussions, proponents of grout assert that it will be cheaper and faster than the current vitrification path. However, this 'cheaper, faster' position does not adequately take into consideration whether anything has changed since past grout efforts failed and relies on a host of assumptions, which are called into serious question by the history of failed grout attempts at Hanford.

Hanford Challenge has been a steadfast advocate for a safe and effective plan to immobilize Hanford's tank waste in glass (or "as good as glass"). Although cost and schedule are important factors when choosing a plan for cleaning up Hanford's tank waste, they are not the only factors. Hanford Challenge believes that safe, long-term storage of Hanford's tank waste is one of the most important factors when deciding on a solution to contain Hanford's waste safely for millennia.

The Department of Energy has yet to successfully demonstrate that it can safely and effectively contain Hanford's tank waste in grout. Like any solution that has yet to be put to the test, and has a clear history of failure, grout would likely to encounter cost overruns, potentially insurmountable technical challenges, and schedule delays. Simply put, we cannot afford more avoidable failures.

As the timeline below shows, treating Hanford's tank waste with grout has been shown to be problematic. Near the end of Hanford's production days in the early 1980's, the grout program was established to deal with a lack of space in underground waste storage tanks. The idea was to remove tank waste, pre-treating it to remove key radionuclides and grout the low-level waste for disposal onsite, not from a cleanup mindset, but because of a storage space issue. Glassifying Hanford's tank waste has always been the plan for the high-level portion of the waste.

From 1983 to 1993, the Department of Energy (DOE) spent over $200 million ($450 million in 2021 dollars) attempting to mix tank wastes with cementitious materials—"grout"—for disposal in large underground vaults on the Hanford site. The grout program was cancelled in 1993 because it was too expensive, technically impractical, and not protective of human health and the environment.

In 1993, the plan to grout the low-level portion of tank waste failed and glass was selected as the cheaper, faster, and more protective waste form. As glassifying tank waste through vitrification encounters more cost increases, delays, and uncertainties, grout is resurfacing as an "easy alternative" to the high-level tank waste treatment problem. However, the original grout program failed for insurmountable technical challenges that remain insurmountable today. Without credible solutions to these challenges, it would be a mistake to waste more time and money chasing this mirage.

Below, we present the "Current Claims and Past Failures" about grout to ensure that these issues are thoroughly reviewed by entities such as the National Academy of Sciences and the Nuclear Regulatory Commission. Thorough review by these entities will ensure that all of the past issues are adequately—and publicly—addressed and used to update cost and schedule estimates. Our goal in highlighting these past unresolved issues is to arrive at an accurate picture of what it would take to grout tank waste.

We will best serve future generations and protect the environment by learning from, instead of ignoring, the past failures Hanford's grout program. We should avoid investing millions of taxpayer dollars on grout when it has yet to overcome the problems that led to its past failure. Successfully immobilizing the worst of Hanford's waste is too important for hastily-made decisions that do not adequately and publicly resolve past performance issues. In that spirit, we present a summary of 'Current Claims and Past Failures' with grout to ensure that these issues are fully researched and addressed before making a decision. Valuable resources for cleanup should not be diverted without first providing validated and technically defensible solutions to the issues that caused the grout program to fail in the past.

Current Claims and Past Failures

Grout Claim #1: Grout is easy to make, especially when compared to glass.

This claim is based on the life experience of many of us—we've poured concrete for a home project and it's easy and straightforward. Very few of us have made glass in a melter.

And it's true, grout is easy to make *as long as you don't put Hanford tank waste in it.* The grout program history shows the extreme difficulty of making a solid, cementitious waste form out of Hanford tank wastes. This difficulty required extremely expensive and technically impractical pretreatment processes. Further, it was judged as the unproven, immature waste form when compared to glass.

In the end, DOE was unable to produce an acceptable grout. Full stop. It did not work.

In 1996, the term "super-grout" came into use.[1] Ironically, the reference was from an Environmental Impact Statement on tank waste treatment and was only mentioned in the discarded alternatives pile. From all accounts and internal conversations with experts this is simply the original formula that did not work with additional dry material thrown in and is yet unproven. Yet, the claim that "supergrout" solves past grout formula problems persist – and no one has produced a tried-and-true formula for what that might be. We believe that the "supergrout" formula needs to be produced, validated, and demonstrated to be able to overcome past grout formula failure for Hanford's specific tank waste.

Grout Claim #2: Grout is protective of human health and the environment.

DOE was unable to demonstrate that grouted tank waste disposed in vaults was protective of human health and the environment. The grout performance assessment was initially rejected by the peer review panel for having unfounded assumptions and failing to show it could meet regulations for protecting groundwater.

The grout waste form was so poor that long-term protection of the environment relied on the vault design—a 44-inch-thick asphalt barrier encapsulating the grout. If the barrier failed, groundwater would be contaminated above regulatory requirements.

The term 'as good as glass' is often used to indicate alternative waste forms at Hanford should only be considered if they perform as good as a vitrified waste. Grout failed, or barely met, leachability indices while glass performed three times better than the requirement. In protecting the environment, glass performed between 100,000 and 1,000,000,000 times better than grout, according to a 1991 Westinghouse report (see p. 10, below).

