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A REVIEW OF METAL-MATRIX ENCAPSULATION OF
SOLIDIFIED RADIOACTIVE HIGH-LEVEL WASTE

by

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ABSTRACT

Literature describing previous and current work on the encapsulation of solidified high-level waste forms in a metal matrix was reviewed. Encapsulation of either stabilized calcine pellets or glass beads in alloys by casting techniques was concluded to be the most developed and direct approach to fabricating solid metal-matrix waste forms. Further characterizations of the physical and chemical properties of metal-matrix waste forms are still needed to assess the net attributes of metal-encapsulation alternatives.

Steady-state heat transfer properties of waste canisters in air and water environments were calculated for four reference waste forms: 1) calcine, 2) glass monoliths, 3) metal-encapsulated calcine, and 4) metal-encapsulated glass beads. A set of criteria for the maximum allowable canister centerline and surface temperatures and heat generation rates per canister at the time of shipment to a Federal repository was assumed, and comparisons were made between canisters of these reference waste forms of the shortest time after reactor discharge that canisters could be filled and the subsequent "interim" storage times prior to shipment to a Federal repository for various canister diameters and waste ages.

A reference conceptual flowsheet based on existing or developing technology for encapsulation of stabilized calcine pellets is discussed. Conclusions and recommendations are presented.

I. METAL-MATRIX CONCEPTS--STATE OF THE ART

A. Overview

1. Introduction

Safe disposal of nuclear wastes ranks as an important problem, the solution of which is necessary for public acceptance of nuclear power. Solidified high-level wastes (HLW) from the reprocessing of spent commercial nuclear fuel, containing most of the fission products and unusable trans-uranium elements, are to be transferred to a Federal waste repository for final isolation. Solid forms of waste are designed to minimize the dispersibility of the nuclides by either aeolian or hydraulic means. The high-level waste is formed in reprocessing operations as an aqueous solution, and the

first product of solidification is a calcine formed by evaporation and heating. The calcine product is thermally stable but is relatively easily dispersed because of its relatively high solubility in water and the powder form usually produced. The poor thermal conductivity and low inherent mechanical strength of the calcine are additional disadvantageous attributes. Considerable effort has been expended on a national scale in the conversion of high-level waste to glass by additional or concomitant steps related to calcination. The advantages of a glass product, with low water solubility and improved thermal conductivity and mechanical strength, are partially offset by the severe conditions required for its formation and its thermodynamic instability. Another solid form of high-level waste that may be acceptable is waste dispersed in a continuous metal matrix.

The objective of this report is to assess the value of encapsulating, into a metal matrix, either a calcine or glass-bead form of radioactive high-level waste from the reprocessing of commercial reactor fuel. The assessment includes a review of the literature on metal encapsulation published through January 1977, a description of the status of the technology, an evaluation of the increase in thermal conductivity of encapsulated waste and its consequences, and discussion of a conceptual-process flowsheet. To a lesser extent, this report addresses the integrity of the encapsulated waste and a comparison of its resistance to dispersion to that of either calcine or glass waste forms. This report identifies the conditions under which the process steps required for metal encapsulation might result in greater advantages in HLW management than from other alternatives.

The metal encapsulation of solidified radioactive waste into a two-phase composite containing 60-70 vol % high-level waste is not a new concept. The concept was investigated in the late 1950s and early 1960s as a potential method of packaging wastes from the reprocessing of military fuels,* but was limited to bench-scale testing. One of the major reasons for the lack of continued development of this method was the inability to utilize the high heat-dissipation capability of the metal matrix. Military wastes have a low volumetric heat generation rate that is due to only moderate burnup, coupled with a rather large dilution of the waste with aluminum and zirconium (a result of dissolution of the cladding during reprocessing). In addition, decisions were made to store the military waste as a liquid in tanks on the reprocessing sites. Therefore, dispersibility during storage, transportation, or on-site handling of solidified waste was of little concern.

Commercial power reactors discharge high-burnup spent fuel; the cladding is removed from spent fuel prior to reprocessing. Reprocessing produces a concentrated liquid waste with a high heat-generation rate. Current Federal regulations require 1) solidification (≤ 5 years) and 2) transport of solidified HLW to a Federal repository within 10 years after reprocessing. Under these conditions, HLW forms that have a good thermal conductivity and that are rather nondispersible are of major interest. For example, severe restrictions upon the size and geometry of HLW canisters may be imposed for short-cooled solid wastes, especially in a FBR fuel-cycle economy, due to the low thermal conductivity of calcine and glass waste forms. The greatest risk

* Military fuels are those fuels reprocessed at Hanford and Savannah River to produce plutonium for nuclear weapons and at Idaho to produce fuel for military propulsion reactors.

of release of radionuclides to the environment has been tentatively identified [NUREG] as accidents during transportation of high-level waste to a Federal repository. Even though the absolute magnitude of any risk is likely to be extremely low [NUREG], regulations may eventually require that only nondispersible forms of solidified HLW be shipped so that reliance against dispersal is not totally placed on the shipping containers. The probability that underground aquifers would ever contact HLW in an underground repository is uncertain. Such a contact, assuming a breachment of the HLW canister, could provide a mechanism for dispersing HLW into the biosphere before all isotopes of the HLW had decayed sufficiently. For spent fuel that is deemed to be a waste in the "once-through" mode, attention to heat evolution and dispersibility may be required; in this case, metal-matrix encapsulation of spent fuel may be attractive but is not addressed in this report. For all of these reasons, it may be desirable to require the solidified wastes (*e.g.*, glass or calcine or spent fuel, *etc.*) to have an improved thermal conductivity and to be in a rather nonleachable (nonwater soluble) and nondispersible form prior to its isolation in a geologic formation.

In principle, metal-matrix encapsulation of commercial solidified waste can serve 1) to increase the thermal conductivity of the HLW form and 2) to produce composites containing either calcine or glass beads and having reduced leach rates and improved mechanical strengths which in combination retard widespread dispersal. The value of the metal-matrix concept is being reassessed to determine if increases in heat transfer and decreases in dispersibility are obtainable under conditions advantageous in cost and safety compared with the existing reference waste forms of glass and calcine.

Finally, some processes used to produce solid forms of HLW require high temperatures, involve highly corrosive media, and produce secondary waste streams that are difficult to manage. The corresponding process considerations for metal-matrix encapsulation are included in this assessment.

2. Brief Review of Current Solidified High-Level Waste Forms

Solidification of high-level waste is required in all current waste-management concepts. Calcination, generally by fluidized-bed or spray methods [BONNER, BJORKLUND-1, ERDA], is used as the first process step in almost all solidification schemes. Calcine taken directly from either of these processes is a dispersible powder with particle sizes ranging from approximately 2 to 500 μm , is rather water soluble (*i.e.*, leachable), contains some residual nitrates, and has poor thermal conductivity properties. The major protective barrier to prevent dispersal of a final solid waste form of calcine to the environment would be very rugged, thick-walled canisters in conjunction with institution of appropriate protective measures to decrease the probability of a canister breachment. Breach of a waste canister containing calcine powder could lead to extensive dispersal, the extent of which would depend upon the environment (*e.g.*, air, water, geologic formation) and the mode (*e.g.*, mechanical impact, fire, internal pressurization) in which the breach occurred. Further processing of calcine to reduce the risk of dispersibility may be required under the guidelines "as low as reasonably achievable" and to limit potential population exposures in the event of an accidental release at areas where HLW canisters are handled or transported. There is probably sufficient justification to institute additional steps for processing calcine as long as improvements can be realized in the dispersibility (*i.e.*, solubility or leachability, particle size), and perhaps the thermal conductivity, properties of calcine.

Shown in Fig. 1 are four generalized high-level waste management alternatives that are considered in this review. This figure is used to summarize the important process steps and their required temperatures to produce packaged solidified HLW.

Fig. 1. Summary of Process Steps and Temperature Required to Produce Solid HLW Forms.

Calcination and stabilization of the solid of residual nitrates is relatively simple, but the only physical barrier against dispersal to the environment would be the thick-walled canister.

Consistent with most borosilicate glass vitrification concepts, Fig. 1 shows a calcination step prior to the formation of glass [BLAIR, BONNIAUD, ERDA, GUBER, MCELROY-1, MCELROY-4]. Exceptions that use a concentrated aqueous HLW slurry as feed for a glass vitrification process include

the German phosphate-glass PAMELA process [HEIMERL, VANGEEL-1] and the English HARVEST [WARNER] process. Glass-making processes differ in particular details, but all require temperatures greater than 1000°C to achieve a satisfactory viscosity of the glass for melting and packaging. Such high temperatures, coupled with liquid phases, may significantly shorten useful equipment life due to accelerated corrosion rates. Some volatilization of fission and activation products can be expected during melting and pouring and may require additives and/or off-gas collection systems for control. Significant corrosion or volatility may contribute to the production of secondary waste streams. The in-can melting process [BLAIR] may be ready for full-scale radioactive demonstrations in the U.S. and will generate factual information to determine the magnitude of these secondary waste streams.

