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ALTERNATIVE WASTE FORM EVALUATION FOR SAVANNAH RIVER PLANT HIGH-LEVEL WASTE

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INTRODUCTION

During the past several years the U.S. Department of Energy (DOE) has conducted extensive research and development programs on the immobilization and permanent disposal of the high-level radioactive wastes from nuclear reactor fuel reprocessing. From this work, a consensus has been reached that the preferred method for disposing of these high-level wastes (HLW) is multibarrier isolation of high-integrity waste forms in engineered, deep geologic repositories.

In these two sessions on Materials for High-Level Waste Isolation, we will be hearing detailed talks on waste form materials and on materials for the other engineered barriers. This lead-off presentation will be an overview of the recently completed evaluation of candidate waste forms for the immobilization of high-level defense wastes in the Defense Waste Processing Facility (DWPF), proposed for construction at the Savannah River Plant (SRP) beginning in 1984 as DOE's first HLW immobilization facility.

The selection of the most appropriate waste form for SRP waste (note that we avoid the term "best," because the "best" waste form material is not necessary in a multibarrier repository) has been a long, arduous task frought with a modicum of notoriety and controversy, as the proponents of the many fine alternative waste forms each gave strong arguments that their form is the best. However, when the entire waste disposal system and all important factors were considered together, the waste form decision proved to be not nearly as difficult as first assumed, as it became primarily

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a consideration of practicality and cost effectiveness. This simplification results because any of the better waste forms would, in conjunction with the repository system, provide more than adequate protection to present and future generations.

This presentation (Slide 1) will include a historical summary of the SRP waste form screening and selection process, a description of the two candidate waste forms, borosilicate glass and crystalline ceramic, resulting from the screening process, and a discussion of the final evaluation of these two forms leading to the selection of the DWPF waste form.

WASTE FORM SCREENING AND SELECTION

The development and evaluation of waste form alternatives for SRP high-level waste began about 10 years ago (Slide 2). During this period, the Savannah River waste forms program has encompassed over 13 waste form types and has involved broad participation by other DOE laboratories, universities and industrial contractors, as well as by the Savannah River Laboratory (SRL).

In 1973, an R&D program was initiated at SRL to investigate glass and concrete as potentially promising categories of materials for immobilizing SRP waste. Based on results of this work, as well as the work on glass forms at Pacific Northwest Laboratory (PNL) and in Europe, borosilicate glass was selected in 1977 as the reference DWPF waste form. Development of a borosilicate glass production process was undertaken at SRL and PNL, and conceptual design of the immobilization plant, the DWPF, was begun by the Du Pont Engineering Department.

In 1979, DOE undertook a multi-year program to develop and evaluate alternative waste forms for both defense and commercial high-level wastes in compliance with recommendations of the President's Interagency Review Group on Nuclear Waste Management. A primary objective of this program was to select the DWPF waste form by FY-1983. The alternative waste forms program is managed by the DOE Operations Office at Savannah River with technical assistance provided by SRL.

An initial screening evaluation of the potential product properties and processing characteristics of the proposed waste forms in 1979 resulted in the selection of seven forms for further development and evaluation for both defense HLW and future commercial HLW.[1] These candidate waste forms were developed and characterized in FY's 1980 and 1981, with emphasis on SRP waste. At the end of FY-1981 they were assessed to select the final two waste form candidates for SRP waste and for other high-level wastes.[1]

The seven alternative waste forms and their developers are listed in Slide 3. The assessment of these seven forms was based on four inputs: (1) comparative tests of waste form performance properties (such as leachability) by the Materials Characterization Center (MCC) at PNL, by SRL, and by the developers; (2) a quantitative analysis of relative processing complexity, reliability, cost and safety by the Du Pont Engineering Department; (3) waste form evaluations by other DOE contractors; and (4) an independent peer review by a panel of materials experts. The assessment yielded the merit rankings shown in Slide 3. Based on these rankings, borosilicate glass and a crystalline ceramic form based on Synroc-D were selected for final evaluation for SRP HLW and for further development for other high-level wastes.[1]