Grout Claim #3: Grout is cheaper than glass.

Again, this appears intuitive since many of us have poured concrete, but it is wrong. The true cost of grout is still unknown because DOE was unable to make it work. But a significant rationale for cancelling the program was that the cost was skyrocketing and there was no end in sight. Life-cycle cost estimates consistently identified glass as competitive with, or cheaper than, grout.

Grout Claim #4: Grout is faster than vitrification.

Similar to cost, the true schedule for grouting Hanford waste is unknown because it failed. But the concept of grout being a faster, cheaper treatment method relies on the image of a very simple mixing facility near a tank farm. Waste is retrieved from a tank, mixed with cementitious materials, packaged, and shipped away.

But that is a mirage. The truth is, extensive characterization and testing is required for each waste type to determine a grout formula. In the past, DOE, while never developing an acceptable formula, estimated it would take at least twenty months to do so for the first grout campaign.

[1] https://www.energy.gov/sites/default/files/nepapub/nepa_documents/RedDont/EIS-0189-FEIS-1996.pdf, p. 443

Then, depending on the characterization and formulation, multiple pretreatment operations (in a large, complicated, multi-billion dollar facility) would likely have to be performed to prepare the waste for grout. The pretreatment step is often ignored in current discussions, but was the Achilles' heel of the first grout program.

Grout Claim #5: Grout is a good option for Hanford because it is successful at the Savannah River Site and West Valley.

Let's just take this claim one step further—Hanford successfully disposed of one million gallons of waste in grout in the late 1980's as a demonstration project. If it has worked at Hanford, SRS, and West Valley, why isn't it being utilized more broadly?

Here's why. SRS and West Valley both chose to remove the overwhelming majority of radionuclides so the waste would meet NRC's Class A waste criteria. Hanford, even with pretreatment, was having difficulty meeting Class C and transuranic requirements. In other words, Hanford planned to dispose an unrealistic amount of radioactivity in grout. Of great concern, as well, is the presence of unacceptable levels of nitrates and nitrites predicted to escape from the grout formula, in exceedance of environmental standards.

What about the one successful grout vault at Hanford? It was not even tank waste, but extremely low-level waste from N Reactor. The radionuclide content was so low that leach testing of the grout was very challenging since it is impossible to detect contamination when it is not present.

Grout Claim #6: The technology for grout has improved remarkably since the DOE last considered it nearly 30 years ago.

Even though grout is now being marketed as the solution for a large portion of Hanford's tank waste, as far as we can tell, not much has changed since the DOE turned its back on grout in 1993. The National Academy of Sciences, in a 2019 review of a DOE (FFRDC) report that listed grout as a cheaper option, stated:

> "The committee finds that, in its current iteration, the FFRDC's analysis:
> a. When taken alone, does not yet provide a complete technical basis needed to support a final decision on a treatment approach;" p. 3 and
>
> "The cost estimates in the FFRDC report are based on technologies that, for the most part, have not yet been fully developed, tested, or deployed for Hanford's particular, and particularly complex, tank wastes, and instead use costs from similar technologies. As a result, there are large attendant uncertainties, suggesting that costs could be much higher than estimated, but are unlikely to be much lower." p. 3
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> "Assessment of waste form performance would have to include consideration of the characteristics of the disposal sites and the transport pathways to receptors over relevant periods of time, as well as be based on the inherent characteristics of the waste form." p. 4

What follows is a detailed chronology of the grout program as it was pursued and rejected at Hanford from 1983 to 2000.

Grout Program Chronology

1983: Grout program conceived to treat and dispose tank waste (Worthington, 1991).

1984: Grout facility performance criteria and design completed (Worthington, 1991).

1985: DOE publishes the first grout performance assessment (Treat, 1985).

1986: DOE decides the existing vault design will not meet RCRA and performance assessment requirements. As a result, it will be used only for the first demonstration run (low radioactivity, nonhazardous phosphate-sulfate from N-Reactor). Future tank waste campaigns will be disposed in redesigned vaults (Worthington, 1991).

1986: Difficulties in planned grout pretreatment technologies begin to appear. The strontium-90 removal technology (SREX) does not work. The solvent is not efficient, radiation degrades the extractant, and it has not been tested beyond bench-scale (Horowitz, 1986).

April 1988: DOE issues Record of Decision for the Hanford Defense Waste Environmental Impact Statement that requires grouting (low-level portion) and vitrifying (high-level portion) of double shell tank wastes (DOE, 1987 and DOE, 1988).

August 1988: Construction of the first grout vault is completed and grout facility startup is initiated (Worthington, 1991).

August 1988-June, 1989: DOE takes nearly one year to fill one vault of approximately one million gallons of dilute sodium decontamination waste from N Reactor (high phosphate and sulfate) (Cline, 1990).

1989-1991: New grout vault design is developed and four vaults are constructed and planned for filling starting in 1992 (Worthington, 1991).

