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RESEARCH AND DEVELOPMENT SUPPORT OF THE HANFORD
SITE TANK WASTE REMEDIATION SYSTEM

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ABSTRACT

The research and development of new technology in support of the tank waste remediation system (TWRS) program at Hanford is largely driven by the unique situation with the Hanford radioactive tank wastes. The operational history at Hanford has involved three different major processes and several major campaigns to recover fission products from the wastes, and has not maintained a segregation of the high-level wastes. The result is a very diverse inventory with very high content of solids of many different chemical constituents and great complexity. The R & D program must not only assure that an acceptable strategy for remediation of these wastes can be put in place, it must also define ways of improving the cost effectiveness of the strategy to make the mammoth task more tractable.

INTRODUCTION

A previous paper presented at this session by Wodrich¹ described the Tank Waste Remediation System (TWRS) which has been recently established to safely store, treat and dispose of the highly radioactive waste at the Hanford site. This paper discusses the nature of the new technology needed to support this program and the factors that determine those needs.

BACKGROUND

Briefly noting the information provided in the previous paper, the TWRS was established to bring together all of the major elements of work that have been ongoing at Hanford to safely remediate 227,000 m³ (60M gal) of high-level radioactive waste that are stored in 177 underground tanks. The wastes are stored in 149 single-shell tanks (SSTs) and 28 double-shell tanks (DSTs), most of which range in size from about 1900 m³ (0.5M gal) to 3800 m³ (1M gal).

No wastes have been added to the SSTs since 1980. Furthermore, because of concern for leaks from some of the tanks, the pumpable liquid has been removed from many of them so the remaining waste is mostly saltcake (precipitated soluble salts from saturated solutions) and sludge (solids insoluble in caustic solutions). Total volume is estimated to be 139,600 m³; about 20 percent is sludge and 80 percent is either liquid or salt cake, but predominantly the latter (i.e. predominantly evaporated, water-soluble solids).

The DSTs contain five different types of waste. Approximately 73 percent of the 113,000 m³ of waste is material pumped from the SSTs (designated double shell slurry [DSS]), much of it concentrated to the limit set by the operating temperature of the evaporator. Fourteen percent is waste from the radionuclide recovery processing, containing considerable organic complexants added to prevent the precipitation of certain species (designated complexant concentrate [CC waste]) ; six percent is neutralized current acid waste (NCAW) from the recent operation of the plutonium/uranium recovery extraction (PUREX) plant; three percent is neutralized cladding removal waste (NCRW) from the same operations, and the remaining one percent is waste from the plutonium finishing plant (PFP).

The tank wastes are hazardous not only because of the fission product (FP) constituents, but also because of the transuranic (TRU) components that are either unrecovered plutonium from the irradiated fuel or higher atomic numbered elements formed by neutron capture without fission of the plutonium. The TRU waste are of considerable hazard because of their very long half-lives and their biological/radiological effects. In addition, some of the process chemical present in the wastes are environmental hazards as non-radioactive wastes and must be considered in determining the strategy for ultimate disposal.

Before establishment of the TWRS, the remediation of the SSTs and the DSTs were considered separately. Basic strategies had evolved for the separate elements of remediation, but they had not been base-lined or endorsed by DOE. Under the new organization, resolution of the safety questions receive highest priority. The need to integrate all tank remediation efforts, including

the mitigation of certain unresolved safety issues with the tanks and their continued safe operation, led to the formation of the TWRS organization.

THE UNIQUE HANFORD REQUIREMENTS

The research and development of new technology for the TWRS program is largely driven by the unique situation with the Hanford radioactive wastes. An "idealized strategy" for the ultimate disposal of tank waste at Hanford is essentially the same as at nuclear fuel reprocessing sites elsewhere in the U.S., as well as in Europe and Japan. These are 1) the encapsulation of the highly radioactive FP and TRU wastes in a minimum volume of a very stable solid form, i.e. one that will retain its integrity and insolubility for many millennia, and storage of this waste in a geologic repository, 2) the immobilization of remaining process waste solids with essentially no radioactivity (albeit probably a "hazardous" waste because of the chemical constituents) and the disposal in a RCRA-approved manner, and 3) the reduction of the activity in the residual water and gas streams to a level that can be released to the environment.