SRP HIGH-LEVEL WASTES AND WASTE FORMS

Before discussing the final evaluation of borosilicate glass and Synroc for the DWPF waste form decision, we would like to describe briefly the SRP high-level wastes. Characteristics of these wastes are given in Slide 4. They are alkaline wastes consisting of an insoluble sludge containing most of the Sr-90 and actinides and a soluble salt containing most of the Cs-137. Slide 5 shows the relative hazard of SRP HLW versus time compared to the hazard of a natural uranium ore body equal in amount to that required to produce the high-level waste.[2] Two curves are shown: the solid curve derived using the current standard ICRP-2 dose factors and the dashed curve representative of the newer ICRP-30 dose factors. The conclusions are the same for both curves. The hazard of SRP waste, dominated during the first 300 years by Sr-90, decreases by about 3 orders of magnitude after a few hundred years to a hazard level comparable to uranium ore and lower than that of many other natural ores. Thus, geologic disposal in a durable solid waste form should ensure that the hazard from high-level waste to future populations is no greater than from existing ore bodies.

The heat generation rate of SRP waste forms versus time has the same functional form as the relative hazard curves. By the time the waste forms are ready for repository disposal, almost all of the heat will be from Sr-90 and Cs-137 and will amount to a total of about 2 megawatts (for 20-year production period), or about 200 watts per canister of borosilicate glass. After several hundred years, the heat will have decayed to a few watts per canister. Again, from the standpoint of the waste form decision, these are relatively small numbers.

The reference glass waste form, Slide 6, consists of borosilicate glass containing 28 wt % waste oxides cast into a stainless steel canister 0.61 m in diameter by 3.0 m high.[3] Forms of this size have been successfully made using simulated waste. The reference ceramic form, also shown in Slide 6, is envisioned to consist of three hot isostatically pressed Synroc forms in carbon steel containers stacked in a 0.61 m x 3.0 m outer canister similar to the glass canister.[4] Synroc forms of this size have not yet been demonstrated.

Several key characteristics of the reference glass and ceramic forms are listed in Slide 7.[4,5] A major difference in the two forms is that Synroc has about a factor of three higher volumetric radionuclide loading due to a higher allowed waste loading and a higher density. For the reference canister design, this higher loading means that about one-third as many waste canisters need to be produced for Synroc as for glass. Mechanical and thermal properties of both forms are comparable and are more than adequate for their intended usage. However, Synroc is expected to have about an order of magnitude lower release rate than borosilicate glass under groundwater leaching in a repository.

FINAL EVALUATION AND SELECTION

The decision between borosilicate glass and Synroc ceramic for SRP HLW immobilization required evaluations of how the waste forms are expected to perform in the various disposal system steps of waste form production, interim storage, transportation, repository emplacement, and repository disposal. Comparative evaluations of the two waste forms (Slide 8) were performed to assess exposure risks for each waste disposal subsystem, production processes, performance properties, systems costs, and conformance with regulations. In the next several slides, key results of these comparative evaluations are summarized.

The chief advantage of borosilicate glass is its simpler, less-expensive and well-developed production process.[6] As illustrated in Slide 9, borosilicate glass preparation is basically a three-step process involving continuous melting of a waste/glass-frit slurry in a ceramic-lined melter and casting the molten glass in steel canisters. On the other hand, the ceramic production process for SRP waste requires many steps, including the handling and transfer of dry radioactive powder (Slide 10). Synroc preparation involves intimate mixing of the waste and Synroc additives, comminution of waste particles, calcination, loading and preheating of primary canisters, hot isostatic pressing, and final canisterization. Other process options, such as in-can uniaxial hot pressing or cold press/sintering, appear to be of comparable complexity.

