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CHEMICAL ENGINEERING DIVISION

WASTE MANAGEMENT PROGRAMS

QUARTERLY REPORT

April--June 1975

by

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ABSTRACT

Consolidation techniques for Zircaloy fuel-cladding hulls were studied including (1) further work on a pyrochemical-volatility scheme for separating the zirconium as the volatile tetrachloride and (2) ignition tests and shock-ignition tests on several Zircaloy materials to further characterize the pyrophoric behavior of Zircaloy and the impact on hulls management. Quantitative results on the reaction with molten zinc chloride are presented. A series of steel-melting experiments examined the compatibility of various crucible materials with the molten steel and provided information on the behavior (distribution) of CeO_2 and UO_2 (used as stand-ins for PuO_2).

Examination of existing information on deep-well injection of industrial wastes and on low-level aqueous wastes from fuel reprocessing led to the conclusions that the technology is generally available from industrial practice, that costs are of the order of 10^{-4} mill/kWh, that environmental effects could be insignificant in normal operation (but could include contamination of groundwater and resources and also stimulation of minor earthquakes in maloperation), that legal constraints may be the most significant barrier to adopting the practice, and that the site of such an operation would best be at a fuel reprocessing plant located at one of the U.S. sedimentary basins.

The conclusions and recommendations from a study of the reliability of high-level-waste canisters are presented.

SUMMARY

Consolidation Techniques for Fuel-Cladding Hulls

A study is in progress to develop a long-term management scheme for the contaminated, Zircaloy-based cladding waste stream that is generated by the chop-leach processing of spent LWR fuel. This program explores and evaluates chemical and mechanical process steps that will consolidate the waste and

circumvent any pyrophoric hazard. Means of reducing the alpha-waste volume include exploratory studies for separating the zirconium from the long-lived alpha-emitters and other radionuclides. Initial work is with unirradiated Zircaloy tubing. The first shipment of irradiated Zircaloy tubing has been received and analytical work initiated to establish the composition of the material, particularly plutonium content.

Two chemical methods selected for initial study provide separation of the zirconium as the volatile tetrachloride: (1) hydrochlorination with anhydrous HCl, and (2) a pyrochemical scheme involving reaction with molten ZnCl_2 . Analytical results have been obtained for recent experiments involving reaction with molten ZnCl_2 . The experiments involved excess and substoichiometric amounts of the molten salt. Essentially complete separation of the zirconium as ZrCl_4 occurs as the reaction with the molten ZnCl_2 proceeds in the substoichiometric case. In the other case, a separate volatilization step following completion of the metal-salt reaction will be needed to remove the ZrCl_4 . The extent of metal reaction ranged from nearly complete (97%) to about 50%; zirconium material balances ranged from 85.5% to 100.2%. Analytical results on the distribution of uranium in the system (added as UO_2 to provide insight into the possible behavior of PuO_2) show that the bulk of the uranium is not volatile and remains with the metal heel. The salt phase in two experiments contained only 0.36 and 0.25% of the uranium charged in two runs; uranium material balances were about 95 and 61%. The use of CeO_2 as a stand-in for PuO_2 appears to have little value.

A management scheme for Zircaloy hulls requires consideration of potential accidents during shipment. Extreme impact conditions were selected for testing to establish limiting conditions for hull-like materials under which the material might ignite. A comparison of energy regimes for this condition with energies generated in "ordinary" accidents was expected to show that hulls do not represent a pyrophoric hazard. Tests referred to as shock-ignition tests were devised and carried out under a special contract. Conditions were selected that resulted in Zircaloy reaching its melting point. Tests were carried out on 600-g portions of unirradiated Zircaloy tubing sections (*i.e.*, loose-packed, 2.5-cm-long sections that resemble hulls). A single test on a 1950-g compact of tubing sections (70% of theoretical density) was included. Each test involved impaction of an aluminum disk (propelled by an explosive charge) into the Zircaloy materials directly, rather than striking a container wall. Impact velocities of 2600 ft/s (792 m/s) and 6700 ft/s (2042 m/s) were used. Some melting of the Zircaloy and evidence of ignition was observed at the higher velocity for both uncompacted and compacted material. The lower-velocity shock test, including one test with 10% zirconium fines in the impacted material, resulted only in mechanical deformation (compaction) of the tubing sections but still represents an extremely high input of energy. Discussions have been started with persons involved in shipping cask accident analysis in an effort to rationalize the question of energy regimes for these tests and ordinary accidents.

In other scouting ignition tests, zinc coating of relatively high surface-volume ratio zirconium materials, such as saw fines and turnings, apparently did not reduce their sensitivity to ignition.

Data on properties of zirconium tubing considered relevant to fines production and/or pyrophoric behavior continue to be surveyed. Hardness measurements on a variety of tubing specimens show a range of values, with irradiation appearing to be the most significant factor in terms of increasing hardness.

A draft of a report summarizing information on the pyrophoricity of zirconium has been completed and is being renewed.

Salvage of Alpha-Contaminated Metals

A program is in progress to identify and test methods for decontaminating metallic materials that have become contaminated with plutonium, with the aim of salvaging the metal. The program is directed toward the decontamination of ERDA-owned equipment and facilities; decommissioned facilities are a major source of this material.

A glovebox facility has been set up for experimental work with plutonium-contaminated metals. Experiments involving the melting of plutonium-contaminated steels have been initiated, and two types of input material have been successfully melted in the new installation. Sampling and analysis of the products has begun.

Supporting steel-melting experiments are in progress using ordinary steel to examine the suitability of crucible materials, to test the effectiveness of slagging materials (using CeO_2 or UO_2 as a stand-in for PuO_2), and to test operating procedures. Ten steel melting experiments have been completed. The tests indicated good compatibility for MgO and high-alumina commercial refractory materials when no salts or slags were added. Use of cryolite as an additive resulted in complete penetration of a MgO crucible. Also, cryolite appeared to dissolve the CeO_2 , which may be advantageous if suitable crucible materials can be found. In general, the molten steel did not appear to wet UO_2 added as a powder phase. The UO_2 was found either as clumps in the crucible (in runs in which the molten steel was poured out of the crucible into a mold) or on the surface of the solidified ingots; the CeO_2 behaved similarly. The presence of test samples of SiC and B_4C appeared to enhance the solubility of UO_2 in steel, possibly due to the reduction of the oxide by the carbon; both carbides dissolved in the steel.

Storage and Disposal of Tritium

Deep-well injection of low-level aqueous wastes from commercial reprocessing of spent LWR fuels has been assessed by a review and discussion of the factors that must be considered in assessing its feasibility. The assessment has been assembled into a draft manuscript, including contributions of ANL personnel and a consulting geochemical engineer. This report summarizes the work which will appear later as a separate topical report. Factors likely to have a significant bearing on the adoption of this disposal practice have been considered in the categories of technology, cost, environmental impact, legal and regulatory constraints, and siting. Examination of these factors indicates that the technology of deep-well injection, extensively developed on other industrial wastes, would require little innovation in application

to low-level aqueous wastes. Costs would be relatively low, in the order of magnitude of 10^{-4} mill/kWh. The environmental impact of normal operation would be small compared with dispersal to the atmosphere or to surface streams; abnormal operation should not produce catastrophic results. Geologically suitable sites are abundant in the U.S., but a well would best be colocated with a fuel reprocessing plant. Currently developing legal and regulatory constraints will be the most important determinant of the feasibility of applying the method.