Commercial disposal of high-level radioactive waste is underway in several European countries. However, most foreign reprocessing sites segregate the waste from the first cycle of extraction of uranium/plutonium products from the fission products and thus have a waste stream that contains perhaps 99 percent of the fission products together with very small quantities of well-characterized process chemicals. Under these circumstances, the task of producing a very concentrated high-level waste form is relatively straight forward.

For several reasons, Hanford operations have not produced segregated waste of this nature. Early separation processes resulted in very large volumes of waste and some of these were subsequently further processed to recover uranium. In addition, select fission products were also recovered. These operations, further increased the volume of wastes and this, together with shortages of tank volume, have resulted in extensive mixing of the highly concentrated fission product waste with a great variety of process chemical wastes. The concomitant neutralization and concentration of these wastes

have produced saturated slurries, solid salt cakes, and sludge. The result is an inventory of waste with a very high content of solids and great complexity. The major constituents (not in order of concentration) are aluminum, boron, calcium, iron, magnesium, sodium, zirconium, carbonates, nitrates, nitrites, phosphates, silicates and sulfates.

Thus, waste remediation at Hanford, if one were to follow the "idealized strategy", is a considerably more daunting task than the initial recovery and purification of plutonium/uranium from irradiated fuel.

Studies have concluded that nearly all the objectives of the "ideal strategy" for Hanford wastes could be achieved if the TRU elements plutonium and americium, and the fission products cesium, strontium, and technetium, could be immobilized in the high-level waste form and removed (or at least minimized) in the low-level waste form.

As a gross approximation, under the basic conditions in which Hanford wastes are stored, the TRU wastes, plutonium and americium, together with strontium, will be predominantly in the solid (water insoluble) phase unless there are complexant agents present which can partially hold these constituents in solution. The cesium will be in the solution (or salt-cake) phase unless particular compounds are present which precipitate the cesium or effectively trap it within a solid lattice. Technetium, depending on the oxidation state within the tank, will be in solution as the pertechnetate anion.

The actual situation is not this simple. These radioactive constituents tend to partially distribute into both the solid and liquid phases, driven by both physical factors (e.g., limited adsorption on solids) and chemical factors (e.g., solubilities dependent on the oxidation state of the particular constituent and the presence of complexants).

THE REFERENCE STRATEGY

In reality, with Hanford waste, the complexity of the waste has forced a compromise on the extent to which the "idealized strategy" noted above can be pursued; i.e. one is forced to accept both 1) a large quantity of non-radioactive chemicals in

the glass matrix (high-level waste), and 2) a residual of radioactive constituents in the low-level waste. The low-level waste is now no longer simply a "hazardous" waste, but rather, a "mixed" waste containing both hazardous and radioactive constituents.

The objective of the research and development program is not only to assure that an acceptable strategy can be put in place, but also to improve the cost-effectiveness of pushing the waste disposal strategy toward the idealized strategy, or some other strategy that provides the optimum solution to the balance among public risk, costs and priorities.

Although a baseline strategy has not been established for TWRS, there is a reference strategy against which alternatives will be judged. This was outlined in the program objectives discussed by Wodrich¹. Figure 1 illustrates the essential elements while Figure 2 is an elementary schematic diagram of the pretreatment options.

The original baseline strategy for DSTs² envisioned a phased approach which built on existing technology to treat a certain portion of the DSS waste (the concentrated supernatant waste from the SSTs) by converting it to grout with no further pretreatment, on the assumption that no extraction of radioactive constituents from this supernatant solution was required. However, there is concern that the amount of cesium still in this waste is sufficiently high that provision for its removal prior to grouting should be considered. Ion exchange technology is the leading contender to accomplish this with a minimum impact on secondary waste volumes. However, other similar process streams for which ion exchange removal of cesium has been successful have had a lower concentration ratio of sodium to cesium. A variety of ion exchange media, both inorganic and organic, have been studied in the effort to maximize both cesium loading and the lifetime of the media in the high radiation environment.

It was envisioned that for DST wastes other than the DSS, the liquid and solid phases would be separated and treated, as the technology was developed. The liquids containing the highest amounts of cesium would be treated for its removal, and the solids of select wastes would be dissolved in acid to form a liquid feed to an

extraction process for removal of TRU constituents. These would go to glass. This approach will remain as the reference strategy but the selection of the extraction process requires further effort. Demonstration of the TRUEX³ has not proceeded beyond the bench scale, and other approaches, including the use of dialkylamides⁴ and bidentate phosphine oxides have been considered.