The next slide (Slide 11) summarizes results of a detailed evaluation of the two processes and production facility requirements by the Du Pont Engineering Department.[6] The processability rating was derived by comparing the processes and conceptual facility designs against 21 quantitative criteria in the general areas of complexity/reliability, personnel safety, quality control and assurance, and resource requirements. The factor of two higher rating for the glass process reflects its clear superiority over the more complex ceramic process. The much lower complexity of the glass process translates into a smaller processing facility and much lower capital and operating costs.

As shown in Slide 12, the offsite exposure and hazards of production are extremely small for either waste form, as a result of remote operation and maintenance plus the multistage containment and filtration in the DWPF.[7] Borosilicate glass has a slight advantage because of its simpler process and avoidance of dry powder handling. The risks of exposure from onsite interim storage of either of the waste forms are also very small. Overall then, the major differences in manufacturing the two waste forms are in efficiency and money, not in risks to the population or environmental impacts.

In evaluating the two candidate waste forms for the transport and repository emplacement steps, essentially identical considerations apply (Slide 13). Exposure risks associated with normal operations or with accidents would be controlled primarily by the shipping or emplacement casks. Risks are very low for both forms, and both offer higher integrity in transport than spent fuel, which is already an accepted transport form.[8] Borosilicate glass and Synroc forms both have the necessary mechanical strength and accident resistance for transport and emplacement. Therefore, cost is the only factor for transport and emplacement that is important to the waste form decision. Because one-third as many Synroc forms would need to be transported to and emplaced in the repository, Synroc has a definite cost advantage over borosilicate glass in these areas. More will be said about costs later in the discussion.

Traditionally, the repository disposal step has received the greatest emphasis in evaluations of waste forms. Three considerations are of primary importance: (1) the effect of the waste form on the repository, (2) the effect of the repository on the waste form, and (3) the risks of human exposure from radionuclides that might be released in repository groundwater.

Slide 14 shows a generic design for a salt repository.[9] The insert illustrates how the DWPF waste canisters might be emplaced in twin rows of holes in the floors of the repository rooms, at a spacing of about 2.3 meters center-to-center between rows and between holes. With a total heat content of about 2 megawatts for the as-emplaced SRP wastes, each DWPF borosilicate glass canister would initially generate an average of 200 watts of heat, and each

Synroc canister an average of 600 watts for repository area loadings of ~39 kilowatts/acre and ~90 kilowatts/acre, respectively. Because there will be considerable variation between canisters, the borosilicate glass canister heat loadings were assumed to be ~310 watts for repository temperature calculations. Results of these calculations are shown in Slide 15.[10] They indicate that, under the assumed conditions, canister-repository interface temperatures should remain under 100°C, and that peak temperatures are obtained about 25 years after waste emplacement, dropping to ambient rock temperatures in the 20 to 40°C range in about 100 years. Higher temperatures would occur for the ceramic waste forms; e.g., in salt the peak surface temperature would be about 160°C.

The other basic inputs to the waste form evaluation in repositories are the assumption that leaching by groundwater is the most likely mechanism for transporting radionuclides from the repository to the human environment, plus the specification of the repository type and its groundwater composition. The most likely repository geologies are salt, basalt, tuff, or granite.

Slide 16 shows comparative data on waste form leaching for simulated SRP waste in simulated groundwaters, obtained using the standard MCC static leaching tests for 28 days.[5] There are several important points to be made from this table. First, the measured short-term leach rates do not correspond to congruent dissolution of the forms, but vary element by element and differently from form to form. The leach rates are higher for strontium in Synroc than in glass, lower for uranium in Synroc than in glass, and about the same for cesium. Second, the leaching differences between better forms such as these tend to be about one or two orders of magnitude. Third, there are not large differences in the values with different leachants, distilled water being generally the most aggressive leachant. Fourth, the leach rates generally decrease by about a factor of 4-10 in going from 90 to 40°C.