A major advantage of a glass monolith HLW form in comparison to a calcine waste form is a lower solubility (*i.e.*, leach rate) and hence a lower dispersibility in the event of canister rupture. A minor advantage of a glass monolith is better thermal conductivity of this glass waste form; its thermal conductivity is higher than that of calcine by a factor of about three to four. Investigations are currently under way to establish the long-term behavior of the glass, which is a thermodynamically unstable system [MCELROY-1, MCELROY-5, MENDEL-1].

Another scheme shown in Fig. 1 should minimize the rate of formation of some detrimental effects of glass. The concept employs small spherical glass beads (approximately 1-10 mm in diameter), rather than large glass monoliths. If glass beads are embedded in a ductile metal matrix, a relatively nondispersible waste form can be produced. The increased thermal conductivity due to the metal matrix reduces the temperature gradients in large-diameter glass monoliths. If appropriate interim storage is used, the lower temperature in the center of glass beads encapsulated in metal should result in a lower rate of devitrification, and hence reduce even further the formation of water-soluble phases. Further, in the event of a canister being breached by mechanical impacts, encapsulation of glass beads in a relatively ductile metal should improve the dispersibility resistance in comparison to more brittle glass monoliths.

The final scheme shown in Fig. 1 is the metal-matrix encapsulation of stabilized, pelletized or agglomerated calcine granules. This concept avoids production of any liquid phases at temperatures above ~600°C but still produces a solid waste form that is not as leachable or dispersible as is calcine. The thermal conductivity of the waste produced by the fourth scheme is also improved by more than a factor of ten. The metal encapsulation process consists of stabilizing calcine by first agglomerating calcine powder, together with appropriate additives and binders that react after sintering with the more leachable and/or hazardous elements, *e.g.*, cesium and strontium, to particle sizes of approximately 1-10 mm diameter. The agglomerated calcine is then sintered at temperatures of 600-900°C to chemically fix the constituents and encapsulated in a metal matrix at temperatures of ~300-600°C, depending upon the metal. The absence of liquid phases at the sintering temperatures should reduce corrosion problems compared to those in glassification processes. Volatilization during the sintering processes should be solvable by technology developed for glass making, spray calcination, or fluidized-bed calcination.

B. Review of Literature on Metal Encapsulation of Solidified Waste

1. Introduction

A review of the work that has been done on the metal-matrix encapsulation of solidified HLW revealed that a large fraction of the metal-matrix encapsulation data obtained by U.S. workers is available in progress reports rather than in the open literature. Such reports are, by their nature, often preliminary and incomplete, and sometimes the data cannot be directly referenced. Relatively few details of the metal encapsulation work done in Europe are available. Some data has been presented at waste management topical meetings. No reports of metal encapsulation studies in Great Britain or the U.S.S.R were found.

Since the first reports of the metal-matrix concept during the late 1950s and early 1960s, only three laboratories in addition to Argonne National Laboratory (ANL) have actively participated in metal-encapsulation studies. These are Allied Chemical (formerly operated by Phillips Petroleum) at Idaho Nuclear Engineering Laboratory (INEL) in Idaho, Battelle Pacific Northwest Laboratories (PNL, formerly operated by General Electric) in Richland, Washington, and Eurochemic at Mol, Belgium. A summary of all the encapsulation work of these groups published through January 1977, and selected publications dated thereafter, is given below. The experimental work performed at ANL used this literature review as a base to identify areas lacking the data required to judge the technical feasibility of metal encapsulation. This work is generally not included here but may be found in [ANL-77-36 and ANL-78-11].

2. INEL - Allied Chemical (Formerly Operated by Phillips Petroleum)

With the purpose of reducing the dispersibility of solid, calcined waste and increasing the thermal conductivity, work was done [RHODES-1, RHODES-2, RHODES-3] to embed simulated calcine ($-60 +100$ mesh Al_2O_3) in an aluminum metal matrix in 1959. Some work was also done with ~ 12 mesh Al_2O_3 in a tin-lead matrix. The fabrication technique consisted of filling a metal tube with Al_2O_3 and heating. One end of the tube was inserted into a beaker of molten metal, and a partial vacuum was applied to the other end. After cooling, examination of cross sections of the composites indicated that the interparticle void space was only partially filled [RHODES-4]. No thermal conductivity or physical strength measurements were reported in this early INEL work, which has been summarized [RHODES-4].

Leach tests at INEL of simulated calcine (i.e., alumina) dispersed in an aluminum metal matrix were reported [WILDING]. Cesium-137 was calcined with the alumina and was used as a tracer for determining cesium leach rates. A whole slug section of the encapsulated alumina containing the ^{137}Cs was sectioned and leach-tested in distilled water at 80°C . The data showed that cesium was leached more slowly ($\sim 40\%$ of the total ^{137}Cs in 600-700 hours) from the metal matrix than from similar unencapsulated alumina ($>70\%$ of the total ^{137}Cs in 1 hr). However, in both cases, the leach rate was rapid in relation to the 30 year half-life of ^{137}Cs . It was concluded [WILDING] that cesium was leached from the interior of the sectioned metal-matrix composite by movement of water through the relatively porous calcined alumina. Hence, the porosity of the dispersed particles (i.e., alumina) was deduced to be important to the leach rate of a calcine-metal matrix composite [WILDING]. This is an

important conclusion that needs to be confirmed or refuted with more quantitative data than those given in the early cursory study [WILDING]. If confirmed, metal encapsulation to reduce HLW dispersal by leaching could be less advantageous if porous waste forms were encapsulated.

A renewed investigation of metal-matrix encapsulation of commercial high-level radioactive waste has taken place since 1973 as part of the AEC/ERDA Waste Fixation Program. Both casting and powder metallurgical fabrication techniques were studied at INEL. Much of this recent work carried out at INEL has been summarized [BERRETH-2], including some of the work done on the sintered glass ceramic HLW form of calcine. None of the recent work involved any radioactive materials [SLANSKY-1 through 6] but rather cold simulated wastes. This renewed metal-matrix work was apparently terminated during FY77 [SLANSKY-6].

Composites (~50-70 vol % waste) of various simulated commercial calcines dispersed in aluminum, zinc, tin-lead, tin-antimony, and aluminum-silicon have been prepared at INEL, essentially by the casting techniques described in Section I.C.1. A metal alloy subjected to extensive study consists of ~82 wt % Al, 12.6 wt % Si, and ~6 wt % Cu [BELL-2]. This alloy is reasonably fluid, has a melting point of ~550°C that is lower than that of pure aluminum, and has produced satisfactory metal matrices. Attempts have failed to fabricate waste composites without any particle agglomeration, i.e., by casting with INEL "as produced" fluidized-bed calcine which contains about 30-50 wt % calcine fines (0.03-0.1 mm diameter [BERRETH-2]) and 60-70 wt % bed material (about 0.1-0.4 mm diameter [BERRETH-2]).

Workers at INEL have found, in agreement with those at Eurochemic [VANGEEL-3], that when calcine fines are present in the calcine at concentrations higher than ~10 wt %, casting methods produced nonuniform,* poor-quality composites that are unsuitable [BELL-1, BERRETH-2]. Beds of smaller particles have more surface area and smaller void or pore size. It is believed that the causes of the poor nonuniform composites are the large fraction of smaller particles of fluidized-bed calcine and the lack of sufficient driving forces for the molten alloy to overcome the surface-tension forces that resist flow to fill the void spaces between the individual calcine particles. The difficulty of dispersing "fines" in a metal matrix is consistent with the fact that, in general, metals do not wet oxides; this would make filling of the void spaces between calcine particles more difficult as the fraction of small particles increases. Definitive data that define the range of particle sizes that resulted in acceptable HLW composites are still needed for various casting fabrication techniques. Some examination of the effects of calcine particle size and height of the casting is under way at INEL [BELL-1].

A solution to the "fines" problem, since acceptable particle-size casting criteria are established, may be an agglomeration process to increase the calcine particle size. Workers at INEL are developing a pelletizing (or agglomeration) process and are searching for appropriate solid additives and

*Nonuniform is used to indicate that regions of the composite existed where the metal phase did not penetrate the waste particles, perhaps in part due to metal channeling.

liquid binders with the goal of dispersing the agglomerated calcine in a metal matrix [BELL-1, BELL-3, BERRETH-1, SAMSEL-1]. A 16-in.-diameter commercial disc pelletizer (the same device described in detail by [GARRETT-1 of PNL) has been secured by INEL and is being used to produce granules of ~1-10 mm in diameter [BELL-3, SAMSEL-1]. This pelletizer is also being studied for agglomeration of fluid-bed calcine from military wastes prior to bin storage [SLANSKY-7].