January 1989: DOE commits to a *"good faith"* effort to meet NRC's requirements for removal of radionuclides for grout in the absence of NRC rulemaking (NRC-DOE, 1989).

May 1989: DOE, Ecology, and EPA sign the Tri Party Agreement. Milestone M-01-00 requires 14 grout vaults be filled by 1994. M-02-00 requires operating a tank waste pretreatment plant by October 1993.

1989: NRC and DOE agree to take inventory of all waste in the tanks and *"demonstrate the largest practical amount of total site activity attributable to high-level waste had been isolated for disposal"* (Lacey, 1989).

1989: Pretreatment capital cost for B Plant is estimated at $1.6 billion at the low end and technically, *"considerable additional development,"* will likely be required for additional pretreatment operations that could increase the cost by hundreds of millions of dollars.

Pretreatment operations costs are estimated at between $150 and $200 per gallon (Wodrich, 1989).

January 1990: Citing 5 U.S.C. Section 533 and 10 C.F.R. Section 2 800-2.809, the Confederated Tribes of the Yakama Indian Nation, State of Washington, and State of Oregon petition the NRC to invoke rulemaking authority and declare all tank waste HLW unless, *"the largest technically achievable amount of activity from each tank has been isolated for vitrification prior to permanent disposal,"* and grout,*"meets temperature requirements for long term stability for low-level waste forms,"* and, *"that any other pretreatment processes (e.g. TRUEX) have undergone appropriate evaluation by the NRC prior to implementation"* (Yakama, 1990).

February 1990: Updated performance assessment finds that grout performance relies on the 44-inch asphalt barrier that encapsulates the grout vault. If the asphalt fails, the PA predicts groundwater concentrations for nitrite and nitrate will be exceeded (McNair, 1990).

1990: DOE acknowledges that source terms and estimates of chemicals to be disposed in grout are based on waste samples from only three tanks (Hendrickson, 1990).

1990-1991: More technical difficulties with pretreatment emerge. DOE's plan relies heavily on a pretreatment technology called TRUEX. Studies show that TRUEX is not practical:

- TRUEX requires acidification of the waste which would corrode tanks (Marsh, 1991).
- TRUEX uses a solvent that cannot separate transuranics because of the *"extreme selectivity of the solvent for these constituents."* (Marsh, 1991).
- The solvent is also very expensive, difficult to purify, can generate harmful products when degraded by radiation, and is not completely combustible even in the high-level vitrification process (Cuillerdier, 1991).
- TRUEX creates foaming problems and crystal growth in the process and has not been demonstrated beyond the bench lab scale (Burris, 1990).

1991: DOE acknowledges that Technetium-99 removal during pretreatment will not work: *"Technetium-99 recovery is technically possible but may not be practical"* (Wodrich, 1991).

May 1991: DOE creates a "new" organization in Richland, the Tank Waste Remediation System (TWRS) to revise its treatment strategy.

1991: DOE decides pretreatment will not be needed for the first 20-25 grout vaults to be filled between 1994 and 2001. DOE estimates 4.4 to 5.4 million curies will be disposed in these initial grout vaults (Wodrich, 1991). However, the body of work on grout is showing pretreatment will likely be required for all waste types, *"Up to this point a satisfactory grout formulation, which meets all physical, regulatory and design requirements, has not been developed for the disposal of DSS and DSSF waste"* (Worthington, 1991). The formulation for the first grout campaign, *"generated excessive heat, creating* *temperatures in excess of design, during curing"* (Worthington, 1991). Alternative formulations have been tested but still, *"resulted in temperature rises due to heat of hydration which exceed the design parameters"* (Worthington, 1991). The heat increases leachability, and the grout does not meet NRC guidelines (NRC, 1991). Alternatives such as pouring in lifts, installing larger exhausters on the grout facility, and pretreatment are being investigated (Worthington, 1991). If the heat problem cannot be solved, *"…the current grout program appears to be in jeopardy"* (Worthington, 1991).

1991: Plans to grout higher activity wastes (e.g., NCAW, CC, and PFP) all exceed TRU requirements (<100 nCi/g) and are planned to be treated via solids washing and the TRUEX process in B Plant. Cesium content and removal requirements will have to be calculated for each grout campaign (Worthington, 1991).

March 1991: Ecology Director asks DOE to drop B Plant since it cannot comply with hazardous waste laws (Ecology, 2000).

June 1991: Grout vault estimate grows to 270 vaults (Hanford, 1991).

June 1991: GAO report says DOE should cancel plans to use B Plant for pretreatment (GAO, 1991).