Data from longer-term tests on borosilicate glass indicate leach rates decrease significantly with time, as illustrated in Slide 17.[10] This effect in borosilicate glass is apparently largely due to oxide layer formation on the glass surface. Initial leaching data for Synroc beyond 28 days indicate that leaching of the ceramic form also decreases with time, partly due to the selective leaching of the more soluble phases first.

The effect of self irradiation, especially atom displacements caused by α-decay, on the waste form's leach resistance is another important factor in assessing the waste form's durability in a repository environment. Radiation effects on borosilicate glass containing SRP waste are very small, based on tests with curium-244 doped glass specimens.[10] The results, shown in Slide 18, indicate that leach rates for highly damaged curium-doped samples are comparable to those for samples doped with plutonium-239 to receive very low alpha doses. The alpha dose at 150 days of the curium-doped sample in Slide 17 corresponds to about 10^6 years exposure in a repository. Similar test data are not yet available for Synroc; however, natural perovskite and zirconolite minerals containing uranium and thorium have been found to be very leach resistant after extensive alpha exposure. (Perovskite and zirconolite are the two key actinide-bearing phases in Synroc.)

Based on the leaching data we have seen and on effective leaching surfaces for the DWPF forms of about five times the geometrical canister area, leached fractions for the DWPF borosilicate glass form are estimated in the 10^{-5} per year range, and for the DWPF Synroc form in the 10^{-6} per year range.

These leaching values were compared against parametric repository risk analysis calculations, performed by Pacific Northwest Laboratory and by Lawrence Livermore National Laboratory (LLNL), to determine whether such leach rates lead to acceptable risks, and whether there is incentive to work towards still lower leach rates. Typical LLNL risk analysis results are shown in Slide 19 in terms of population dose integrated over 10^6 years (left ordinate) and number of premature cancer deaths over the same period (right ordinate).[11] The "90% confidence level" curves represent a combination of worst-case values for the key release and transport parameters, while the "best-estimate" curves are representative of median values for these parameters. The results indicate that: (1) the dose effects are extremely small over the entire range of release rates; (2) doses tend to be insensitive to release rate for poor repository conditions; and (3) for conditions where dose is sensitive to release rate, the doses are already negligibly small. Even for a relatively poor repository, less than one premature cancer death was calculated over a million years.

Another important factor in the waste form decision is the ability of the waste forms to meet the draft criteria and regulations proposed by the Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC) for high-level waste disposal, as embodied in those agencies' drafts of 40 CFR 191 and 10 CFR 60. This question is addressed in Slide 20.[12] EPA puts system requirements on radionuclide effects from both waste form manufacture and waste form disposal. As shown earlier, dose effects from the DWPF can be held to about 10^{-6} of the EPA requirements almost regardless of the waste form. Similarly, for either borosilicate glass or Synroc DWPF forms, "worst-case" repository releases would be about 10^{-6} of the allowed EPA health effects. Even over a million years, the best-estimate health effects are still only about 10^{-2} of the EPA 10,000 year values.

NRC puts a few direct criteria on the waste form itself, requiring that it not be liquid, dispersible, combustible, pyrophoric, explosive, chemically toxic, or a criticality hazard. Essentially any of the waste forms examined by DOE meet these criteria. NRC puts its disposal system requirements in terms of package requirements, asking for zero radionuclide release from the package for the first thousand years, and 10^{-5} per year thereafter. The first requirement is taken to be largely an overpack requirement. Since NRC states that the main purpose of this requirement is to isolate the waste form from the repository during a high-temperature phase, it should presumably apply only in the special case where high-heat waste forms are used in the repository, and not for low heat SRP waste. The second requirement of 10^{-5} per year fractional release rate is probably met by either borosilicate glass or Synroc, but again, this is an overall package requirement. The package designers have placed only a 10^{-4} per year requirement on the form alone, easily met by either waste form.