In one pelletizer run the feed consisted of 58.5 wt % bed and 31.5 wt % fines calcine plus 10 wt % metakaolin and a water binder [BELL-3]. Pellets sintered at 600°C had a pellet density of 2.5 g/cm³ and a bulk density of 1.4 g/cm³ (i.e., 44 vol % void space), a slightly lower density than the calcine. In another agglomeration process under active investigation at INEL, ~10 wt % metakaolin is added, primarily to fix after sintering the cesium as CsAlSiO₄, and a 3:1 volume ratio of phosphoric-nitric acid is added as a wet binder to fluidized-bed calcine; this is followed by firing of the agglomerated granules at 200-800°C [SAMSEL-1]. Preliminary data indicate that the leach rate of the stabilized calcine granules after firing at temperatures above 600°C is lowered to the leaching rate range of typical borosilicate glasses ($\sim 10^{-5}$ g/cm²-day). This is several orders of magnitude lower than the leaching rates of untreated calcine. The enlarged stabilized calcine granules (~1-10 mm in diameter) can then be readily embedded in a metal matrix [SLANSKY-4, SLANSKY-5]. Leach rates of aluminum metal-matrix composites of untreated or unstabilized calcine containing <10 wt % fines have been reported as 1×10^{-3} to 4×10^{-4} g/cm²-day at 25°C [BERRETH-2], which is several orders of magnitude lower than leach rates of unencapsulated, untreated calcine. The stabilized calcine granules are in a relatively unleachable form, and the leach rate of a metal-matrix composite is expected to be comparably low.

The extent of reaction of dispersed calcine with the metal matrix is of interest. As a basis for a safety and handling analysis, the extent of thermal contact resistance barriers at the HLW particle/metal-matrix interfaces must be known, as well as 1) pressurization of HLW canisters due to volatile products caused by radiation and reaction products and/or product outgassing and 2) oxidation of the matrix-metal phase which could be accompanied by a loss in mechanical strength and/or leach resistance. Some thermochemistry has been investigated at INEL [SAMSEL-1] using differential thermal analysis (DTA) techniques coupled to a mass spectrometer off-gas analyzer to identify off-gases. The results of one DTA run are shown in Fig. 2. Curve III is for crushed, stabilized calcine granules mixed with aluminum metal powder in a helium atmosphere. No exothermic thermite-type reaction was observed to 800°C, indicating a probable compatibility. However, further testing is required for confirmation [SAMSEL-1].

Some DTA data have been reported for mixtures of untreated calcine and aluminum powder in air [BERRETH-2]. Small exothermic reactions were observed between a simulated commercial (AGNS) calcine and aluminum at temperatures $\geq 830^\circ\text{C}$ (Fig. 3). However, DTA experiments in an argon atmosphere showed even less of a reaction, indicating that an external source of oxygen reacting with the aluminum may have been the cause of the observed reaction. For conclusions to be made, more definitive DTA data will be required, especially with candidate metals other than pure aluminum.

Fig. 2. Differential Thermograms of Stabilized Calcine. Curve I is for a powdered granule, dried at 200°C, prepared with a phosphoric-nitric acid-metakaolin binder. Curve II is for AGNS bed calcine (+50 mesh) with *in situ* acid binder addition. Curve III is for a powdered granule (the same as in Curve I) mixed with 50 wt % aluminum powder in He [from SAMSEL-1].

Tests have also been made at INEL using powder metallurgical techniques. Untreated calcine was intimately mixed for 1-5 hours with powdered metals (1:1 weight ratio), cold pressed at $\sim 2.8 \times 10^8$ Pa (4×10^4 psi), and sintered in an inert (Ar, N₂) atmosphere for ~ 30 minutes. Powdered aluminum (600-620°C sintering temperatures) and powdered iron (900-980°C sintering temperatures) were each tried [BERRETH-2]. Powdered Zn, Pb-Sn, Al-Ti, and Fe-Ti were also examined. Metal-matrix products using these metals contained between 30 and 80 wt % calcine. The sintered aluminum matrix composites gave values of thermal conductivity that agreed with those obtained with specimens produced by casting techniques. In general, all measured thermal conductivities of metal composites, summarized in Table 1, have been found to be approximately proportional to the percentage of metal phase in the composite. However, more data are required to definitely establish the correlation.

Some preliminary mechanical strength tests of sintered, but not cast, composites indicated that compressive strengths were greater than 2×10^7 Pa (3000 psi), which is comparable to that of concrete. Calcine particle size appeared to have little effect upon density and strength of the composite when this powder metallurgical technique was used [BERRETH-2]. However, the compressive strength was somewhat dependent upon the type of metal employed since iron was $\sim 25\%$ stronger than aluminum in 50 wt % dispersed HLW form phases and 50 wt % metal [BERRETH-2].

Fig. 3. Differential Thermograms of Untreated Calcine in Air. Lower curve is of calcine-aluminum metal mixture; upper curve is of pure powdered aluminum [BERRETH-2].

The leach rate of sintered metal composites placed in 25°C water for 95 hours was $\sim 3 \times 10^{-3}$ g/cm²-day. This is about a factor of ten greater than those of composites produced by casting but a factor of 10-100 lower than that of ordinary untreated calcine. This observation is also consistent with the porosity of sintered metal specimens being greater than that of cast composites. Further improvements in the thermal conductivity, mechanical strength, and leach rate of sintered composites are, in principle, possible by increasing the percentage of metal phase to reduce the amount of particle-particle contact of calcine. However, this would be achieved at the cost of increasing the total waste volume as well as the added expenditure for additional metal. The leach rate can probably be decreased relatively easily by using agglomerated calcine granules in which selected isotopes have been combined with additives to reduce their leachability. The thermal conductivity and mechanical strengths of sintered composites are likely to be sufficient so that probably no improvements in these properties will be necessary.

Another calcine stabilization concept [BERRETH-2, BERRETH-3, SAMSEL-2] being developed at INEL is primarily aimed at decreasing leachability of calcine. The concept seeks to alter the calcine form prior to encapsulation by mixing "glass-making" additives (calcium and sodium borosilicate and aluminosilicate fluxes) with the calcine, agglomerating, and firing at ~ 800 - 1000°C to produce a sintered-glass ceramic product containing 50-67 wt % calcine. This waste form has shown, prior to encapsulation, a cesium leach rate as low as $\sim 10^{-8}$ g/cm² day, four orders of magnitude less than that of untreated

TABLE 1. Thermal Conductivities for Simulated Calcines Encapsulated in Metal Matrices

<u>Dispersed HLW Phase</u>						
Metal Phase	vol %	wt %	<u>Thermal Conductivity^a</u>		Alloy Melting Point, ^b °C	Reference
			Melting Composite, W/m-°C	Pure Alloy, W/m°C		
<u>Cast Specimens^c</u>						
60% Pb, 40% Sn	~70 ^d	---	4.5 (150°C)	---	~240	DEMIER-2 BARTON
100% Sn	~70 ^d	---	13.8 (40°C)	59	232	DEMIER-2 BARTON
97.5% Pb, 2.5% Sb	~65 ^e	---	12 ^f	30	326	VANGEEL-1
84% Pb, 12% Sb, 4% Sn	~60 ^d	---	10 ^f	24	239	VANGEEL-3
90% Pb, 10% Sn	~70	---	g	36	~300	VANGEEL-3
88% Al, 12% Si, <0.7% Fe	~66 ^e	---	32 ^f	168	575	VANGEEL-3
100% Zn	---	42.5 ^h	23 (200°C)	110	420	BERRETH-2
96% Zn, 3.9% Al, Trace Cu, Mg	~70	---	g	113	385	VANGEEL-3
<u>Sintered Specimens</u>						
Al	---	50 ^h	36 (200°C)	209	660	BERRETH-2
Fe	---	50 ^h	10 (200°C)	63	1536	BERRETH-2

^a1 W/m°C = 0.578 Btu/hr.ft.°F.

^bThe phase diagrams of M. Hansen in *Constitution of Binary Alloys* (McGraw-Hill Book Company) provide information on melting points for other compositions.

^cThe alloy compositions are wt %.

^dDispersed phase was primarily Al₂O₃.

^eDispersed phase was LOTES granules [VANGEEL-5].

^fTemperatures of thermal conductivity measurements were not given.

^gNot reported.

^hDispersed phase was primarily simulated ZrO₂ calcine, typical of military fuel wastes.

calcine/metal-matrix composites [SAMSEL-2]. It is also reasonably hard, intrinsically strong, and resistant to thermal shock when compared to glass. The thermal conductivity of the ceramic waste form is intermediate between that of glass and calcine so that a metal matrix is still required with it to avoid high centerline temperatures if short-cooled wastes are used. Encapsulation of a sintered-glass ceramic waste form in a metal phase having low corrosion rates provides another technique for producing a very good waste form, if the method of producing the sintered glass ceramic can be kept simple. This encapsulation concept has been demonstrated on a laboratory scale [ANL-77-36] and sintered-glass ceramic waste forms have been produced [BERRETH-2, BERRETH-3, GARRETT-1, SAMSEL-2].