For the SSTs⁵, the initial problem is retrieval of the predominantly solid waste without adding water to potentially leaking tanks. Under the DOE Office of Technology Development various methods of robotic mining of the waste with minimum water addition are being studied. An alternative approach is to surround the tanks with an impervious barrier, such as frozen earth, vitrified soil, or mixed constituents pumped into the soil to render the, nearly impervious. Under this condition, one can envision the use of placer mining techniques to mobilize the solid. During initially phases of the program, once the slurry mix from select tanks, which contained relatively little cesium, was removed from the tank, the sludge (water insoluble) and salt cake (water soluble) would be separated. The supernatant solution would be mixed with constituents to form grout, and the solids would be sent to the Hanford Waste Vitrification Plant (HWVP) where it would be mixed with constituents to form glass (the high-level waste form). In the later phases of the program, waste containing greater amounts of cesium would undergo washing of the salt cake/sludge mixture and removal of any cesium in the liquid phase. The cesium would be combined with the solid sludge and sent to the HWVP for vitrification. As the program matured, greater volume reduction of high-level waste would be achieved by constructing a central processing facility that would permit removal of technetium, TRUs and strontium from the sludge, and incorporating just these constituents in the glass. There is a strong economic driver for this waste volume reduction because the cost of permanent storage of each individual "log" of glass is very high and the projected number produced under the present reference scenario is greater than the space allocated to the Hanford wastes in the initial high-level waste repository. The most promising approach is the use of macrocyclic polyethens (crownethers)⁶ in solvent extraction systems. This approach too

will doubtless be part of the reference strategy for the new program.

An important new element in the present reference strategy is the focus on the resolution of tank safety concerns, primarily;

1. tanks generating flammable gases that are retained and episodically released at rates resulting in a temporary explosive composition in the tank head space (e.g. Tank SY-101)
2. tanks that possibly contain sodium, nickel ferrocyanide, together with an oxidant (sodium nitrate/nitrite), in conditions that might lead to a runaway exothermic reaction
3. tanks that possibly contain organic constituents together with oxidants (sodium nitrate/nitrite), which might lead to uncontrolled exothermic reactions.

The destruction of organic constituents in the waste is an approach common to the remediation of each of these risks of an uncontrolled exothermic reaction in these tanks. Consequently, organic destruction is a part of the reference strategy, and it is highly probable that it will be in the new base line strategy of the program. A wide variety of technologies have been considered, but no clearly superior approach has been established. A process that can be accomplished in the liquid phase, at nominal pressures and with relatively rapid kinetics would have obvious engineering advantages for tank wastes. Processes capable of producing large amounts of free radical, such as sonification, electrical discharge and intense UV-ozone reactions may have potential in this regard, but have not been demonstrated for high-level waste compositions.

TECHNOLOGY PLANS

The establishment of a baseline strategy requires responses to the following fundamental questions, which will impact the selection of the optimum cost-effective strategy for ultimate remediation of radioactive tank wastes.

- 1) What will be the ultimate land use of the site?
- 2) "How clean is clean enough?"
- 3) What are the required characteristics of the high-level waste form sent to the off-site repository?

4) What standards will be used for specifying acceptable low-level wastes which also contain non-radioactive hazardous waste constituents?

As noted by Leo Duffy⁷ in his recent statement² to the Senate, a Priority Model is being developed which incorporates such factors as risk, regulatory drivers, and cost. The model is intended to assist decision-makers evaluating alternatives for addressing competing program priorities with limited resources. Thus, one can envision that the baseline strategy of the TWRS program may change over the life of the program as changes in costs, regulatory drivers, and perceived national risk/priorities change. In the meantime, assessment and characterization are being conducted as required by law; the "bias toward action" philosophy is being implemented to the greatest possible extent.

THREE TECHNOLOGY LEVELS

Because the baseline strategy may need to respond to a changing set of criteria, the preparation of the TWRS Technology Development Plan recognizes the required flexibility by dividing the activities into three levels as noted by Wodrich¹, namely:

1. technology required to implement the present baseline processes within the program present strategy;
2. alternate technologies that could achieve major improvements if successfully developed or provide backup support where the present requirements are uncertain;
3. technologies supporting significantly different program strategies that could have significant positive impact on the cost effectiveness of the total program.

An example of a Level 1 technology is the acid dissolution of sludge for the extraction of TRU, strontium, and technetium as noted earlier.