Reliability of High-Level-Waste Canisters

Conclusions for this study are summarized in the text.

I. CONSOLIDATION TECHNIQUES FOR FUEL-CLADDING HULLS (N. M. Levitz, I. O. Winsch, B. J. Kullen, T. F. Cannon)

A. Introduction

This program concerns the development of methods for the safe and economic long-term management of the Zircaloy cladding* waste steam generated in the reprocessing of spent LWR fuel by the chop-leach process. The cladding is contaminated with long-lived alpha-emitters, fission products, and neutron-activation products. Current attention is being given to the potential of a pyrophoric hazard from Zircaloy, particularly in the form of finely divided metal. Consolidation processes that transform the waste so that it can be classified and treated as a nonpyrophoric, non-alpha-bearing waste ($<10 \text{ nCi g}^{-1}$) are being identified, tested, and evaluated. The processes should also provide for the collection of the alpha-emitters in a compact form, amenable to storage, disposal, or further processing. Monitoring of the waste and the various process streams for plutonium content has been identified as a problem needing further development. Identification of methods for salvaging the Zircaloy for reuse remains a secondary goal. The plan of work includes review and evaluation of the literature to assess the state of knowledge and technology, an experimental phase, and a flowsheet and concept design phase that will identify process options. Resolution of the pyrophoricity question will be emphasized in the work this fiscal year.

Experimental work continues to stress methods that provide a separation of the zirconium as the volatile tetrachloride, namely, hydrochlorination with anhydrous HCl or reaction with molten ZnCl_2 .¹ Efforts continued on the development of information related to the potential ignition of Zircaloy materials for characterization and test purposes. An on-site source of material has been found, and the first acquisition of material was completed. The Zircaloy has had exposures to 6600 and 33,000 MWd/metric ton uranium. Gamma scans are being used as an initial means of characterization. Two irradiated test pieces have also been received from ORNL. Other off-site sources have been virtually discounted, because of either cost or restrictions stemming from proprietary interests.

A draft of a report has been completed that summarizes the information gathered to date on the question of the pyrophoricity of zirconium and the impact on the handling of cladding waste. This report will be issued after further editorial review.

B. Pyrochemical Studies

A number of pyrochemical (molten metal/molten salt) process flow sheets appear to be applicable to the processing of Zircaloy hulls, with process selection being dependent on program objectives. Processes under initial consideration are intended (1) to transform the Zircaloy into a form that

* Cladding hulls are the short Zircaloy tube segments. Extraneous fuel element hardware such as Inconel grids and nozzles are included in the waste stream. Zircaloy is a zirconium-based alloy containing tin, iron, chromium, and sometimes nickel.

no longer represents a potential pyrophoric hazard, and (2) to effect a separation and concentration of the long-lived alpha-emitting nuclides. It is also desired to maximize the recycle of process reagents and thereby reduce significantly the overall volume of alpha-bearing waste.

1. Oxidation of Zircaloy with ZnCl_2

Experimentation has continued on the use of ZnCl_2 as an oxidizing agent, the main reaction being $\text{Zr} + 2 \text{ZnCl}_2 \rightarrow \text{ZrCl}_4 + 2 \text{Zn}$. The intent is to separate the ZrCl_4 by volatilization, leaving the actinides in the residue. The zinc would be rechlorinated and reused, effecting a net reduction in waste volume. The feasibility of the reaction was indicated in the previous quarterly report.¹ In the three experiments to date (ZZ-1, -2 and -3), ZnCl_2 , Zircaloy-2 tubing sections (previously oxidized at 350°C for two hours), CeO_2 , and UO_2 fines were charged to a tungsten crucible positioned in an inductively heated, tilt-pour furnace. The system was held at a temperature of 500°C for five to six hours. About 1 g of CeO_2 was charged in each experiment as a substitute for PuO_2 , but this addition later proved to be of little value since interference by tantalum, tungsten, and nickel made it difficult to analyze for CeO_2 . About 5 g of UO_2 fines (-80 mesh) was added in each experiment to determine the distribution of the uranium in the oxidation step and to provide insight into the expected behavior of plutonium (PuO_2). The detailed analytical results are presented in Table 1.

In Run ZZ-1, the quantity of ZnCl_2 used to oxidize the Zircaloy was about a factor of three greater than stoichiometric, and no agitation was provided. Only 43.5% of the zirconium in the charge was oxidized to ZrCl_4 ; this is represented by the zirconium found in the salt layer (with excess ZnCl_2) and that which volatilized and was recovered from upper, cooler portions of the furnace. An additional 46.5% of the Zircaloy tubing was disintegrated by the attack of the ZnCl_2 but did not react to form ZrCl_4 .

In Run ZZ-2, slightly less than the stoichiometric amount of ZnCl_2 was used, and some agitation (~400 rpm) was provided. About 80% of the zirconium in the charge was oxidized to ZrCl_4 . Since there was no excess ZnCl_2 in this experiment, the ZrCl_4 volatilized from the crucible and was recovered as a condensed phase from the upper region of the furnace, as in the earlier experiment.

About 120% of the stoichiometric amount of ZnCl_2 was used in Run ZZ-3 and resulted in oxidation of 82.5% of the zirconium to ZrCl_4 . Agitation of the melt was provided as in ZZ-2. Only 3.2% of the original charge of Zircaloy was found unreacted in the heel. The overall zirconium material balance was only 85.5%.

The zirconium material balances in these early tests are somewhat low because the design of the equipment did not provide for efficient collection of the volatilized ZrCl_4 . A condenser for ZrCl_4 has been fabricated and installed for use in later tests.

The uranium analytical results for the salt phase in Runs ZZ-1 and -3 indicate that only 0.36 and 0.25% of the uranium charged was present in

Table 1. ZnCl_2 Oxidation of Zircaloy-2 Tube Sections
Temperature: 500°C

Run No.	Charge ^a		Metal Heel + Crucible					Salt				Material Balance	
	ZnCl ₂ , Zr-2,		Zinc, g	Uranium		Zirconium		Zirconium		Uranium		Zirconium	Uranium,
	g	g		g	% of charge	g	% of charge	g	% of charge	g	% of charge	%	%
ZZ-1	300	29.8	9.6	4.1	93.5	13.44	46.5	12.54	43.5	0.16	0.36	90.0	93.9
ZZ-2	300	106.4	102	NA ^b	-	21.0	20.2	83.0	80.0	NA ^b	-	100.2	-
ZZ-3	390	109.0	138	2.7	61.0	3.2	3.0	87.5	82.5	0.11	0.25	85.5	61.3

^a The charge in each experiment included 5 g UO_2 and 1 g CeO_2 as stand-ins for PuO_2 .