July 1991: DOE white paper seriously questions the viability of grout and recommends considering vitrification for low-level wastes:

- *"For NCAW waste at least 90% of the Cs-137 would need to be removed from the LLW stream before grouting in order to meet NRC HLW requirements for the site."*
- Organics in tank wastes are increasing grout leachability and interfering with setting and curing, *"Their presence in wastes for grouting is, therefore, undesirable. Removal is, however, extremely difficult."*
- *"Pretreatment costs are shown to be high. They are higher in many cases than the remainder of the costs of disposal as grout. The unit cost of potential pretreatment is so high and sufficient uncertainties exist in the grout program to justify the instigation of a program to study disposal forms alternative to grout as a fallback position. The best alternatives are presently all seen as being vitrification processes…a program to develop one or more of these processes…should be undertaken at the earliest opportunity."*
- *"One way to overcome the need to remove specific elements from wastes before grouting, is to dispose of the waste in forms other than grout. Such processes should produce disposable waste forms where the leachability has been reduced to the point where it is of no concern. Processes such as producing glass in containers or in situ vitrification would fix some elements in a form with extremely low leachability, while volatilization and/or destroying others, such as nitrites and organics, and thereby coincidentally removing them in the waste."*
- *"Glass is the chosen solidification form for HLW, based on its low leach rate and high durability. Its use has been demonstrated in a number of countries including*

the USA, France, Germany, Japan, the USSR and the UK and a wide literature exists. The glass process is subject to fewer problems than competing processes of similar durability. Glass manufacture is a technology with a long pedigree…based on well developed, clearly demonstrated large scale experience. Those attributes which make glass attractive as a HLW disposal form apply equally to its use with LLW. Little or no new development is required to adapt existing technology to low level waste disposal. Vitrified LLW will be a highly stable, low dispersal waste form with a projected ANS 16.1 leach index of 13-15, which greatly exceeds the NRC recommended value of 6.0 and no nitrite or organic content."

- *The best alternatives are presently seen as being vitrification processes, particularly in-situ vitrification"* (Worthington, 1991).

October 1991: Westinghouse Hanford Company publishes the Hanford Site Tank Waste Disposal Strategy to evaluate uncertainties with B Plant as a pretreatment option and the integration of SST and DST wastes. The document will lead to an integrated baseline disposal program with *"firm cost and schedule information"* in 1992. The report:

- Adds *"early cesium ion exchange"* capability to the Hanford Waste Vitrification Plant (HWVP) resulting in an estimated 2-year delay for HWVP.
- *"Disposal of low-level waste in a cementitious waste form (grout) as directed by the HDW-EIS will proceed as scheduled. The ability to dispose of LLW is critical to overall program success in that it frees up tank space that is needed for downstream pretreatment operations as well as interim waste collection."*
- Grout will go forward as planned but, *"Technology programs to develop alternative LLW forms, which could reduce costs or improve waste form performance, will continue to be evaluated."*
- *"The capability to remove additional cesium from the LLW (double shell slurry DSS/double shell slurry feed DSSF) will exist concurrent with HWVP startup."*
- *"Further isotope removal (e.g. technetium, iodine, etc.) is not practical today; development would be required."*
- *"Providing cesium ion-exchange capability in the near term is essential to the complete remediation of high-heat NCAW waste as well as to reduce tank space concerns. This capability is needed to bring the decanted supernatant and sludge-wash solutions into compliance with DOE goals for radionuclide content in grout feed. It will also be needed for pretreatment of complexant concentrate waste."*
- In the intermediate term, the report envisions selective leaching and waste blending pretreatment capabilities, *"These processes are relatively straightforward chemistry but need to be engineered for Hanford's specific waste types and in-tank applications."*
- In the long-term, DOE continues to plan on using TRUEX and organic destruction (in the 2008-2010 timeframe). To support long-term pretreatment a TRUEX pilot plant is planned for 1992.
- Concurrent with grout disposal activities, *"the evaluation of advanced treatment and alternative LLW forms will be initiated. The goal of this evaluation will be to provide improvements to the approved waste form, reduce the hazardous*

constituents, and/or enhance the long-term performance of the LLW form. In the long-term, treatment processes that lower waste toxicity and alternative LLW forms that reduce disposal cost and/or improve waste form performance could be implemented."

- *"A number of SSTs and DSTs contain high concentrations of organic complexants. This organic material may adversely impact the performance of the LLW form. Thus, it is necessary to destroy the majority of this organic material."* Multiple technologies to accomplish this will be considered.
- *"Continuing technology development is needed to support LLW disposal. Currently, about one year is required to formulate and demonstrate an acceptable waste form for each waste type incorporated into grout. The incentives for developing alternative LLW forms are decreased waste form volume, which reduces operating and disposal costs, and enhances waste form performance."*
- *"Characterization is one of the key program elements that provides the technical foundation for the specific processes used in grouting of tank wastes. Lack of a comprehensive chemical and physical properties database for all tank wastes has been identified as a significant risk factor contributing to uncertainties in the tank waste disposal program."* Forecasts *"13 years or more"* to characterize all the wastes. Laboratory resources also have to be upgraded to support characterization (WHC, 1991).