2. PNL-Battelle Pacific Northwest Laboratories (General Electric)

Early work on metal-matrix waste encapsulation was also reported by Hanford workers [DEMIER-1, DEMIER-2, BARTON] who described studies in 1959-1960 using a simulated calcine waste dispersed in Al, Zn, Cd, Zn-Sn, Cd-Sn, Sn, Pb, and Pb-40 wt % Sn. These early encapsulation techniques consisted of first prefilling a steel tube with the simulated calcine, immersing one tube end in a container of molten metal or alloy, filling the void spaces between calcine particles with the molten metal (using either vacuum or pressure differences across the tube), and then allowing solidification to occur. A wire mesh was used to retain the calcine particles during the filling operation; this is essentially the same concept as is described in more detail in Section I.C.1.

Qualitative conclusions from these early studies [DEMIER-1, DEMIER-2, BARTON] were that Sn and Pb-40 wt % Sn produced satisfactory calcine/metal-matrix composites. At the casting temperature employed, the other metals or alloys either would not flow into void spaces between the calcine particles (particle size distribution not given) or would react excessively with the simulated calcine (with subsequent outgasing). All but Sn and Pb-40 wt % Sn resulted in poor and visibly nonuniform calcine-metal matrices. Thermal conductivity values (Table 1) for Sn and Pb-Sn metal matrices were measured and are consistent with more recent Eurochemic data [VANGEEL-3] for similar alloys. No data obtained with radioactive materials were found in this early work.

During the current AEC/ERDA Waste Fixation Program at Battelle (PNL), begun in 1973, there has been renewed interest in the metal-matrix encapsulation of commercial waste. Current examinations have been limited to nonradioactive materials. Initially, simulated calcine coated with pyrolytic graphite was embedded [GRAY-1, GRAY-2] in an aluminum matrix, using a tube-casting method as described above. More recent work [SUMP-1, SUMP-3, SUMP-4, MCELROY-6, MCELROY-7, MCELROY-8] has employed casting of aluminum (at $\sim 700^\circ\text{C}$), lead (at $\sim 400^\circ\text{C}$), or manganese-bronze (at $\sim 950^\circ\text{C}$) with simulated calcine (Al_2O_3) and 1 1/2-mm borosilicate glass beads; manganese-bronze was selected because of its potential high resistance to water corrosion. Lead casting composites were fully penetrated with lead. The higher casting temperatures of $700\text{--}750^\circ\text{C}$ used for aluminum composites caused some softening of the glass, as well as some glass-aluminum reaction [SUMP-3].

In-canister gravity sintering (see Section I.C.2) [SUMP-1, SUMP-2, SUMP-3] is a powder metallurgical technique under active laboratory-scale investigation at PNL. Specimen sizes have generally been 2 1/4 in. OD x 3 1/2 in. long. Metal-matrix composites of iron, copper, bronze, brass, and various steel alloys have been gravity sintered. Stainless-steel powder and the gravity sintering method are expected to receive the most attention in the near future [SUMP-1, SUMP-2, SUMP-4]. In gravity sintering studies, only Al_2O_3 has been used as a simulated HLW. Only observations from visual examination have been reported, not detailed data on thermal conductivity or leach rates of metal-matrix composites produced by either casting or gravity sintering. The most current progress report [MCELROY-8] indicates mechanical impact testing has begun.

Work on calcine agglomeration techniques using a disc pelletizer or agglomerator [GARRETT-1] and a fluidized bed [GRAY-3] has been reported. Both techniques were aimed at producing HLW particles with a satisfactory intrinsic strength and size for coating application and handling, prior to encapsulation in a metal matrix. The optimum operating parameters of the 16-in.-diameter disc pelletizer are being determined for different feed materials [GARRETT-1]. Additions of up to ~50 wt % glass frit to simulated calcine (Types PW-4-b and c), using water as a binder, have produced granules with sufficient green strength for transfer to a sintering process. Sintering at 650-1000°C has produced very good waste forms (~1-3 mm diameter) for subsequent coating application [GARRET-1, GARRET-2]. These sintered glass ceramic waste forms are expected to exhibit a good leach resistance and can be directly encapsulated in a metal-matrix composite to produce suitable waste forms. Studies are planned characterizing the properties (*i.e.*, strength, porosity, leach resistance, *etc.*) of these waste granules before and after coating and encapsulation on a metal matrix [CHIKALLA].

A fluidized-bed agglomeration technique [GRAY-3] that has been demonstrated consisted of adding a small amount of a sodium silicate binder solution to a slightly fluidized bed of spray calcine powder (size distribution ~1-10- μm diameter) at 200°C. Agglomerated granules of ~150 μm were obtained and were subsequently coated with 1 μm of nickel.

Work using cold pressing and extrusion of simulated calcine (PW-7a) has been reported [ROSS-2]. In this concept, up to ~40 wt % glass frit was mixed with a liquid HLW sludge that had been denitrated (*e.g.*, with formic acid). Denitration is a prerequisite in order to prevent excessive surface deposits of friable soluble nitrate salts after sintering. The mixture is either extruded and chopped into pellets or cold pressed and then sintered at ~900°C. Problems with excessive cracking have been encountered during the sintering or drying stage for extruded calcine mixtures. Only very little data on the physical properties have been reported to date [ROSS-2].

Currently, [CHIKALLA] at PNL is investigating a "multibarrier" concept of waste management. This is illustrated in Fig. 4 [MCELROY-1]. The first barrier would be achieved by producing thermodynamically stable crystalline

Fig. 4.

Multibarrier Waste
Form [MCELROY-1].

phases of certain toxic waste elements by modifying the normal calcination operation. For example, addition of chemicals to HLW solution prior to calcination can produce a "supercalcine" with a low leach rate [MCCARTHY]. "Supercalcine" (or calcine) would then be agglomerated into granules and sintered in order to make the powder less dispersible. A glass frit might be added to ordinary calcine at the agglomeration stage as an alternative to producing supercalcine in order to increase the leach resistance and hence form a barrier against dispersal. The second barrier would be the application of an impermeable coating (*e.g.*, Al_2O_3 , Ni, SiC, SiO_2 , Cr_2O_3 , Cr_7C_3 , and/or pyrolytic graphite) on each waste agglomerated granule. A summary of the coatings under development has been given [GRAY-4]. These coated pellets would then be placed in a metal matrix that would serve as a third barrier and provide impact resistance against dispersal. The outer canister wall would serve as a fourth barrier.

The multibarrier concept has been introduced to obviate any leach or dispersal problems and to provide adequate thermal conductivity and shock resistance. Experiments to obtain leach rate, thermal conductivity, and mechanical shock resistance data are in progress [CHIKALLA, MCELROY-6, MCELROY-7, MCELROY-8]. Gravity sintering (or vibrator compaction) and casting fabrication techniques are being examined. It should be noted, however, that a gravity sintering process is unlikely to produce a high-density metal matrix, and only 30-65% of the theoretical density is expected [SUMP-1]. The residual porosity can provide a pathway for leaching due to interparticle contacts. Metal-matrix waste composites containing rather nonleachable waste forms (*e.g.*, coated particles, "supercalcine") are likely to be required if it is desired to use gravity sintering to produce final composite waste forms with a low leachability. Composite fabrication by casting (*i.e.*, less porosity) may not require dispersed waste forms with as low a leach rate in order to achieve a comparable composite leach rate.

4. EUROCHEMIC - Mol, Belgium

Calcine and phosphate glass beads, including radioactive glass beads, have been embedded [VANGEEL-1, VANGEEL-2, VANGEEL-3, VANGEEL-4, VANGEEL-5] in various metals and alloys. By a process called the LOTES process [VANGEEL-5], simulated calcine has been produced in a modified fluidized-bed or stirred-bed reactor as a conventional oxide. The LOTES process involves the conversion of nitrates into phosphates prior to solidification and subsequent calcination in a stirred-bed reactor. The LOTES process results in a phosphate-based product with particle sizes up to ~ 3 mm, larger by factors of ~ 30 -100 than INEL fluidized-bed oxide calcine and with leach rates of cesium and strontium lower by factors of $\sim 10^3$ [VANGEEL-5]. The larger particles are primarily due to the much lower fluidizing velocities of a stirred-bed reactor and can be directly encapsulated in a metal matrix. Phosphate glass beads of ~ 5 -mm diameter encapsulated in metal composites have also been produced using the PAMELA process [HEIMERL, VANGEEL-1]. Successful radioactive runs have produced ~ 8 kg of phosphate glass beads containing HLW fission products with an activity totaling $\sim 4 \times 10^4$ curies. Pilot-size lead alloy composites containing about 5 kCi of fission products in the glass beads have been prepared [VANGEEL-1].