The final factor to be considered in the waste form decision is total cost of disposing of SRP high-level waste. Estimated costs in millions of FY-81 dollars for the steps in the immobilization-disposal system are listed in Slide 21 for the reference borosilicate glass and Synroc forms.[13] There are three important points to be made from this table. First, the total cost for borosilicate glass is lower than for Synroc. This is true when the different spendout schedules for the two waste forms are discounted by 10% to present values. (Discounting is necessary in comparing costs between the two forms because the DWPF startup time for borosilicate glass, 1990, precedes that for the ceramic form by two years.) Second, costs associated with manufacturing the waste form (i.e., development, DWPF capital, operating, and canister procurement) are significantly higher for Synroc. Third, costs associated with transportation and emplacement are lower for Synroc because fewer forms are required. However, this partial advantage is not enough to offset the higher costs of manufacturing and would be mostly lost if the NRC 1000-year waste package requirement is relaxed for defense waste.

SUMMARY

Summarizing the results of the waste form evaluation (Slide 22):

- Risks of human exposure are comparable and extremely small for either borosilicate glass or Synroc ceramic.

- Waste form properties are more than adequate for either form.

- The waste form decision can therefore be made on the basis of practicality and cost effectiveness.
- Synroc offers lower costs for transportation and emplacement.
- The borosilicate glass form offers the lowest total disposal cost, much simpler and less costly production, an established and proven process, lower future development costs, and an earlier startup of the DWPF.

REFERENCES

1. The Evaluation and Selection of Candidate High-Level Waste Forms. USDOE Report DOE/TIC-11611, United States Department of Energy, Savannah River Operations Office, Aiken, SC (February 1982).

2. W. L. Marter. Relative Hazard of DWPF Reference Glass Canister: ICRP-2 Versus ICRP-30. USDOE Report DPST-82-475, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (June 1982).

3. R. G. Baxter. Description of DWPF Reference Waste Form and Canister. USDOE Report DP-1606, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (June 1981).

4. J. L. Butler, J. S. Allender, T. H. Gould, Jr.. Description of a Ceramic Waste Form and Canister for Savannah River Plant High-Level Waste. USDOE Report DP-1626, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (March 1982).

5. J. A. Stone, J. S. Allender, and T. H. Gould, Jr. Comparison of Properties of Borosilicate Glass and Crystalline Ceramic Forms for Immobilization of SRP Waste. USDOE Report DP-1627, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (April 1982).

6. J. B. Dunson, et al. Assessment of Processes, Facilities and Costs for Alternative Solid Forms for Immobilization of SRP Defense Waste. USDOE Report DP-1625, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (April 1982).

7. J. C. Huang and W. V. Wright. Comparative Risk Assessments for the Production and Interim Storage of Glass and Ceramic Waste Forms - Defense Waste Processing Facility. USDOE Report DPST-82-327, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (April 1982).

8. R. A. Moyer. Comparative Transportation Risk Assessment for Borosilicate Glass and Ceramic Forms for Immobilization of SRP Defense Waste. USDOE Report DPST-82-294, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (April 1982).

9. Bechtel Group, Inc. Conceptual Reference Repository Description (CRRD): Drawings. Volume V, ONWI-258, Office of Nuclear Waste Isolation, Battelle Memorial Institute, Columbus, OH (1981).

10. M. J. Plodinec, G. G. Wicks, and N. E. Bibler. An Assessment of Savannah River Borosilicate Glass in the Repository Environment. USDOE Report DP-1629, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (April 1982).

11. H. Cheung, et al. Post-Closure Risks of Alternative SRP Nuclear Waste Forms in Geologic Repositories. USDOE Report UCRL-53269, Lawrence Livermore National Laboratory, Livermore, CA (1982).

12. D. E. Gordon, P. L. Gray, A. S. Jennings, and P. H. Permar. An Assessment of High-Level Waste Form Conformance with Proposed Regulatory and Repository Criteria. USDOE Report DPST-82-410, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (May 1982).

13. W. R. McDonell. Comparison of SRP High-Level Waste Disposal Costs for Borosilicate Glass and Crystalline Ceramic Waste Forms. USDOE Report DPST-82-346, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, SC (April 1982).