November 1991: Ecology issues a report from consultants Brown and Caldwell that shows pretreatment poses serious technical challenges and threatens the viability of the grout program:

- Recommends canceling plans to use B Plant for pretreatment.
- Finds that DOE's current plan *"relies on several unproven technologies, including TRUEX, SREX, and in-tank or mobile cesium ion exchange technology."* Therefore, a two-phase approach is recommended. The first phase (primarily in-tank), will include sluicing, sludge washing, settle/decant separation, filtration, and cesium ion exchange. The second phase will occur in a new pretreatment facility and include settle/decant separation, filtration, cesium ion exchange, organic destruction, strontium ion exchange, acid dissolution and TRU removal, *"In addition, grout feed preparations may require technetium removal, nitrate removal, and chromium reduction to limit chromium's toxicity and mobility in the grout."*
- *"In general, while the limitations on the constituents sent to the grout have not been quantified, the grout must have limited heat generation to prevent cracking of the waste monoliths. Therefore, because of their propensity for heat generation, cesium and strontium must be removed."* Organics also need to be removed or destroyed because they *"can inhibit proper grout formation…"*
- *"Many of the pretreatment processes recommended are in early stages of development, or have unresolved problems. There is, therefore, a degree of uncertainty related to the maturity of each technology, and whether the process can be developed in time to meet TPA milestones."*

- *"Alternatives resulting in the lowest level of grout radioactivity remaining in the grout should be pursued. Grouting has been performed successfully on phosphate-sulfate wastes, and has been tested on DSSF waste. It has not been tested on the other DST wastes discussed in this report"* (Brown and Caldwell, 1991).

1991: Westinghouse publishes a review of the tank waste treatment system to provide a basis for recommending alternatives that should be considered in a Supplemental EIS that will be performed to incorporate the SSTs into the treatment program. The report shows grout as a poor waste form that is more expensive than immobilization in glass:

- *"High-temperature conversion of LLW fraction to leach-resistant form. Incorporating the LLW fraction in a silicate-based glass destroys many environmentally objectionable waste components (e.g. nitrates, nitrites, and organic materials) and produces a relatively low-volume waste form that is effectively resistant to water leaching of radionuclides."*
- *"Glass in sulfur provides the most effective overall treatment for onsite disposal. The option allows for bulk handling of a high-performance compact waste form. The process uses existing industrial scale equipment and designs. The waste performs from 100,000 to 1,000,000,000 times better than disposing of tank waste in grout. Glass in sulfur has the lowest life cycle cost for disposal."*
- The study finds that the largest environmental risk is associated with residual wastes in the tanks and recommends in-situ vitrification of residuals. The second largest risk comes from the low activity waste form: *"Whether the DOE spends $1 billion or $100 billion to remediate the tank waste, the long-term impact to the environment does not change by more than 2 orders of magnitude, unless the DOE processes tank farm residues. Following treatment of tank residues, the next most important improvement to the environment comes from improving the release from the waste disposed onsite (LLW fraction). Following the improvement of tank farm residues and LLW form, improving of separations performance results in insignificant improvement to total releases (e.g. 10^{-10} fraction of stabilizing and dome fill of initial wastes"* (Boomer, 1991).

December 1991: DOE acknowledges that grout is in trouble, *"…inadequate integration among related tank waste programs and insufficient management systems to identify critical environmental, safety, and health issues…a need to consider contingencies to the current grout program and feed preparation strategy for the vitrification plant"* **(**Tseng, 1991).

December 1991: DOE cancels plans to utilize B Plant for tank waste pretreatment due to challenges related to making the facility compliant with current regulations, (HEAL, 1993).

January 1992: One of the existing grout vaults at Hanford fails a leak test (Wisness, 1992).

March 1992: PNL publishes a study of the compressive strength and leachability of samples taken from the first full-scale grout vault. However, the researchers experience trouble analyzing the samples for leachability because they do not contain sufficient contaminants. Discussion of leach indices *"...is made difficult because of the absence of any regulated quantities of hazardous components and the low concentration of radionuclides."* The maximum dose rate of the grout was only 0.3 mrem/hour, *"The low initial inventory of nuclides in the grout resulted in very low concentrations in the leachates, often indistinguishable from background activity."* The researches decided to use sodium as a conservative indicator in the leach test and it failed the leach test in all but one case. The samples passed the compressive strength tests (Martin, 1992).

May 1992: Grout performance assessment is rejected by DOE's peer review panel (Cook, 1992).

June 1992: Grout program estimate is 32.3 million curies and 57 million cubic feet of grout disposed in 270 vaults of currently uncontaminated 130 acres (DOE, 1992).

June 1992: PNL releases results of a study on the durability of different wastes in Hanford grout formulations:

- Simulants of the waste for the 1988 pilot grout effort were tested and, *"The leach resistance and compressive strength decreased with increased curing times and curing temperatures. The osmotic pressure within the grout may have been sufficiently high to cause localized microcracking, thereby reducing strength. Cracking due to increases in internal pressures caused by salt crystallization also may have occurred as the samples cooled from their curing temperatures to room temperature."*
- *"DSSF grouts are unique in their composition and their intended purpose. The hydration reactions for DSSF grout are expected to be quite different from those for conventional concretes. Other complicating factors include the high salt content in the waste and high curing temperatures."*
- *"Under the expected disposal conditions, the temperature of the grout will peak twice. The first peak will result from hydration heat, and the second will result from radioactive decay heat. 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 and 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, the osmotic pressure caused 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."*
- In some cases nitrate leachability actually increased over time, *"...the amount of nitrate leached from the sample cured for 6 months at 75 ^{o}C is more than 4 times greater than the amount leached from the sample cured for 1 month."*
- *"If the extent of microcracking were severe, the effective surface area available for leaching under saturated conditions could have increased significantly*" (PNL-7835, 1992).