^b Not available at time of report.

the total of the vaporized and poured salt. Apparently, the crucible heels contain the bulk of the UO_2 , as shown by analytical results. Uranium material balances were about 94 and 61%.

In summary, the oxidation of zirconium in Zircaloy-2 to ZrCl_4 and its subsequent separation from components that do not form volatile chlorides appear feasible by reaction with ZnCl_2 at 500°C . Uranium, added as UO_2 , appears to react to a slight extent, but its behavior may not be like that of PuO_2 . Experiments with PuO_2 will be required to determine its behavior in this system.

C. Ignition and Other Miscellaneous Tests on Zircaloy

1. Shock-Ignition Tests on Zircaloy

Information on whether hulls would be pyrophoric in the event of an accident during shipment is pertinent to the development of a hulls-management scheme. The behavior of the hulls is considered to be related to the energies involved in the postulated accident. Tests were devised which provided energy levels considerably above those expected in "typical" accidents. In related work, the capability of casks used for shipment of nuclear fuel to withstand accidents is being investigated* in a new program at the Sandia Laboratory; mainly cask-drop and impact tests are being made, with reported velocities ranging up to 250 mph (367 ft/s, 112 m/s). Tornado missile effects which represent higher energy regimes, *e.g.*, velocities to 360 mph (528 ft/s, 161 m/s), are also under study at Sandia.*

Shock-ignition tests** were carried out on small batches of unirradiated, chopped (2.5 cm long) Zircaloy tubing sections. The material was hydrided and autoclaved to more nearly simulate spent hulls. Seven tests were made, six with ~600-g batches of loosely packed tubing sections, and one test with a 1950-g compact (about 70% of theoretical density). Variations in batch makeup included the addition of zirconium fines (10 wt % of the metal charge) and the addition of sand (50 wt % of the metal charge).

The plate impact test configuration for the shock-ignition tests is shown in Fig. 1; details of the plate projector are shown in Fig. 2. Each test involved impacting (by explosive charge) an aluminum disk at high velocities, 2600 or 6700 ft/s (792 or 2042 m/s), into a mass of tubing confined in a heavy-walled [1/2-in. or 3/4-in. (1.3 cm or 1.9 cm)-thick] pipe section; testing was limited to these velocities, although other velocities were considered. No shown is a 3-in. (7.6-cm) diameter undercut section of the 5-in. x 5-in. (12.7 x 12.7 cm) aluminum impact plate which is actually the projectile that impacts the Zircaloy mass.

Instrumentation consisted of thermocouples drilled into the thick-walled container and high-speed motion picture cameras, but neither provided

* Leon Wilson, Sandia Laboratory, personal communication to Norman Levitz, ANL (August 1975).

** Tests were conducted by Shock Hydrodynamics, North Hollywood, California. Zircaloy test materials were prepared by Teledyne Wah Chang Albany, Albany, Oregon.

Fig. 1. Setup for Plate Impact Test

Fig. 2. Details of the Plate Projector

much quantitative information; the thermocouples broke off soon after the impact plate struck the sample, and filming was severely hampered by the hulls being confined in the heavy-walled container. A single test, made with only a sheet metal container which disintegrated during the test, provided a somewhat informative photographic record. Test conditions and results are summarized in Table 2. The data obtained with the thermocouples are shown in Fig. 3. Calculations made by H. Anderson* preliminary to the tests are summarized in Table 3. The melting point ($\sim 1850^{\circ}\text{C}$) of Zircaloy was expected to be reached in the tests at the higher velocity. The calculated maximum temperature reached is indicated in Table 3 as the shock temperature. The release temperature is the temperature of the metal after release of the shock pressure to atmospheric pressure; release temperatures are plotted in Fig. 4.

The tests at lower impact velocity resulted in only mechanical deformation (compaction) of the tubing sections, whereas some melting of tubing sections occurred for both the uncompacted and compacted material at the higher impact velocity. The motion picture of the high-velocity impact test made with the thin-walled primary container showed ignited tubing sections, but it could not be ascertained whether any sections burned completely to the oxide.

The addition of fines caused an internal energy surge (compare Fig. 3a and Fig. 3b) indicative of the fines igniting, but the tubing sections did not ignite. The test with fines and water showed evidence of the reaction being quenched (compare Figs. 3b and 3d); individual tubing sections were cool to the touch immediately following the test. Inspection of the sample with sand tested at the high velocity gave no indication that the sand had served to ameliorate the reactions; definite evidence of melting of Zircaloy was seen.

This test program was successful in outlining the energy levels that ignite Zircaloy tubing. Ignition occurred with a test impact velocity of 6700 ft s^{-1} (2042 m s^{-1}) but did not occur at 2600 ft s^{-1} (792 m s^{-1}). Remaining work includes an evaluative comparison of these shock energies (from high impact velocities) with energies provided by more conventional accident conditions, *e.g.*, truck accidents (100 ft s^{-1} , 30 m s^{-1}) or aircraft accidents (300 ft s^{-1} , 91 m s^{-1}). Other work planned includes examination of the Zircaloy materials which underwent the shock tests to gain more insight into the effects of the tests.

The above tests were all conducted on unirradiated material. The pyrophoricity of irradiated and unirradiated Zircaloy needs to be compared.

2. Miscellaneous Ignition Tests

Treatment of Zircaloy hulls with an inert coating such as zinc was considered a process option to mitigate the pyrophoric hazard. Earlier, simple ignition tests were performed to observe the behavior of zinc-coated

* Shock Hydrodynamics.

Table 2. Shock-Ignition Tests

Test Conditions of Zircaloy Hulls	Impact Velocity, ft s ⁻¹	Measured Temperature Rise, °C	Comments
Autoclaved, unconfined	6,700	---	Film shows burning particles; recovered pieces confirm that burning occurred.
Autoclaved	6,700	---	Recovered pieces show evidence of burning, oxidation, compaction. Sand on which compacted pieces fell showed evidence of scorching.
Autoclaved, hydrided	2,600	22	Recovered pieces showed no evidence of melting, burning.
Autoclaved, hydrided, 10% fines	2,600	121	Recovered pieces showed no evidence of melting, burning.
Autoclaved, hydrided; Compact	6,700	162	Recovered pieces showed evidence of melting, etc. On top surface, delamination of compact also evident.
Autoclaved, hydrided, 10% fines, 15% water	2,600	24	No evidence of heating. Some recovered pieces were actually cool to touch immediately after test.
Autoclaved, hydrided, 50% sand	6,700	101	Evidence of heating, melting. Sand on which one compact piece fell showed evidence of scorching. None of the interior sand showed evidence of melting or scorching.