An example of a Level 2 technology, one that could effect a major improvement if successfully developed, would be a process to remove these radioactive constituents from alkaline solutions/slurries, such as the selective leaching using KMnO_4 -Al with NaOH. This is of prime interest because avoiding acid dissolution

of sludge would significantly reduce the final waste volume.

Another possible (Level 2) approach to reducing the volume of high-level waste would be to extract major amounts of non-radioactive constituents from the feed to vitrification process. The allowable loading of waste in the glass is seldom set by the quantity of fission products but rather by the allowable concentrations of the oxides of aluminum, chromium, and phosphorous.

DRIVERS OF ALTERNATIVE STRATEGIES

Many situations that might lead to a change in the baseline strategy for TWRS can be envisioned. For example, tighter restriction on performance requirement for the waste repository, could force consideration of methods to reduce the volume sent to the repository thus driving the need for more efficient separations processes. Possibly even the reconsideration of concepts to transmute the TRU portion of the waste would need to be revisited. These are examples of a Level 3 technology required to support an alternate strategy.

Conversely, a relaxation of the RCRA regulations on allowable landfills would probably result in renewed interest in in-situ vitrification of the tanks⁸ and the need for an investment in the development of the concept of vitrifying from beneath the tank - similarly, a Level 3 technology.

The uncertainty in the ultimate disposition of the repository issue may also lead to the need to develop the technology to immobilize the high-level waste for interim storage on site until the uncertainty is resolved. Total calcination of the waste and storage in a monitored retrieval storage system would immobilize the waste and also destroy the organic constituents.

The development of the Priority Model noted above could place added interest in compact processing units, modular waste treatment modules⁹ which could be deployed in the vicinity of the tanks to be remediated, and tailored to pretreat the particular waste composition in those tanks. The concept might avoid the need to construct a large central processing facility and provide the flexibility to accommodate new technology as it

is developed in response to significantly different waste being pretreated.

The removal of the radioactive constituent may not always be the critical step in successful pretreatment. Risk-based standards may also dictate a limitation on non-radioactive constituents in the present low-level waste form, grout. Chromates and nitrate are such constituents which may jeopardize the acceptability of this waste form. Processes to remove chromium and destroy the nitrate in the grout feed may be required.

CONCLUSIONS

Research and development in support of TWRS must be structured to support the present aggressive Hanford cleanup schedule, but it must also be very much in tune with the possible shifting of strategies, and indeed must take the lead in considering ways to change the approach to make the mammoth task more tractable and cost effective.

This must be a national effort. The process for enlisting the ingenuity of the national laboratories within the DOE complex, as well as academic and industrial organizations, is being developed thorough the use of National Technology Working Groups to assist in the development and prioritization of the strategies and supporting technology for the TWRS.

REFERENCES

1. D. D. WODRICH, "Hanford Site Tank Waste Remediation System", WHC-SA-1545-FP, Westionhouse Hanford Co. April 1992, To be presented at SPECTRUM '92 (August 1992)
2. M. J. KUPFER, A.L. BOLT, J.L. BUULT, Process and Facility Options fo Pretreatment of Hanford Site Tank Wastes, SD-WM-TA-015 rev 0. August 1989. Westinghous Hanford Company, Richland, Washington
3. W. W. SCHULTZ and E. P. HORWITZ, "The TRUEX Process and the Management of Liquid TRU Waste," Separ. Sci. & Tech. 1988, 23, (12 & 13): 1191-1210

4. M. K. CHMUTOVA, N. E. KOCHETKOVA, B. F. MYASOEDOV, "Polydentate Neutral Organophosphorus Compounds as Extractant of Transplutonium Elements," J. Inorg. Nucl. Chem. Vol 42, pp 897-903.
5. K. D. BOOMER et.al. "Systems Engineering Study for the Closure of Single-Shell Tanks" WHC-EP-0405 Vol 1 and 2 Westinhouse Hanford Company, Richland, Washington 1991
6. J. S. BRADSHAW, R. M. IZATT, J. J. CHRISTENSIN, K. E. KROKOWIAK, B. J. TARBET, R. L. BRUENING, S. J. LIFSON, "Stable Silical Gel-Bound Crown Ethers: Selective Separation of Metal Ions and a Potential for Separations of Amine Enantiomers," Inclusion Phenom. Mol. Recognit. Chem. 1989 7(2): 127-136.
7. LEO P. DUFFY, Statement to the Committee on Governmental Affairs of the United States Senate, April 9, 1992
8. (ISV of underground tanks - from Bill bonner)
9. Modular Waste Treatment Report.