June 1992: PNL publishes a study on 1987 pilot scale DSSF grouts finding that elevated cure temperatures harm grout performance:

- *"The temperatures peaked out at 105 ^oC and the calculated temp rise was 81 ^oC."*
- Grout strength was lower than comparable lab bench scale tests (1040 psi vs 1430 psi).
- *"Grouts cured at higher temperatures were less resistant to leaching than those cured at lower temperatures. The total amount of nitrate leached from a sample cured at 71 ^oC was 56% less than from a sample cured at 101 ^oC."*
- *"Because all the grouts tested reached the same maximum temperature during the calorimetry testing, it appears that they have reached the 'boiling' point of the pore solution. For the temperatures to increase any further, the grouts must be cured in a pressurized system."*
- The grout exceeded the nitrate leach requirement of 6.0: *"The nitrate leach indices ranged from a low of 7.5 to a high of 8.4. It is apparent that increased curing temperatures resulted in a more leachable grout."*
- *"Most of the samples cured under unsaturated conditions in the ovens were cracked, with some crack extending the length of the sample. The cracking was due to drying shrinkage, since the samples lost about 10% to 20% of their original moisture during curing"* (PNL-7929, 1992).

June 1992: PNL publishes a report using DSSF simulants to determine if waste concentration and/or dry blend formulations could be altered to control the heat of hydration: *"Minimizing the temperature rise during curing is desirable for reducing thermal stresses on the vault and to limiting the detrimental effects on grout leach resistance."* The tests were unsuccessful at controlling the heat of hydration: *"All the grouts prepared with undiluted DSSF had temperature rises exceeding 45 ^oC…it is evident that the waste concentration contributes significantly to the overall heat generation."* The only method to control the heat of hydration was to dilute the waste by a factor of 100 (PNL-7860, 1992).

June 1992: PNL publishes a study of the durability of Hanford grouts. To attempt to control the heat of hydration, grout formulations with 40% limestone were tested which reduced the heat but produced *"lower strength"* grouts:

- *"Compressive strengths decreased with increased curing temperature."*
- *"Leach resistance decreased with increased curing temperature and curing time, with curing time having the greatest effect at the lower temperature."*
- *"Waste concentration (dilution) had a major, positive effect on leachability, i.e., leach resistance increased for the grouts prepared with dilute DSSF."*
- *"The two most significant factors affecting the grout properties were the slag-to-cement ratio and waste dilution"* (PNL-7838).

June 1992: DOE sends a grout issue paper to Ecology and EPA ahead of a meeting of the agencies to determine how to proceed with the failing program stating, the *"feasibility of*

Hanford grout not yet demonstrated (e.g. characteristics, formulation, and PA uncertainties)." The memo continues:

- *"The estimated radioactivity level for Hanford grout much higher than SRS and West Valley (Class C vs Class A). Total estimated at Hanford is 32.3 M curies in 270 vaults."*
- Due to the high radionuclide content, identifying a suitable grout formulation continues to elude DOE:
  - *"Estimated radionuclide concentrations at high end of previous international grout experience."*
  - *"Bench-scale testing on-going with actual waste."*
  - *"No pilot plant operations planned using actual waste prior to full scale grout production."*
  - *"Full scale grout successfully demonstrated with phosphate sulfate waste (PSW; low radioactivity) and similar grout formulation. However DSS/DSSF waste has greater radionuclide and organic concentrations and associated concerns with both radiolytic heat generation and heat of hydration."*
  - Formulation development for tailoring the first campaign is estimated at 20 months and all future campaigns will require tailoring as well.
- Grout may not meet Land Disposal Restriction requirements: *"Insufficient tank waste characterization data (i.e. organics) are available to conclusively evaluate LDR problem for all tanks."*
- To meet NRC and EPA performance requirements, the asphalt barrier cannot fail: *"depending strongly on assumption of diffusion barrier (fourty inches of asphalt and aggregate mixture) to remain effective for more than 10,000 years."*
- 270 or more grout vaults is a de facto land use decision without NEPA coverage since the HDW-EIS only foresaw 44 vaults (Anttonen, 1992).

September 1992: DOE requests delays to TPA grout milestones based on the Yakima (now Yakama) NRC petition, the peer review required rewrite of the grout performance assessment, and *"ongoing problems associated with the heat of hydration of the grout and the need to pour grout campaigns in lifts."* DOE predicts a 5-10 year delay in initiating grout operations.