Eurochemic's casting method is slightly different from INEL's casting method. Details are given in Section I.C.1. Alloys that have been tested include (wt %): 90 Pb - 10 Sn; ~ 95 Zn - 4 Al - 1 Cu - 0.03 Mg; 87.3 Al - 12 Si - 0.7 Fe; 97.5 Pb - 2.5 Sb; 84 Pb - 12 Sb - 4 Sn, with the latter three used more commonly [VANGEEL-3]. Thermal conductivities (Table 1) of waste-metal composites using the aluminum or lead alloys are higher by factors of ~ 30 and ~ 10 , respectively, than the thermal conductivity of glass (~ 1 W/m°C). Glass typically has three to four times higher thermal conductivity than does untreated calcine. Preliminary leach tests of LOTES granules dispersed in the lead alloy indicated leach rates of $\sim 10^{-6}$ g/cm²-day for cesium and strontium, which is much lower than for untreated calcine. Cylindrically shaped metal-matrix composites (cold runs) of up to 15-cm diameter by 50 cm have been produced [VANGEEL-3].

The process currently being studied at Eurochemic involves the continuous vitrification of the high-level liquid waste to phosphate glass beads, followed by incorporation of these beads into a lead metal matrix [VANGEEL-1, VANGEEL-3]. The product is referred to as a "vitromet" and the process as PAMELA [VANGEEL-1]. The phosphate glass beads containing ~ 30 wt % fission product oxides are produced at 1000°C. The beads are formed by dropping molten glass onto a rotating, cooled, stainless steel disc. The beads are about 5 mm in diameter and have an initial leach rate of about 3×10^{-5} g/cm² day. The beads have been incorporated into a molten metal alloys (e.g., 84 wt % Pb, 12 wt % Sb, and 4 wt % Sn) which were maintained about 50°C above its melting temperature. For lead alloys, this is sufficiently below the softening temperature of the phosphate glass (400°C) that no deformation of the beads was observed. This composite (70% glass, $\sim 30\%$ metal) was then solidified into the "vitromet" block as a final waste form.

The final lead composite has some self-shielding (estimated to be >90% for 600 keV photons in 50-cm-diameter vitromets [VANGEEL-1]) and has excellent mechanical stability. The leach rates ($\sim 10^{-5}$ g/cm² day) of the "vitromets" are essentially the same as for phosphate glass beads [VANGEEL-1]. However, the surface area of the waste form available for leaching is greatly reduced, and the primary area exposed is the lead alloy rather than the waste. Long-term product behavior studies are in progress to evaluate the chemical compatibility of a canister and vitromet, mechanical properties, radiation damage, corrosion resistance, and leach resistance [VANGEEL-1].

Some preliminary details of these tests have been reported. For example, preliminary data (Table 2) on tensile strengths, charpy impact values, and compression strengths indicate that a vitromet has a better mechanical stability than does a glass monolith. In drop tests (from ten meters), canisters of a glass monolith suffered severe fracturing while the vitromet showed no cracks [VANGEEL-1]. The ductile lead thus absorbs much of the impact energy and would contribute to decreasing the dispersibility risks. Preliminary leach-rate data indicate that cesium and strontium are each preferentially leached out of phosphate glass beads at a rate of $\sim 10^{-5}$ g/cm²-day. The corrosion rate of a pure lead-alloy matrix is approximately the same as that of the phosphate glass beads. It is tentatively concluded that corrosion resistance of the vitromet is governed by the matrix material and not by the dispersed granules [VANGEEL-1]. This may be in disagreement with the early cursory experiments in Idaho [WILDING] using composites that consisted of aluminum and ¹³⁷Cs tracer in simulated calcine. Limited compatibility tests using an electron microprobe and X-ray spectrometry of the lead metal matrix and glass beads interface have revealed no appreciable reaction. Some diffusion (~ 40 μ m) of lead into the glass beads was detected when held for <72 hours at 50°C above the melting point of lead but is not considered serious. No cracking of the glass beads was observed because lead contracts less upon solidification than do the glass beads (Table 2). Glass beads were recovered from composites by heating the vitromet slightly above the melting point of the lead and allowing lead to drain away. Radioactive damage studies of phosphate glass beads using ~ 4 Ci of ²⁴²Cm/g have been started [VANGEEL-1]. Thus metal encapsulation of glass beads in lead alloys appears to be a plausible waste solidification alternative for which much experience has been acquired in the past several years, including some radioactive pilot testing.

C. Metal-Matrix Fabrication Techniques

1. Casting Techniques

Two different techniques have been successfully employed to disperse solidified high-level waste into a metal matrix. A method used by U.S. researchers is shown in Fig. 5 [BERRETH-2]. This method has also been tested by Eurochemic [VANGEEL-3]. A high-level waste canister is first filled with granular, solidified waste such as calcine. The canister and its contents are then heated to approximately 50°C above the melting point of the alloy being used, air is evacuated from the canister, and the molten alloy at approximately 50°C above its melting point is introduced into the evacuated canister through a tube. The molten alloy flows into the packed bed of waste

TABLE 2. Some Mechanical Properties of Glass Beads, a Matrix Alloy and a Metal Matrix Composite [from VANGEEL-1].

Material	Tensile Strength, kg mm ⁻²	Compression Strength, kg mm ⁻²	Charpy Impact, kg cm ⁻²	Elasticity (Modulus), kg cm ⁻²	Expansion Coefficient, °C ⁻¹
Vitromet ^a	0.4	230	0.43	---	28.8·10 ⁻⁶
Phosphate Glass	---	~8	---	665	1.1·10 ⁻⁵ (<400°C) 4.0·10 ⁻⁵ (>400°C)
Lead-1% Sb	2.4	300	4.3	1500	28.8·10 ⁻⁶

^aVitromet consists of phosphate glass beads dispersed in a lead-1 wt % antimony alloy.

granules and fills the interstices with metal phase. A wire mesh or screen is used to prevent the waste granules from floating prior to solidification of the molten alloy. The alloy is allowed to solidify, forming a metal-matrix waste form inside a container that serves as the primary canister during storage. Since the metal phase only fills the void spaces of the bulk granules, the increase in volume over the volume of the packed calcine granules alone is minimal. This report assumes that there is no increase.

A slightly different technique has been developed by Eurochemic [VANGEEL-1, VANGEEL-3] and is shown in Fig. 6. In this method, the canister is first filled with the alloy at ~50°C above its melting point. Solidified waste granules or glass beads are then pneumatically transported via a central tube into the waste canister containing the molten alloy. An inert gas (argon or nitrogen) purge is used to force the granules through the tube, away from the bottom of the submerged central tube, and into the molten alloy. The granules or glass beads are generally less dense than the alloy and rise through the molten metal until retained by the wire mesh in the upper part of the canister. The displaced alloy is recovered for use in the next canister. This technique may help eliminate the possible requirement that HLW granules be force-cooled when they are transferred into a canister prior to addition of the metal alloy.

It is not possible to disperse untreated or as-produced fluidized-bed calcine by either of these two casting techniques [BERRETH-1, BERRETH-2, VANGEEL-3]. Also, if more than approximately 10 wt % of the calcine consists of fines (*i.e.*, particles with diameters of ~0.03-0.1 mm), neither casting technique consistently yields a uniform waste composite. The failure is generally attributed to the poor wetting of the granular oxide by the molten alloy. Penetration of the bed of granular solid calcine waste by the molten alloy becomes increasingly more difficult as the waste particle size is reduced. When the molten alloy does not uniformly fill the entire bed of calcine, a waste form of unpredictable and variable thermal conductivity, leach rate, and mechanical strength results.

Fig. 5. Conceptual Process for Molten-Metal Matrix Formation [BERRETH-2].

The technical solution that results in acceptable products from either casting process is the use of a large fraction of larger (0.1-10 mm) solidified waste granules. The fluidized-bed calciner used at INEL produces waste granules containing ~50 wt % fines (0.03-0.1 mm) with only ~50 wt % of the granules large enough (0.1-0.4 mm) to cast directly [BERRETH-2]. Eurochemic has produced acceptable waste forms with 1-5-mm-diameter granules. More experimental data are needed to define which range or distribution of HLW sizes is castable. Efforts at INEL and PNL are aimed at introducing an additional process step of particle agglomeration after calcination in a standard fluidized-bed or spray calciner. A conceptual flowsheet of an encapsulation process is shown in Fig. 7 [MCELROY-1]. Untreated calcine is fed into a particle agglomerator (pelletizer) where a binder and stabilizing

Fig. 6. Technique Developed at Eurochemic to Incorporate Vitreous Granules into Molten Lead Alloy [VANGEEL-3].

Fig. 7. Conceptual Metal-Matrix Process [MCELROY-1].

additives (*e.g.*, phosphoric acid and metakaolin) are added. The agglomerated waste granules ($\sim 1-10$ mm) are then added to the casting container for further stabilization, *i.e.*, removal of the binder, residual nitrates, and volatiles by heating. The stabilized granules are then encapsulated in metal as previously described. Additional details are given in Section I.B.2.