Fig. 3. Temperature Versus Time of Instrumented Shock-Ignition Tests

Table 3. Calculated Properties of Shocked Zircaloy Hulls

Impact Velocity, ft s ⁻¹	Shock Pressure, kbar	Internal Energy, cal g ⁻¹	Shock Temperature, ^a °C	Release Temperature, °C
Compacted Zr Hulls, $\rho_0 = 4.22 \text{ g cm}^{-3}$				
11,000	310	423	2,696 (all melt)	1,917 (all melt)
8,000	190	257	1,845 (partial melt)	1,830 (solid)
3,000	45	45	386 (solid)	384 (solid)
Uncompacted Zr Hulls, $\rho_0 = 1 \text{ g cm}^{-3}$				
11,000	109	893	7,223 (all melt)	5,576 (all melt)
8,000	52	518	3,704 (all melt)	3,319 (all melt)
3,000	10	83	524 (solid)	517 (solid)

^a Melting point of Zr is 1,845°C.

tubing.¹ Coating was achieved by holding the sample in a zinc bath for 10-15 min at 575°C. Use of a gas-oxygen torch (~1400°C) resulted in oxidation of the coated tubing, similar to that experienced with unoxidized material but no ignition occurred. A less intensive heat source, *i.e.*, a match (estimated temperature, 500°C), had no effect on the coating.

In current work, single ignition tests with zinc-coated, Zircaloy saw fines and turnings, using the gas-oxygen torch, resulted in spalling of the zinc, probably as the oxide, and ignition of the Zircaloy materials. A match had no visible effect. Thus, zinc coating of hulls does not appear to appreciably alter the ignition properties of Zircaloy materials and does not appear to reduce the pyrophoricity of fines.

Scouting tests involving water and 1-in.-long tubing sections included heating quickly in air to 800°C followed by (1) spraying with atomized water or (2) immersing in a beaker of water. No signs of ignition were noted. The heating resulted in an oxide coating on the specimens. It is cautioned that these results should not be extrapolated to larger systems since application of water to zirconium fires has resulted in dissociation of the water followed by a hydrogen explosion.²

3. Hardness of Zircaloy-2 Tubing

Physical properties of Zircaloy-2 which may influence the generation of fines and thereby be related to the pyrophoricity question are of process interest. No correlation or relationship between hardness or embrittlement and fines production has been found in the literature, but until such work is done, information on the properties themselves is of interest. Hardness data on several Zircaloy-2 materials have been assembled (see Table 4).

Fig. 4. Computed Maximum Final (Release) Temperature Produced by Impact of Zircaloy Hulls

Table 4. Rockwell Superficial Hardness of Zircaloy-2 Tubing

	Hydrogen, ppm				Oxidized	Autoclaved ^b	Nonautoclaved ^b	Unirradiated ^c	Irradiated ^d
	~25 ^a	100	250	300					
Rockwell Hardness 15N	62	60	60.7	60.4	57.5	63.75	63.15	58.8	63.8

^a Off-the-shelf Zircaloy-2 tube.

^b Autoclaved and nonautoclaved Zircaloy-2 tubing supplied by General Electric.

^c Zircaloy-2 cladding material for irradiation (identified in footnote d).

^d Zircaloy-2 irradiated in VBWR to 1×10^{21} - 1.5×10^{21} nvt, > 1 MeV, described in reference 3.

Sections of 1/2-in.-OD x 1-in.-long (1.3 cm x 2.5 cm) Zircaloy-2 tubing were hydrided* at 600°C to produce material with 100, 250, and 350 ppm hydrogen content; in comparison, the hydrogen content of Zircaloy-2 tubing from light water reactors has been reported to be 50 to 200 ppm. Rockwell Superficial Hardness tests were run on this material, on tubing oxidized at 350°C for two hours, and on General Electric autoclaved and nonautoclaved Zircaloy-2 tubing. A value for irradiated Zircaloy-2 has been obtained from the literature for comparison.

The hardness values cover a range of 57.5 to 63.8 but are not fully consistent. For example, the stock tubing containing little hydrogen (25 ppm) was somewhat harder than the tubing with higher hydrogen contents. No trend with increased hydrogen content was noted, which was unexpected. The values for the hydrided material may be low because of annealing occurring during the hydriding procedure, which included a period at 600°C. Little difference was noted between the autoclaved and nonautoclaved material supplied by General Electric, although the hardness values were among the highest obtained; these values were comparable to that reported for the irradiated sample. Irradiation appears to slightly increase hardness, as expected.

* Preparation of hydrided samples by E. Veleckis, Chemical Engineering Division, ANL, is gratefully acknowledged.

II. SALVAGE OF ALPHA-CONTAMINATED METALS

(T. J. Gerding, I. O. Winsch, T. Cannon, N. Levitz)

Development work is in progress on decontamination methods for waste metal contaminated with alpha-active elements, particularly plutonium. This waste is accumulating at ERDA facilities as a result of upgrading and/or replacing equipment and the decommissioning of entire alpha facilities. Current regulations require the controlled storage of waste that contains long-lived alpha activity at levels above 10 nCi g^{-1} of waste. The economics associated with this storage concept provides an incentive for reducing the volume of waste needing specialized care. Chemical/mechanical surface cleaning offers an opportunity to reduce the volume of alpha-contaminated metal materials. However, the analytical uncertainty associated with sampling irregularly shaped materials (*e.g.*, equipment items) after chemical/mechanical surface cleaning suggested the conversion of the material to standard forms (ingots, slabs) more likely to be homogeneous, in order to increase analytical reliability. Melting and slagging techniques were selected to achieve program objectives.

A glovebox facility has been set up for work with plutonium-contaminated metal. Experiments involving the melting of plutonium-contaminated steels have been initiated.

A. Melting of Plutonium-Contaminated Steels

A glovebox facility with support systems is operational for steel-melting experiments associated with the program on salvage of plutonium-contaminated metals. To date, two types of source material have been melted. The first sample was 200 g of clean carbon steel with powdered PuO_2 added to an average concentration of 500 ppm. The second sample was 200 g of steel from a plutonium-use area that was surface contaminated at 10^6 dpm total alpha. The surface contamination of this sample was fixed and was associated with rust, paint, and chemical deposits of unknown composition.

Both samples were melted in a modified Brew Furnace (Model 1064-C), using the same procedure. The metal sample, contained in a MgO crucible, was heated to about 1000°C , with the pressure maintained at $\leq 100 \text{ } \mu\text{m Hg}$ ($\leq 13 \text{ Pa}$) by continuous evacuation of the system. The sample was then heated to 1500°C under a helium atmosphere. The steel was kept molten for one hour and then was allowed to solidify in the crucible.

Sampling of the product ingot and the crucible material is nearly complete, and the attendant analyses are under way. The product ingot is sampled by making a series of cross-sectional cuts through the ingot to obtain a number of thin discs (1-2 mm thick by 3.2 cm dia). These sections are being examined by autoradiography (using cellulose nitrate film), radiation counting, and conventional radiochemical analysis. The sampling and analysis are designed to provide an indication of PuO_2 separation from the product ingot by inclusion in the dross, or in the crucible, or (as was the case with UO_2 -steel, see Section B) the extensive physical separation of the PuO_2 from the steel. The results for these experiments are pending.