The grout peer review panel required DOE to:

- Rewrite the performance assessment.
- Justify each assumption about the long-term performance of grout.
- Perform sensitivity analyses.
- Justify calculations for the peak release of radionuclides to the environment.
- Compare contaminant release results to compliance requirements.
- Demonstrate that ground water is protected (Wagoner, 1992).

September 1992: Revision 2 of the TPA delays LAW grout vault completion until 1996.

November 1992: DOE estimates that one-third of total grouted radioactivity will be disposed in the first four vaults. DOE estimates this is 4.48 million curies (including decay daughters, 8.87 million curies). This estimate was based on a 14.6 million curie total estimate although total curie estimates range from 14.6 to 60 million curies (92-LLB-001, 1992).

December 1992: Memo compares Hanford to DOE's grout programs at Savannah River and West Valley:

- Both SRS and West Valley remove radionuclides (cesium and strontium) until the waste meets Class A requirements. *"At Hanford, for reasons which escape rational thought, the decision was made to include the cesium and strontium in the low-level waste…with all the consequent restraints upon its near surface disposal. Instead of the simple containment systems in use at SRS and WVDP, a complex, engineered, environmental containment system, incorporating diffusion barriers which must isolate the waste from the environment for 10,000 years has been developed (or, more accurately, is still being developed)."*
- *"Resources which could, and should, have been diverted to the development of a more viable system, are still tied up trying to justify past decisions and somehow produce a Phoenix from the program's ashes."*
- *"The politically motivated effort to meet TPA milestones for the grout program is based upon the assumption that the chosen route will work. This is clearly unlikely to be the case. Wisdom and concern for the long-term environmental viability of the current approach should lead to the rapid construction of a facility to remove cesium and strontium from all Hanford waste before disposal of the low-level fraction as grout."*
- *"The only other, presently logical, viable alternative is conversion of the cesium containing LLW to a vitreous form. Such vitreous forms are inherently stable and have acceptably low dissolution and release rates to the environment. This approach removes the need for the development and construction of complex, expensive, engineering barriers of unprovable speculative life"* (Memo, R.E. Worthington to General Dogsbody).

1993: DOE requests TPA Milestone M-01-00 that required filling 14 grout vaults by 1994 be changed to a date of To Be Determined.

1993: Hanford Defense Waste EIS includes SSTs in retrieval and treatment, dramatically changing the scope of treatment facilities (Ecology, 2000).

March 1993: GAO issues a report about the management of Hanford's tank waste treatment program:

- The estimate of grout vaults has grown to 240.
- DOE is *"…basing its pretreatment plans on untested technology."*
- *"The technical feasibility of DOE's approach to dispose of low-level waste has yet to be demonstrated."*

- *"DOE is facing technical uncertainties with the grout process. When radioactive materials are grouted, heat is produced, and generally speaking, the amount of heat rises with the level of radioactivity. If the temperature rises above 90 degrees centigrade, the grout may not effectively immobilize liquid wastes. As a result, DOE may have to change the grouting process or process the low-level waste in another pretreatment sequence to remove more radionuclides. A DOE internal document, dated December 1992, stated that the feasibility of the grouting process has yet to be demonstrated."*
- *"Even if the process works from a technical standpoint, the contents of the low-level waste have raised questions about the appropriateness of using grout vaults as a disposal method. The low-level waste designated for disposal in grout vaults will contain materials that have a high level of radioactivity. On the basis of an October 1990 Westinghouse analysis of the radionuclide content of DST waste, the grout in each vault could contain about as much radioactivity as would be contained in eight canisters produced by the high-level vitrification plant."*
- Tc-99 (210,000 year half-life) and I-129 (16 million year half-life) continue to be worrisome, *"The manager of Hanford's grout facility acknowledged that these radioactive materials will eventually leak into the ground, but he stated that they represent a small fraction of the total radioactive content of the grout vaults. DOE claims the grout vaults will retain the waste for up to 10,000 years but acknowledges that this is an assumption not based on empirical evidence."*
- *"Westinghouse's draft study implies that DOE's current approach is not the best, in part because the grout facility was not designed to handle wastes from both the single-shell and double-shell tanks. The draft study states that an improved approach would be to vitrify low-level waste, mix the vitrified product with sulfur polymer cement, and pump the mixture into large near-surface vaults like the five DOE has already constructed."*
- *"Technical and regulatory uncertainties in grouting Hanford's waste are also not resolved. Because the waste DOE intends to grout contains long-lived, high-level radioactive waste components that will eventually leak into the environment, grout vaults may not be an acceptable approach for final disposal of the waste"* (GAO, 1993).