Efforts with a calcine waste form at Eurochemic are directed at modifying the calcination process itself in order to reduce the fraction of small particle sizes produced. Stirred-bed reactors that employ lower fluidizing velocities and hence less particle attrition are being examined [VANGEEL-3].

Some scouting casting experiments using a modified version of the INEL and Eurochemic casting techniques with pure lead have been performed at ANL [ANL-78-11, ANL-77-36]. The major objective was to produce a waste composite in which an outer layer of pure metal, or a protective metallic envelope, isolated the outermost waste granules from the canister wall. The protective envelope can serve as an additional protective barrier to retard dispersibility (1) by leaching if a relatively corrosion-resistant alloy is used and (2) by mechanical shocks due to impacts in event of a breach (*i.e.*, corrosion or mechanical) of the primary HLM canister.

In the ANL experiments [ANL-77-36], both agglomerated calcine (simulated with 1-4 mm diameter Al_2O_3 pellets) and borosilicate glass beads were dispersed in pure lead matrices. Thin-walled stainless steel beakers, prefilled with solid lead, were used to simulate a high-level waste canister. A (1 mm by 1 mm) stainless wire mesh was formed into a cylindrical basket smaller than the beakers. Granules or glass beads were placed in the baskets and the baskets were closed. The lead-containing glass beads and a 2 1/2-in.-OD by 2 1/2 in.-long casting containing Al_2O_3 pellets dispersed in a lead matrix are shown in Fig. 8. Lead was observed to have fully penetrated the beds of waste forms. The protective annulus that would isolate the outermost waste granules or glass beads in the event of a premature canister mechanical failure or accelerated corrosion is clearly observable. Work is required to establish the dispersed-waste particle-size distribution that can be employed with this technique.

2. Powder Metallurgical Techniques*

In principle, powder metallurgical techniques should be capable of directly incorporating calcine, including the large fines fraction in untreated calcine, into a metal-matrix composite, thereby eliminating a separate agglomeration step. However, other processing steps (*i.e.*, mixing, blending, pressing, sintering) would be required, all of which would add to the complexity of hot-cell operations. Sintering of the composite at a temperature below the melting point of the metal offers the potential of employing higher-melting matrix metals than could be used with casting techniques. For example, if a simple and safe method were available to produce powdered forms of iron from failed contaminated equipment or powdered Zircaloy from cladding wastes, it might be possible to dispose of these waste streams together with the high-level waste. However, an entire process must be evaluated to establish if any net processing simplification can be realized.

For these reasons, potential powder metallurgical fabrication techniques were surveyed. The objective was to identify powder metallurgical processes that are most likely to merit future development if current casting techniques or alloys become inadequate. Details are given in the Appendix.*

Processes or techniques identified as offering various degrees of potential were cold pressing-sintering, cold extrusion-sintering, molding-sintering, vibratory compaction-sintering, hot isostatic pressing, and extrusion. However, all of these methods would require additional development in order to properly evaluate whether or not they could be used to produce

*More details on powder metallurgical fabrication techniques are given in the Appendix.

(a)

(b)

Fig. 8. Sectioned Castings in a Thin-Walled Stainless Beaker of (a) 5-mm Glass Beads and (b) 1-4-mm Al_2O_3 Pellets Dispersed in a Lead Matrix. ANL Neg. No. 308-78-180.

adequate metal-encapsulated waste forms. Processes deemed not appropriate for radioactive hot-cell application were swaging, hot rolling, impact forging, explosive compaction, and drawing.

Battelle Pacific Northwest Laboratories is currently examining the potential of a vibratory compaction technique, referred to as in-canister gravity sintering [SUMP-1]. The technique requires an initial loading of a HLW canister with the waste form (calcine or glass beads) and the addition of metal powders of smaller particle size than the waste forms. A vibratory device is used to assist in packing the metal matrix powder into the void volumes of the bed of waste particles. The compacted powder mixtures of metal and waste form will be ~30-65% of theoretical density, depending upon the effort expended at sizing the metal powder for the sizes of the waste forms. The container then is sealed and sintered at temperatures sufficiently low so that no excessive outgassing of the waste forms occurs. The resulting metal-matrix encapsulated waste forms will be porous but will have been produced by a process that may be readily adapted to hot-cell application. Note, this fabrication process has some of the same concepts as used in the in-can glass-making process [BLAIR] under development at PNL.

Cold pressing and sintering have been examined [BERRETH-2, ROSS-2]. Details of these studies are given in Sections I.B.2 and I.B.3. Also examined was cold extrusion and sintering (1/2-in.-diameter bodies) of mixtures of denitrated calcine and glass frit [ROSS-2]. In the first experiments, excessive cracking during the sintering process was identified as a problem to be solved. However all of these concepts were limited to small-scale (perhaps only scouting type) experiments such that much yet remains unknown about their potential applicability.

3. Comparison of the Casting and Powder Metallurgical Techniques

The combination of a calcine stabilization-agglomeration process and a casting technique employing low-melting alloys (*e.g.*, lead, aluminum) appears to be the most straightforward process for the encapsulation of high-level radioactive waste into a metal matrix. Further demonstration of the agglomeration or granulation process for calcine, resulting in a simultaneous improvement in the leach rate (*i.e.*, lower leach rate) of the waste forms after sintering, is still required. The agglomeration step is required to increase the calcine particle size (*i.e.*, decrease the fines fraction of the waste to ~10 wt %) so that the casting techniques will produce uniform waste composites. A low leach rate of the waste forms may be required to maintain a satisfactory leach rate of the composite after fabrication if it is found that the leach rate of the composite is in part controlled by the point contacts of individual waste granules in a bed of waste granules. Interconnections could provide a mechanism for high leach rates after casting (see Section I.C). Glass beads are initially a low-leach-rate waste form and should be directly dispersible into a metal matrix with no major problem, once they are made.

A potential problem with casting of a metal is shrinkage during solidification. This can result in the formation of interconnected shrinkage cavities around the waste particles which could increase the susceptibility to leaching as well as affect the mechanical strength. Shrinkage causing fracturing of brittle dispersed waste forms may be possible too. The

possibility that a small gap might form between the metal-matrix composite and the inner canister wall due to shrinkage also exists. This gap could produce a thermal contact resistance problem. The effect and extent of shrinkage of cast metal alloys will have to be examined further.

Powder metallurgical fabrication techniques depend upon the particular process being considered, but all appear to require much more extensive development to be workable than do the agglomeration-casting fabrication techniques. For example, there will be porosity in cold-pressed and sintered pellets of waste composites. Although it may be possible to limit this porosity, especially with liquid-phase sintering, this needs exploratory research. The large fraction of calcine fines should pose no insurmountable problems. Proper blending can result in the calcine particles being surrounded by matrix metal, although blending techniques applicable to hot cells will probably require some development.

Hot isostatic pressing of calcine-metal matrices appears to be a potentially useful concept. Leaching of the product would be more restricted than in products of other powder metallurgical techniques due to the additional densification obtained by pressing. This would be especially true if nickel or copper is used as a matrix metal and a nickel can is used during the hot isostatic pressing step, thereby bonding the corrosion-resistant can (required in the hot isostatic press operation) to the matrix. Such a composite could effectively increase the time until water would have access to the high-level waste composite, *i.e.*, the can would have to corrode first. In order to minimize the number of steps, development studies would have to be concerned with designing good tolerances of the can to cermet body during fabrication to permit direct loading into high-level waste canisters. However, adaptation of hot isostatic pressing equipment for use in hot cells needs extensive examination.

It is our opinion that encapsulation of solid-waste forms in a low-melting, relatively corrosion resistant, alloy-utilizing metal-casting technique offers the most direct route for demonstrating metal encapsulation as a viable waste-solidification alternative. The major process steps (*i.e.*, agglomeration, sintering, casting) have had various degrees of examination so that estimates for the potential application to hot-cell operation requirements could probably be made. In fact, Eurochemic has even demonstrated a casting concept with radioactive phosphate glass beads in a remotely operated casting process [VANGEEL-1].

D. Mechanical Strengths of Metal-Encapsulated Waste Forms

1. Introduction

Reasonable mechanical strength of HLW forms is a desirable safety feature to mitigate the consequences of accidents during the transportation and handling of HLW canisters. The maintenance of the integrity of the waste form under normal and accident conditions should reduce the likelihood that small particles of waste would form and represent a risk of dispersion by both hydraulic and aeolian means. However, once the high-level waste form is isolated in a geologic formation, mechanical strength is of much less importance since the geologic formation assumes the role of container and acts to retard dispersal to the environment. Transportation accidents probably

represent the greatest risk for a release of radionuclides to the population [NUREG]. Arguments favoring good mechanical strength are probably strongest for scenarios of the transportation of HLW from interim storage to the final Federal repository.