Experimental work will continue to establish the distribution of PuO_2 in the product ingot of a melting operation. Subsequent effort will be directed toward optimizing techniques for decontaminating metals. Methods to be considered include: cleaning the feed material prior to melting, the use of extractive slags during melting, and the removal of surface layers of the ingot after melting if distribution studies indicate that the plutonium is concentrated at the surface.

B. Supporting Studies

A series of steel-melting experiments (Runs SM-1 to 10) has been completed using CeO_2 or UO_2 as a stand-in for PuO_2 . Reports by Shaw⁴ and Mautz, *et al.*,⁵ which were compilations of information on uranium decontamination of steels and stainless steels by smelting, served as a guide in planning this work. Steel sections were melted in various crucible materials, and both the disposition of the CeO_2 or UO_2 and the compatibility of the crucible material were determined. The bulk of the experiments were made without slags or other additives; exceptions were Run SM-3, which involved cryolite as a salt layer, and Runs SM-9 and -10 in which test sections of SiC and B_4C were added (suggested by a refractory manufacturer as candidate crucible materials). For several experiments, commercial refractory brick materials were made into crucibles. Melt periods ranged from 1 to 2.5 h. Pouring of the molten metal into a mold was instituted after Run SM-4. Previously, the steel had been allowed to solidify in the crucible, resulting in cracking of the relatively thin-walled crucible, even with slow cooling. Pourout of the steel allowed better evaluation of the crucible from a compatibility standpoint.

The experiments were conducted in an inductively heated furnace rated at 20 kW and 4.2 kHz; the furnace has a tilt-pour feature. An argon atmosphere was maintained in the furnace during each experiment.

Table 5 shows the experimental conditions and crucible compatibility, and Table 6 shows the analytical results for the melting experiments completed to date. The charge weight for the steel ranged from 226 to 477 g. Approximately 0.5 g of CeO_2 or UO_2 was used in each experiment. Analytical difficulties were experienced with cerium in the first three experiments, and subsequently UO_2 replaced CeO_2 as a stand-in for PuO_2 .

The slip-cast MgO crucibles appeared to be compatible with the steel melt, although slightly melted by the steel when no additives were used. Complete penetration of the MgO crucible wall occurred with cryolite present as a slagging material. Cracking of these crucibles occurred when the steel was allowed to solidify in place rather than being poured into a mold.

The crucibles fabricated from refractory brick* appeared to be compatible with the steel- UO_2 melts, and only the "Guidon" refractory showed some wetting by the steel. The "Ruby" crucible appeared to be the most compatible in the dressing experiments performed to date.

Analysis for cerium in Runs SM-1 and 2 indicated that the cerium concentrated on the surface of the ingot. However, in SM-3, it appears that the cryolite slagged out the cerium; a small amount of cryolite salt trapped inside

* Harbison-Walker Refractories Co.

Table 5. Conditions and Results of Steel Melting Experiments

Run No.	Crucible Material	Time, h	Temp, °C	Argon Pressure, mm	Charge			Weight of Metal Recovered, g	Crucible Weight		Comments
					Steel, g	CeO ₂ , g	UO ₂ , g		Initial, g	Final, g	
SM-1	MgO	1	1475	500	226	0.5	-	227	198	198	Crucible cracked at gas-metal interface during cooldown; crucible shows no attack.
SM-2	MgO	2	1515	705	470	0.5	-	475	220	220	Crucible cracked at gas-metal interface during cooldown; crucible shows no attack.
SM-3 ^a	MgO	2	1515	750	465	0.5	-	466	275	-	Complete penetration of crucible by cryolite at salt-metal interface.
SM-4	MgO	2	1400	820	477	-	0.5	478	132	-	Cooled with crucible at 30° angle. Some metal adherence to crucible. Crucible cracked as metal ingot was removed.
SM-5	MgO	2.5	1545	830	467	-	0.5	467.5	148	148	Metal poured into mold. Crucible intact, showed little indication of reaction.
SM-6	Ruby ^b	1.33	1525	825	465	-	0.5	468	987	990	Metal poured into mold. Crucible showed no evidence of attack. UO ₂ found adhering to crucible.
SM-7	Copur ^c	1.33	1525	825	475	-	0.5	472	1102	1104	Metal poured into mold, one metal bead found adhering to crucible. Crucible showed no evidence of attack. UO ₂ found in clumps on crucible wall.
SM-8	Guidon ^d	1.33	1525	820	475	-	0.5	470	1140	1144	Metal poured into mold. Metal bead and some UO ₂ found adhering to wall. Crucible wall showed some wetting by metal.

(Contd.)

Table 5. (Contd.)

Run No.	Crucible Material	Time, h	Temp, °C	Argon Pressure, mm	Charge			Weight of Metal Recovered, g	Crucible Weight		Comments
					Steel, g	CeO ₂ , g	UO ₂ , g		Initial, g	Final, g	
SM-9 ^e	Ruby ^b	2.0	1535	810	469	-	0.5	471	990	989	Metal poured into mold. Some metal beads and UO ₂ clumps found at bottom of crucible. Crucible wall showed no attack.
SM-10 ^e	Ruby ^b	2.0	1525	815	469	-	0.5	480	988	988	Metal poured into mold. Some metal beads and UO ₂ clumps found adhering to wall. Crucible shows signs of wetting.

^a 75 g cryolite (3NaF·AlF₃) added.

^b Harbison-Walker high alumina refractory brick material, Al₂O₃-89.7%, Cr₂O₃-10%, SiO₂-0.1%, Fe₂O₃-0.1%.

^c Harbison-Walker chrome refractory brick material, Al₂O₃-20.3%, Cr₂O₃-32.5%, MgO-33.5%, SiO₂-2.4%, Fe₂O₃-10.9%, CaO-0.4%.

^d Harbison-Walker Magnesite refractory brick material, MgO-62.7%, Cr₂O₃-18.1%, Al₂O₃-5.4%, SiO₂-1%, Fe₂O₃-12%, CaO-0.8%.

^e SiC and B₄C test samples added to steel melts.