September 1993: The Hanford Tank Waste Task Force issues its final report. The report includes the following principles that are widely perceived as unfavorable to continuing the grout program:

- *"The high cost and uncertainty of high-tech pretreatment and R&D threatens funding for higher performance low-level waste form, vitrification, and cleanup."*
- *"Use the most practicable, timely, available technology, while leaving room for future innovation. Keep a folio of technological options and make strategic investments over time to support a limited number of promising options. Give up further research on unlikely options. When a better option becomes known through an open and credible systems design and R&D process, be willing to adopt it."*

- *"Put wastes in an environmentally-safe form, using retrievable waste forms when potential hazards from the waste may require future retrieval and when retrievability does not cause inordinate delays in getting on with cleanup."*
- *"Let the ultimate best form for the waste drive decisions, not the size nor timing of a national repository."*
- *"Minimize transportation of radioactive and hazardous materials to and from the site to reduce the risks to the public and the environment; evaluate decisions in light of how much and what materials will be used in the course of the cleanup because of potential consequences for communities along the transportation corridor"* (TWTF, 1993).

Tank Waste Task Force small group discussions included the following:

- *"Minimize transport! Which lowers overall risk!"*
- *"Can't rely on off-site disposal."*
- *"Need to minimize irreversible/irretrievable disposal."*
- *"Long term stability of low level waste."*
- *"Grout doesn't adequately protect public, workers, and environment."*
- *"Reduction of waste volume (grout is issue here)."*
- *"Minimizing use of land for disposal" (TWTF, 1993).*

October 1993: Shortly after the Tank Waste Task Force report is issued, DOE cancels the grout program in favor of LAW vitrification after having spent over $200 million on grout. Revision 3 of the TPA includes a target date of 2028 to complete vitrification of all tank wastes. Milestones M-01 through M-03 require: constructing a LAW pretreatment plant by November, 1998 and beginning operations in December, 2004; initiating construction of the LAW vitrification plant by December 1997 and initiating operations by June 2005.

January 1995: Tom Grumbly (EM-1) sends memo recommending the feasibility of privatizing the treatment of Hanford tank wastes to Secretary O'Leary.

1995: Grout performance assessment finds that Hanford waste types are untested and grouts may crack: *"Double Shell Slurry Feed (DSSF) waste cementation has only been demonstrated with waste solutions containing up to 5 M sodium and 3 M nitrate and nitrite. The formulation was at least partially driven by the need to maintain the fluidity of the grout, while pumping to the vault, and to minimize the heat generation during curing. In particular, workers found that the high heat of reaction between the aluminum in the waste and the blast furnace slag would be the cause of undesirable exotherms during curing in the vault leading to potential cracking"* (Kincaid, 1995).

April 1995: Tri-City Herald publishes result of call-in answers to the question: *"Should DOE be allowed to scrap the Tri-Party Agreement and write its own cleanup rules?"* Yes-39, No-100.

February 1997: DOE releases ROD for TWRS EIS favoring phased implementation coinciding with privatization.

August 1998: DOE issues contract to BNFL for privatized tank waste treatment facilities.

December 1998: As part of its contract with DOE, British Nuclear Fuels Limits (BNFL) publishes a study of alternatives to the planned vitrification of the low-level portion of tank waste. The study evaluates alternative vitrified LAW waste forms (e.g., cullet, gems, or small monoliths) and alternative LAW waste forms (e.g. cementitious). The study finds:

- Cementitious waste forms generated 4 times volume of vitrified waste forms.
- Moving to cementitious form would add $50-100 million and *"The schedule would probably be deleteriously impacted by between one and two years…"*
- *"The major risks with the cementation options are associated with the presence of organic compounds regulated by the Universal Treatment Standards (UTS) (40 CFR 268.48) and the need for nitrate/nitrite destruction. The concentrations of UTS-regulated organic compounds are not currently known, and additional pretreatment to destroy these compounds may be required if their concentrations are sufficiently high to otherwise preclude land disposal of ILAW."*
- *"…uncertainty exists as to the applicability of these processes for destroying UTS regulated compounds."*
- *"The nitrate and nitrite leachability of the cement ILAW has been found to be close to the contractual maximum of six, and destruction of these compounds may be required given the small margin for error. Significant development would be required to resolve the engineering uncertainties associated with applicable processes. There would remain significant operational risk given the relative technical immaturity of the processes."*
- *"Develop and optimize the cementation concept to facilitate a more equitable cost and technical comparison with vitrification."*
- *"Assess the feasibility of disposing the cement ILAW, particularly with respect to its volume."*
- *"Cementation remains a viable treatment alternative to vitrification albeit with significant risk associated with potential additional pretreatment requirements."*
- *Technetium-99 separation requirements based on an assumed glass waste form, "Adoption of alternative waste forms may, therefore, require revision of the separations requirements."*
- *"Tc-99 separation requirements would require revision to account for its leachability from the cement waste form. The extent of revision is difficult to predict…"*
- Grout results in between 4 and 4.4 times as much waste as vitrification.
- Recommends a plasma arc calcination process for nitrate destruction. The high temperature process would generate an aqueous solution of hydroxide salts that also would have to be grouted, *"Calcination is a high temperature (800-1000 C) process generating an off-gas similar in volume and composition to that from vitrification."*
- Grout capital costs will be *"no less than"* 79 to 94% of cost for the vitrification baseline.

- Grout operational costs will be *"no less than"* 73% to 108% (more expensive) than the vitrification baseline (Arm, 1998).

May 2000: DOE terminates BNFL contract.

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