Metal encapsulation of HLW (as calcine or glass beads) can result in increased mechanical strength. Limited data on the improvements have been obtained by INEL for some calcine specimens encapsulated in sintered iron and aluminum composites [BERRETH-2]. The data showed that iron composites, on a relative scale, may be slightly (~20%) stronger than aluminum. No absolute mechanical compressive strengths were obtained. However, compressive strengths of sintered composites, which were slightly greater than that of concrete, depended upon the fraction of calcine in the total composites, decreasing as the fraction of metal decreased. The particle size of calcine appeared to have a negligible effect on the strength or final density of the composites. Idaho Nuclear Engineering Laboratory has not reported detailed data on cast specimens, but did report that calcine fines concentrations above 10 wt % weakened metal-encapsulated waste forms, probably by restricting the flow of the metal phase into the bed of calcine during fabrication [BERRETH-2].

Some preliminary Eurochemic data (Charpy impact values, tensile and compression strengths) of glass beads dispersed in a lead alloy (vitromet) have been given in Table 2 [VANGHEEL-1]. These data showed that lead metal-matrix/glass beads had a higher mechanical strength than a corresponding phosphate glass monolithic block (Table 2). A qualitative example was also given. A 10-meter drop test of high-level waste canisters with glass beads dispersed in a lead alloy did not produce any cracks, probably due to the ductility of lead. Under the same test, glass monoliths suffered severe fracturing due to their brittle nature [VANGHEEL-1]. More quantitative data on fracturing of borosilicate glass monoliths during mechanical impacts have been reported [SMITH].

2. Conclusions

Definitive data do not yet exist on the mechanical strength of metal-encapsulated waste forms. The ductility of the metal phase should allow some impact shock energy to be adsorbed, with a corresponding reduction in the extent of fracturing. A method of testing glasses and concrete forms of military waste sludges for impact strengths has been described [WALLACE-1], but none exist for metal-matrix composites. Criteria for testing of waste forms will have to be developed in order to establish a relationship between strength and safety.

E. Chemical Reactions Between HLW Forms and Metal Matrices

1. Introduction

Chemical stability of HLW forms is desired in order to predict the physical properties of waste forms during all storage time periods of interest. Reactions between the metal matrix and the waste form are not desirable; such reactions could lead to excessive pressures from 1) a gaseous reaction product or 2) vapor formation because of an excessive heat release. Reactions could also lead to chemical changes of the waste form, producing excessive amounts of leachable components, a weakening of the mechanical strength, or a major

change in heat transfer properties. If reaction rates remain unknown, accurate predictions can be made of the dispersal of waste to the environment for different geologic transport models.

Only very limited data exist for the reaction of calcine with metal alloys. Thermodynamically, Al_2O_3 is more stable than many fission product oxides in the calcine. Hence a potential for a thermite-type reaction exists at the interfaces of the calcine and aluminum matrix. Some differential thermogram data exist [BERRETH-2, SAMSEL-1] for the interaction of aluminum metal powder and simulated calcines in air and inert atmospheres. The data are given in Fig. 2 and 3. These were obtained by heating mixtures of calcine and powdered aluminum metal. A small exothermic reaction (Fig. 3) was observed to occur at about 830°C [BERRETH-2]. Differential thermograms in inert atmospheres did not show an exothermic reaction. This indirectly implies that a source of oxygen may have been the cause of the former reaction. The direct applicability of these data from high-surface-area metal powder to cast aluminum-calcine composites needs further examination. A preliminary conclusion is that air storage of aluminum metal composites at temperatures restricted to less than 550°C may be safe [BERRETH-2]. However, it is clear that more definitive data need be obtained since a mixture of aluminum metal and fission product oxides is thermodynamically unstable, like glass. No chemical reaction data for lead alloys and calcine were found. Lead is not *a priori* expected to be reactive with calcine but this needs to be examined.

Testing of chemical stabilities with metal matrices of phosphate glass beads and lead alloys has been reported [VANGEEL-1]. Electron microprobe and X-ray analyses of the glass-metal interfaces have shown no significant chemical reaction for rather short 72-hour exposures at temperatures of approximately 380°C . Some diffusion of lead into the glass to a depth of about $40\text{ }\mu\text{m}$, but not vice versa, was observed at the interface. However, the glass constituents remained homogeneous for the duration of the test, and the preliminary conclusion is that there will be no problems. Further testing with much longer exposure times is required, and this is believed to be in progress [VANGEEL-1].

2. Conclusions

Preliminary data have indicated a measurable reaction rate between aluminum and simulated calcine. The corresponding study on lead-glass showed little, if any, interaction. Examination of the chemical reactions between agglomerated calcine (containing additives) and aluminum metal has been reported. The thermodynamic instability of a system of calcine and aluminum may prevent the use of aluminum as a matrix material, but more definitive data establishing the reaction rate at the waste-aluminum interface should be obtained as early as possible so that alternative metals or alloys, if necessary, can be emphasized. Data given elsewhere in this report indicate that lead should be a leading candidate metal. Interactions of lead alloys and calcine at the interface should be examined.

F. Radiation Stability of HLW Forms Encapsulated in Metal Matrices

1. Introduction

High-level waste is a source of very intense alpha, beta, gamma, and neutron radiation due to the concentration of decaying radionuclides. In most metal encapsulation development programs, fabrication techniques and product characterization are being examined using inactive simulated high-level waste forms. Depending upon future HLW criteria, studies of the effects of radiation damage in the HLW forms may be required to prove the concept of metal encapsulation. Radiation damage could cause energy storage in a waste composite, buildup of helium pressure as the actinides decay, and the swelling of a metal matrix--possibly accompanied by a loss of mechanical strength or breach of the outer HLW canister.

Radiation can cause energy to be stored in solids (including high-level waste). It would be undesirable for stored energy to accumulate at low storage temperatures (*e.g.*, during interim water basin storage) and to be suddenly released (causing dispersal of the waste) with a change in storage temperature or conditions (*e.g.*, during transport to a geologic site). A recent report [ROBERTS] concluded that there is probably no serious energy storage problem for high-level waste in the form of a borosilicate glass, calcine, calcine embedded in aluminum oxide particles, or calcine fused with silica. No studies have been done of the metal matrix-encapsulated waste, but metals themselves are not expected to be a source of stored energy.

The effect of an internal pressure buildup in either a high-level waste composite or a canister due to helium (from decaying isotopes) or out-gases (from residual nitrates or water) released as a function of time should be considered. Some data on these phenomena has appeared for borosilicate glasses [TURCOTTE] and calcine [RINDFLEISCH], but no data have been reported for metal matrix composites. Lower maximum temperatures and lower temperature gradients will exist in metal matrices, both of which may slow diffusional release mechanisms. It is noted that for small glass beads or small granules of calcine dispersed in a metal matrix, diffusion lengths for helium to reach a free surface are shorter than with monolithic waste forms. Metal matrices (*e.g.*, lead alloys) may be ductile enough to absorb any increased stress due to the formation of helium bubbles at the waste-metal interface as the actinides decay. Metal matrices are thus expected to reduce fracturing and hence not increase the surface area, as has been observed in large glass monoliths after pressurization by helium [NEWMAN].

2. Conclusions

No definitive data concerning radiation stability for metal-encapsulated waste forms have been reported. Efforts at INEL and PNL have been limited to inactive, simulated calcine. Studies with radioactive phosphate glass beads encapsulated in lead are in progress at Eurochemic [VANGHEEL-1]. Data of this type will be needed to evaluate the long-term behavior of metal-encapsulated HLW forms. Radiation studies have a lower priority than do the development of fabrication techniques and the characterization of waste composites for mechanical strength, leach rate, and chemical interactions.

G. Leachability of High-Level Waste Forms*

1. Introduction

Ultimately, decisions involving the final disposal or isolation of high-level waste (HLW) from commercial fuel reprocessing are likely to include consideration of the dispersibility of the final solid waste form. Leaching of nuclides from waste is an important mechanism of potential dispersal to the biosphere. Low leach rates are necessary when there is any reasonable probability that water will contact the waste material. Extremely low leach rates could prevent moving groundwater from exceeding the maximum permissible concentration levels for the radionuclides present if water should ever contact the waste. The alternative, proving that it would be impossible for the water to contact the radioactive species, seems unachievable. Waste forms that are relatively inert to groundwater but may be dissolved by simple but aggressive chemicals appear to possess useful properties for final disposal.

No material is absolutely insoluble. The concentration of radionuclides in, for example, drinking water is one measure of solubility. Thus, an acceptable degree of waste fixation might be said to exist if the concentration of a specific radionuclide in the leaching medium never exceeds the maximum permissible concentration [MPC] in drinking water for that radionuclide. A maximum permissible leach rate (MPLR) of a solid has been defined [BARNEY] as follows:

$$\text{MPLR} = \frac{\rho}{\sum_i \frac{[K_i]}{[\text{MPC}]_i}} \left(\frac{F}{A} \right) \quad (1)$$

where: ρ = density of the solid (kg/m³)
 $[K_i]$ = concentration of component i in the solid (Ci/m³)
 F = flow rate of the water (m³/sec)
 A = surface area of the solid (m²)
 $[\text{MPC}]_i$ = maximum permissible concentration of i in water (Ci/m³)

The [MPC] in curies per liter for some typical radionuclides in water [BARNEY] are: ¹³⁷Cs (2 x 10⁻⁸), ⁹⁰Sr (3 x 10⁻¹⁰), and ¹⁰⁶Ru (1 x 10⁻⁸).