Table 6. Analytical Results of Steel Melting Experiments Using CeO₂ or UO₂ as a Stand-In for PuO₂

Run No.	Crucible	Charge			Cerium Distribution					Uranium Distribution					Acid Etch	
					Ingot					Crucible		Ingot				
		CeO ₂ , g	UO ₂ , g	Steel, ^a g	Crucible, ppm	Top, ppm	Side, ppm	Bottom, ppm	Inside, ppm	Dross, g	Filings, g	Top, ppm	Side, ppm	Bottom, ppm	Inside, ppm	Top Side, g
SM-1	Mgo	0.5	-	226.2	3300	1000	900	3300	80	-	-	-	-	-	-	-
SM-2	MgO	0.5	-	470	300	200	2.9 x 10 ⁵	-	60	-	-	-	-	-	-	-
SM-3	MgO	0.5	-	465	-	50	-	130	160 ^b	-	-	-	-	-	-	-
SM-4	MgO ^c	-	0.5	477	-	-	-	-	-	0.34	-	.095g ^d	-	-	-	2.34 x 10 ⁻⁴
SM-5	MgO ^e	-	0.5	467	-	-	-	-	-	0.024	-	.233g ^d	-	45	-	1.16 x 10 ⁻²
SM-6	"Ruby"	-	0.5	465	-	-	-	-	-	0.401	0.007	7	<1	-	<1	1.7 x 10 ⁻³
SM-7	"Copur"	-	0.5	475	-	-	-	-	-	0.41	0.008	7	-	<1	<1	<1 x 10 ⁻⁴
SM-8	"Guidon"	-	0.5	475	-	-	-	-	-	0.42	0.002	<1	-	7	<1	2 x 10 ⁻⁴
SM-9	"Ruby" ^f	-	0.5	469	-	-	-	-	-	0.41	0.007	14	-	7	20	2 x 10 ⁻³
SM-10	"Ruby" ^g	-	0.5	469	-	-	-	-	-	0.39	0.016	81	-	82	82	7 x 10 ⁻⁴

^a Cerium content 80 ± 60 ppm^b Cryolite salt trapped in ingot had a cerium content of 3000 ppm^c Ingot not poured, UO₂ on surface^d Analysis of etching solutions^e Ingot poured, UO₂ on surface^f 0.5g SiC and 0.6g B₄C added to melt^g 4.6 g SiC and 8.9 g B₄C added to melt

the steel ingot contained 3000 ppm cerium. In the subsequent experiments in which UO_2 was used, the analyses indicate a good drossing effect, with about 94% of the UO_2 migrating to the crucible walls and the remaining activity being mainly on the surface of the ingots.

Analytical results for SM-9, in which SiC and B_4C samples unexpectedly dissolved in the steel, show 20 ppm uranium in the interior of the ingot in comparison with <1 ppm in the previous melts. In SM-10, SiC and B_4C additions were a factor of 9 and 15 greater, respectively, than in SM-9. The analyses of sections of the poured ingot showed the uranium content to be uniform at about 81 ppm. The results of these two experiments, in which different amounts of SiC and B_4C were added, indicate that the carbides reduced some of the UO_2 and that the uranium then dissolved in the steel.

Observations made after the melting experiments tend to indicate that the UO_2 was not being wetted by the steel melt and was drossed out in easily removable clumps on the crucible walls. The use of powdered UO_2 as an additive may not adequately simulate a surface contamination layer of UO_2 , and the preparation of steel samples that are surface-contaminated with UO_2 is being considered for subsequent support studies.

Another Harbison-Walker refractory, "Korundal XD," a high-alumina brick (90.3% Al_2O_3 , 9.2% SiO_2 , 0.2% Fe_2O_3 , and <0.1% each of TiO_2 , CaO, and MgO) was to have been tested in these experiments, but has not been available. It is postulated that the performance of this refractory, which also contains about 90% Al_2O_3 but contains no Cr_2O_3 , would be as good as or better than the "Ruby" refractory.

A number of slags, listed below, are to be tested for removal of UO_2 from steel melts, and compatibility test with the refractories tested to date will be performed.

CaO·SiO₂
CaO·MgO·SiO₂
CaO·Fe₂O₃
SiO₂·B₂O₃

Fullam's⁶ work in the decontamination of radioactive steels showed the above-listed slags to be compatible with the high-density Al_2O_3 crucibles used in these studies, and decontamination factors of 1000 were obtained using slag-to-metal ratios of 2.5. It is hoped that in the future experiments good decontamination factors may be obtained at a maximum slag-to-metal ratio of 0.1 to provide a feasible process which does not provide an increase in waste material. Flowsheets involving conceptualized drossing/slugging techniques are under development for processing PuO_2 -contaminated steels.

III. STORAGE AND DISPOSAL OF TRITIUM (L. E. Trevorrow)

A. Introduction

The general objective of this project has been to evaluate options in the management of tritium formed in light water reactor fuels. If tritium is not removed from spent fuel by processes such as the Voloxidation process⁷⁻⁹ before the fuel is dissolved in aqueous acid, a major fraction is expected to appear in the low-level aqueous waste (LLAW) streams of fuel reprocessing plants. The disposal option being evaluated in this work is deep-well injection of LLAW, *i.e.*, the emplacement of the liquid waste in deep-lying (>1000 ft, >305 m) permeable aquifers. The possibility of disposal of LLAW from commercial reprocessing of spent LWR fuels by deep-well injection rather than biospheric dispersal has been previously considered,^{10,11} but many of the requirements and consequences relevant to adopting this disposal method, if explored, have not been documented. In the previous quarterly report,¹ a detailed discussion of the geologic considerations determining the choice of a deep well site was presented.

In the present work, existing information on deep-well injection of industrial wastes and on LLAW have been analyzed to determine the factors, within the categories of technology, economics, environmental impact, law, and siting, that are most likely to significantly affect the adoption of this disposal method. This work, carried out by ANL personnel and a consulting geochemical engineer,* has been described in a manuscript that will be published later as a separate report. The discussion presented below is a condensation of that report.

B. Technology of Deep-Well Injection

Review of the technology of deep-well injection of wastes included the requirements imposed by the volume of the waste; the chemical, physical, and biological nature of the waste; and design, operation, and monitoring considerations. It is concluded from this review that the method should be as applicable to LLAW as it has been applicable (with apparent success) to wastes of the chemical industry. The need for technical innovation in its application to LLAW seems to be small or nonexistent. In fact, the LLAW promises to be less noxious than some of the chemical industry wastes (*e.g.*, alkalies, chromates, nitrates, phosphates, sulfates, alcohols, ketones, phenols, organic cyanides, and chlorinated hydrocarbons)¹² discharged into deep wells. Because of the very low concentrations of dissolved solids in LLAW, the technique can probably be applied with less pretreatment than is required for many wastes presently being injected by industry. The relative chemical purity of the waste, except for nitric acid content, may result in the requirement of an ionic additive to prevent the dispersion of clays that could result in plugging of formation pores. Perhaps the main requirement for modification of normal injection technology may result from the accumulation (plate-out) of radioisotopes (present in trace concentrations) in piping and equipment, leading to the necessity for developing operating procedures for handling equipment different from that normally used in the operation of oil-industry or waste-disposal wells but not unknown in the nuclear process industry.

* Professor D. L. Warner, University of Missouri (Rolla).

C. Economics

The total capital and operating costs for deep-well injection of LLAW were estimated to be of the order of magnitude of 10^{-4} mill kWh⁻¹. This cost may be compared with a recently quoted value of 0.05 mill kWh⁻¹ allotted for the total contribution of waste management to the fuel cycle.¹³ The limited accuracy of the cost estimate should be noted, however. The difficulty of arriving at an accurate cost is related to the change in the value of the dollar, the rapidly changing costs of goods and services, the variation in cost with the depth and geological characteristics of sites, and changing requirements.

The cost quoted above for successful practice of deep-well injection of LLAW can be compared with the cost for exposure incurred from biospheric dispersal of the tritium. The cost for dispersal can be calculated from an estimate¹⁴ of the annual whole body dose of 3700 man-rem for exposure to tritium discharged at a 5 metric tons of uranium/day fuel reprocessing plant and from the recent, interim assignment of a value of \$1000 per whole-body man-rem.¹⁵ On these bases, for conventional methods of tritium disposal, the cost of exposure is about 1×10^{-2} mill kWh⁻¹.

The cost for deep-well injection could increase greatly, however, if maloperations should occur that would result in public exposure to tritium. Accordingly, the effect of an upper limit accident was estimated: Escape of 100% of the low-level aqueous wastes injected from a 5 metric tons of uranium day⁻¹ reprocessing plant into a public water supply could result in a maximum population dose, based on continuous consumption, of 3×10^5 man-rem yr⁻¹ corresponding to a cost, based on \$1000 (man-rem)⁻¹, of 0.8 mill kWh⁻¹.

D. Environmental Impact

The environmental effects induced by the nature of the method are, in every case, modification of the groundwater system and introduction into the subsurface of fluids with a chemical composition different from that of the natural fluids. These effects do not necessarily result in an impact on the biospheric segment of the environment and, in fact, are normally designed to have no effect on the biosphere. The most important environmental impacts that could occur in individual cases, as a result of unplanned, adverse incidents, are degradation of high-quality groundwater, contamination of resources, and the stimulation of earthquakes.

The impact of greatest concern is the contamination of potable water. Concepts of the worst case of contamination of potable water indicate that the normal low-level waste from a 5 metric tons of uranium day⁻¹ reprocessing plant has the capacity to expose almost 7000 persons per day to the water contaminated to the Public Health Service nitrate limit for drinking water. Also, a worst-case maloperation, in which 100% of the low-level aqueous waste from a 5 metric tons of uranium day⁻¹ reprocessing plant escapes into a public water supply and is consumed continuously, has the capacity for a maximum individual whole-body dose of 600 rem yr⁻¹ and a maximum population dose of 3×10^5 man-rem yr⁻¹.

If the disposal can be carried out as intended, however (*i.e.*, without adverse incidents), the exposure of the biospheric segment of the environment to the constituents of LLAW is expected to be nil compared with the estimated annual dose of 3700 man-rem/yr incurred from dispersal of LLAW from a 5 metric tons of uranium day⁻¹ reprocessing plant to the atmosphere or to surface streams.

E. Siting

The suitability of a site for deep-well injection of wastewater can be assessed by consideration of a number of types of information: (1) consultation of recorded information on stratigraphy, structure, and lithology (composition and texture) of rock strata; (2) the properties of the natural subsurface water in the area (*e.g.*, chemical composition, viscosity, pressure, and compressibility); (3) data on the mechanical properties of the rock units, such as porosity, permeability, compressibility, temperature, and state of stress; (4) the hydrodynamics of the subsurface region (*i.e.*, the flow of natural water and its relevance to waste containment); and (5) the resources of the region and the possible effects of waste injection on their value.

Data describing the subsurface of a region may be obtained, prior to drilling, from records of state geologic surveys, oil and gas agencies, water-resources agencies, and private companies. Retrieval, by automatic data processing techniques, of geologic and subsurface engineering information that would be useful in site evaluation has not yet become generally available.

Data on a particular well can be obtained, as drilling proceeds, from analysis of rock samples and formation fluids, from a large number of borehole geophysical logging techniques that have been developed, and from tests that involve pumping fluid into or out of the well at various stages of completion.

Predictions can be made, with varying accuracy, on the response of the aquifer to injection, including effects on subsurface flow of natural fluids in the region of influence, effects of pressure, the rate and direction of flow of the waste, the possibility of hydraulic fracturing of the overburden, and the stimulation of earthquakes.

The areas of the U.S. most likely to have geologic properties suitable for deep-well injection are the sedimentary basins. The sum of the areas of these basins is great, indicating an abundance of areas that offer suitable geologic properties. Recorded descriptions of the sedimentary basins of the eastern and middle sections of the U.S. are available in detail, but some of the basins of the far western section of the country are less well explored and described. Recorded information on U.S. basins would serve only for preliminary assessment of the suitability of a region, and would have to be followed by more detailed analysis of a particular site of interest.

Present attitudes toward transport of liquid radioactive wastes and economic factors suggest that a well for disposal of LLAW would best be located at the fuel reprocessing plant which is the source of the LLAW.

F. Legal and Regulatory Constraints

Legal and regulatory constraints may be the most formidable barrier to the application of deep-well injection for disposal of LLAW. This conclusion is made not necessarily in anticipation of prohibition, but in anticipation of the time, effort, and expense that may be needed to satisfy the requirements of review and regulation.

The laws and regulations of the state, if adequate, when judged by Federal guidelines, would be a primary consideration. At present, state laws that apply to deep-well injection vary from those that address pollution control in general to those that are detailed and apply specifically to waste wells. In a few states, waste wells are prohibited either by law or by regulation.¹⁶ In several states, laws and regulations applying to waste wells may be expected to develop further in the near future. Recent Federal guidelines, expressed in EPA Administrator's Decision Statement No. 5,¹⁷ and public laws PL 92-500 and PL 93-523 may be expected to influence greatly the course of future developments in state laws and regulations. Waste wells within states without adequate laws and regulations for waste wells would be regulated by a Federal agency. In any case, for disposal of LLAW produced by a commercial reprocessing plant, it is expected that because of the origin of the waste, the Federal regulating agency would be NRC and that a state with adequate regulatory structure would share the regulatory responsibilities with NRC.

A waste well that is installed at a fuel reprocessing plant in conjunction with the construction of the plant would be described in the environmental impact statement of the plant and would be examined as part of the environmental impact review of the plant and its facilities. It is expected that although NRC and a state government agency would eventually regulate any operations of such a waste well, the review would include representatives of several agencies, including the state government involved, USGS, and EPA. On the other hand, the application for a waste well to be installed at an already-operating commercial fuel reprocessing plant would probably involve filing an application that would be reviewed by representatives of the agencies mentioned above. This review would be expected to result in a recommendation to proceed, to desist, or to initiate a more extensive review. The latter could include preparation of a draft environmental review by the applicant; that review would serve as a basis for a draft environmental review prepared by NRC and circulated to other agencies for review and a public hearing; finally, an environmental impact statement would be prepared by NRC.

In addition to the need to operate within state and Federal legal structures, civil legal action based on civil law could be expected in cases where waste injection results in claims of civil grievance.

IV. RELIABILITY OF HIGH-LEVEL WASTE CONTAINERS (W. Seefeldt, W. Mecham)

A. Purpose and Scope

The purpose of the container reliability studies is to identify as quantitatively as possible the reliability against failure and leakage of the canisters used to contain high-level wastes in a glass or calcine form.

Container degradation due to internal metallurgical characteristics, thermal and mechanical events occurring during transport and handling (but not major events such as earthquakes and tornadoes), and interactions with internal and external environments were considered. Environments included are interim storage of solidified wastes at a reprocessing plant, transport from a reprocessing plant to a Retrievable Surface Storage Facility (RSSF), interim storage at the RSSF, and transport to the ultimate disposal site.

The study requires that reference systems be established prior to the determination of canister reliability. Three storage concepts have been developed by Atlantic Richfield Hanford Company (ARHCO) for application to an RSSF. These concepts will be part of the reference system. In addition, waste compositions, canister material and fabrication methods, coolant compositions, and mechanical and thermal events should be selected for the reference systems.

The three concepts of interim storage at the RSSF are:

- (1) The Water Basin Concept, in which canisters are stored bare in a water pool,
- (2) the Air-cooled Basin Concept, in which canisters are overpacked in mild steel and stored and cooled in air moving by thermal convection, and
- (3) the Sealed Storage Cask Concept, in which canisters are overpacked in mild steel, encased in a freestanding concrete shield placed outdoors on a concrete pad, and cooled by thermal convection.

The sequence of events to be considered for reference was 10 years of interim storage under water at a reprocessing plant, followed by 100 years of interim storage at an RSSF, together with transfer from both facilities. In addition, 40 yr of interim storage under water at the reprocessing plant followed by shipment to the ultimate disposal site is included.

Initially, the two waste forms to be considered for incorporation into the reference systems were calcine and glass, but no specific compositions were established for reference purposes. Through discussions with the Division of Waste Management and Transportation (DWMT), two modes of heat transfer for the calcine form were established: with and without internal fins. This was later reduced to the mode with fins.

B. Preparation of Summary Report

A draft summary report was completed during this reporting period. A summary of the report, the conclusions, and recommendations presented in the report are included below.

1. Summary

Available information was obtained from Battelle Northwest Laboratories (BNWL) and ARHCO on (1) the three conceptual designs of the Retrievable Surface Storage Facility and (2) the known properties and behavior of glass and calcine waste forms.

Methodologies for establishing and expressing reliability were examined to establish a viable technique that was compatible with available time and effort. It was concluded that a quantitative evaluation of reliability is not possible now because of the lack of significant pertinent information.

A thorough review was made of mechanisms by which the reference canister alloy (stainless steel type 304) could be subjected to localized failure. The reference exposure sequences were analyzed to identify conditions leading to stress corrosion cracking, sensitization, and intergranular corrosion.

The cooling of canisters after they are filled with glass introduces substantial stresses due to different coefficients of expansion of glass and the canister alloy. Natural stress-relieving mechanisms of creep and/or glass flow are not effective. Reference normal water conditions during storage and shipment do not lead to cracking, but minor deviations of conditions render canisters susceptible to cracking.

Residual nitrates and moistures in calcine were identified as sources of canister stresses; reduction of residuals during processing or as a post-filling treatment reduces the severity of this effect.

The properties of glass and calcine were examined to determine potentials for intergranular corrosion effects. The complex chemistry of the multicomponent systems did not permit definite judgments, although some constituents are capable of forming low-melting eutectics or volatile species that can migrate. Experiments are recommended to elucidate waste form-canister interactions.

Methods of eliminating adverse effects were studied. These included the selection of alternative canister materials and waste forms, precasting of glass before canister loading, stress relief of a glass-container canister by a subcooling method, alternative sequences of process operations, and the elimination of water cooling.

2. Conclusions

The principal conclusions of the study are:

- (a) The reliability of canisters fabricated of stainless steel type 304L and used in conformity with the reference conditions

may, in fact, prove to be sufficiently high. However, quantitative information supporting such a conclusion is lacking.

- (b) The reference design is not detailed or firm enough at this time to identify clearly the bases for choices of design from among state-of-the-art options or for the specifications for quality control of high-performance canister material. Similar deficiencies are noted for the conditions during transportation of high-level wastes.
- (c) Insufficient information is available on basic, long-term properties of the waste forms and of their interactions with canister materials.
- (d) Current information from corrosion science, including consultations with experts such as Professor Staehle, Ohio State University, is insufficient to allow predictions of behavior for prolonged periods under very mild conditions. Absence of empirical test results and lack of adequate theoretical bases of such phenomena as stress corrosion (for materials susceptible to it) inhibits the development of "good" designs.
- (e) Although reliability analyses have been applied practically and successfully in several industries, applications to chemical corrosion or to radiochemical systems for extended periods have not yet been reported.
- (f) A brief review indicates that the rules of the ASME Boiler and Pressure Vessel Code, Section III, cannot be used for stainless steel type 304L canisters because of (1) the inability to qualify the final closure welds and (2) the excessive temperatures during reference filling operations (in the case of the glass waste form).

3. Recommendations

- (a) A system engineering analysis of the solid waste storage canister should be carried out, to include all steps including procurement, filling, shipping, and storage at the reprocessing plant and the RSSF. Such an analysis should include definition of design options for containment, transfer, cooling, surveillance, quality control, etc. The results of such an analysis would be a reference canister whose behavior in the waste handling environment would have been subjected to systematic examination at all stages and whose design would meet identified criteria according to information presently available. This analysis could be part of a systematic analysis of various options for high-level waste storage. The analysis should be sufficiently flexible to include consideration of (a) air vs. water cooling at the processing plant and in shipment casks, (b) various cooling times at which operations are

conducted (*e.g.*, liquid-to-solid conversion and shipment to the RSSF), and (c) additional operations at appropriate cooling times to enhance reliability or to take advantage of the rapid decline in decay heat with time (*e.g.*, overpack addition prior to disposal, and repackaging in larger canisters at late stages).

- (b) A materials chemistry study of calcine-canister interaction should be carried out for all operations involving the combination of these materials. Included in this work would be the properties of calcine and their relation to its history and composition, the chemistry of the canister material (corrosion), migration of fission products in thermal gradients that affect corrosion, and the practical effects on containment. This study would interface with work on solidification of wastes and postsolidification treatments. Similar studies are needed for the glass form. The results of this work would allow estimates of the reliability of containment of waste to be made where internal effects are critical.
- (c) Consideration should be given to modifying existing waste forms or developing new waste forms to yield compositions that are more stable (in the case of glass), or more conductive (in the case of calcine). Increased stability will remove possible doubts about corrosive effects attributable to long-range changes (*e.g.*, devitrification).

Methods of enhancing the long-term stability of glass by intentionally inducing crystallization by appropriate additives should be examined. Further, the existing body of technology that has been applied to the fabrication of commercial micro-crystalline glass-ceramics that are more stable than glass should be considered for application to wastes.

- (d) There is increasing evidence that stainless steel (Type 304L) may not be the best canister material because of its susceptibility to stress-corrosion cracking. Systematic and practical corrosion studies of alternative candidate materials should be conducted and should be based on the results of the systems analysis suggested above. These studies would allow estimates of the containment of waste to be made where the external effects predominate.

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