From the relationship given by Eq(1), it is possible to devise experiments to determine whether or not specific waste forms have acceptable leach rates. However, it should be noted that flow rates (or the absence thereof) of slow-moving groundwater are often difficult to estimate. Further, the surface area of the waste form may change significantly during the time intervals of concern in these measurements.

Leaching of radionuclides from solid waste forms by water can be examined by laboratory experiments. Many of the reported studies on leaching of waste have employed simulated high-level waste incorporated into glass.

* K. F. Flynn of Chemical Engineering Division, Argonne National Laboratory, Argonne, Illinois, was a major contributor to this section.

Methods for standardized leach-rate determinations have been developed and reported [MENDEL-2]. There is some controversy on the degree to which prolonged and semiautomatic laboratory tests simulate the field conditions, and only a few field studies have been reported [MERRITT]. Mechanisms have been proposed that relate leach rates to established mass-transport theories [GODBEE]. Expressions taking into account diffusion and concentration-dependent dissolution appear to give good agreement with laboratory data. However, the exact mechanisms of leaching remain largely unknown.

Reduction of the concentration of radionuclides along the migration path from the waste to the active biosphere is expected because of radioactive decay and delay of ionic movement by sorption on the geologic environment. Models for such transport have been reported [BURKHOLDER] based on laboratory transport and leach rates. Calculations based on these theoretical considerations indicate that the maximum rate of mobilization of radioactive material will occur when water first contacts the waste form, regardless of the age of the waste or the mechanism of containment failure. Experimental results have largely confirmed this conclusion [BURKHOLDER]. However, models of this type tend to follow a classical approach and to neglect such variables as inter-particle contact, non-constant leach rates, and gradual devitrification. As a result of these limitations, calculations based on mathematical models lead to, at best, qualitative conclusions.

Since the specific conditions present at terminal storage have not yet been defined, it is necessary to determine leach rates under significantly different (laboratory) conditions. The leach rate data accumulated in this fashion are largely of value in making comparisons of various waste forms. The absolute values will need to be established under test conditions bearing more resemblance to the likely repository sites as the latter are defined.

2. Leach Rate Data

Leach rates for non-radioactive simulated waste forms have generally been measured with distilled water at temperatures between 25 and ~99°C. Accelerated leach rates have been determined by crushing the samples and hence greatly increasing the surface area. In very little work with simulated waste forms has the acidity (alkalinity) and/or the salinity of the aqueous leaching media been varied. A relatively large number of solid materials have been studied, including glasses, cements, bitumens, and metal matrices, in order to compare their relative leachabilities. In the case of a metal matrix, it is also necessary to study the corrosion and porosity of the metal in the leachant as part of the overall leachability of this solid waste form. Further application of leach rate data from laboratory measurements to field conditions will require an understanding of the effects of temperature, acidity (alkalinity), and salinity (*i.e.*, ion concentrations) in the aqueous medium as well as temperature, physical structure, and corrosion characteristics of the solid matrix.

A way to view leach rate data is to calculate the time t_n , to leach away a given thickness, Δx , of a waste form. An estimate can be obtained from

$$t_n = \frac{\rho \Delta x}{L} \quad (2)$$

where L is the leach rate, $\text{g/cm}^2\text{-day}$, and ρ is the density of the solid waste form [WALLACE-2]. This expression can be used to estimate the time required for a constant leach rate, ignoring end effects, to leach away a thickness Δx of long cylindrical HLW forms [WALLACE-2]. A plot of this relationship is given in Fig. 9. For example, a 30.5-cm-diameter waste form with a $10^{-5} \text{ g/cm}^2\text{-day}$ leach rate would require $\sim 20,000$ years to be leached away entirely.

For oxide waste forms, cesium and strontium are the most easily leached elements in the radwaste matrix. Hence ^{137}Cs and ^{90}Sr are the radionuclides usually determined in the leachant because they also have relatively long half-lives (~ 30 years). Typically, cesium and strontium are preferentially leached by a factor of 2 to 4 faster with respect to the bulk solid, whereas the transuranic elements are relatively nonleachable [MENDEL-2].

Calcine has a high leach rate compared with borosilicate glass [ORNL]. The leach rate of untreated calcine in a sintered metal matrix (a calcine to metal weight ratio of 1 to 1) is somewhat lower than the leach rate of unencapsulated calcine. The factor of ≥ 20 improvement in the leach rate [BERRETH-2] is low and is attributed to the high probability of particle-particle contact in the metal matrix and the porosity of the matrix, resulting in continuous paths for leaching. The leach rates of unencapsulated calcine can, however, be dramatically reduced by incorporating the calcine into a sintered-glass ceramic material containing up to 67% calcine by weight [BERRETH-3, SAMSEL-2]. Improvement of leach rates by factors of up to 10^6 compared to calcine have been observed [BERRETH-2]. Metal encapsulation of these waste forms should yield significant reductions in leach rates. Attempts have also been made to reduce the leach rate of the calcine by coating the particles with an inert material such as SiO_2 and Al_2O_3 [GRAY-3]. The coated waste particles would subsequently be incorporated into a metal matrix, giving at least two barriers of leach-resistant material. The estimated leach resistance of the coated particles is at least 10^3 lower than that of glass, but cannot be measured above background with the sensitivity of current techniques [CHIKALLA].

The PAMELA process developed by the Gelsenberg Company in cooperation with Eurochemic [HEIMERL] converts the high-level wastes into phosphate glass beads that have an initial leach resistance comparable to a borosilicate glass. The beads are incorporated into a metal matrix (84% Pb, 12% Sb, 4% Sn). This process disperses the low-leach-rate glass beads in the high-thermal-conductivity metal in order to retard or prevent glass devitrification and maintain a desirable solid waste form. The information available in the literature to date indicates that some combination of low leach rate for the waste and high thermal conductivity of the matrix is necessary if low overall leach rates are to be obtained for a metal-matrix product.

Agglomeration of the finely divided spray calcine using commercial-type agglomerators seems to result in substantial improvement in leach characteristics if glass frit is added [ROSS-2]. Work is also being done to improve the leach-rate properties of the calcine by the use of additives prior to calcination [MCCARTHY]. If work of these types is successful and if particle size can be controlled, it may be possible to directly produce an acceptably leach-resistant material for incorporation into a metal matrix without resorting to the high temperatures required for the production of glass.

Fig. 9.

Lifetimes Versus Cylinder Radius
for Various Leach Rates Assuming
a Density of 2 g/cm^3

A compilation of the leach rates of various waste forms is presented in Table 3. A bar graph comparing the principal waste forms is given in Fig. 10. These materials contain from 0-100% waste (e.g., industrial glass vs pot calcine). Leach rates in Table 3 are for both total mass and for specific ions. The lack of clarity in reporting does not always allow identification of what some data represent. Nevertheless, for a given material, the leach rates are in qualitative, order-of-magnitude agreement. These data can be used as a guide for typical leach rates and, if coupled with Eq(2) or Fig. 9, a perspective of the implications of leach rates can be obtained for given materials. For the example of a phosphate glass with 10^{-5} g/cm²-day total mass leach rate [VANGEEL-1], $>10^4$ years (4.1×10^6 days) would be required to leach away an entire 30.5-cm-diameter cylinder. This assumes a constant leach rate and a glass density of 2.7 g/cm³. Meanwhile, many radio-nuclides in the waste would have decayed to non-toxic levels during this time period, mitigating the consequences of leaching.

Fig. 10. Comparison of Leach Rates for Various Waste Forms

TABLE 3. Leach Rates for Various Waste Forms

Waste Form	Leach Rate (g/cm ² day)	Test Conditions	Reference
Pot Calcine	10 ⁻¹	25°C-H ₂ O	[VANGEEL-2]
Fluid Bed Calcine	10 ⁻¹	25°C-H ₂ O	[VANGEEL-2]
Pot Calcine	10 ⁻²	25°C-H ₂ O	[ARH]
Fluid Bed Calcine	10 ⁻²	25°C-H ₂ O	[ARH]
Cement	10 ⁻² -10 ⁻³	25°C-H ₂ O	[MENDEL-2]
Al Metal Matrix-Sintered	3 x 10 ⁻³	25°C-H ₂ O	[BERRETH-2]
Concrete	10 ⁻³	25°C-H ₂ O	[BERRETH-3]
Al Metal Matrix-Cast	10 ⁻³ -10 ⁻⁴	25°C-H ₂ O	[BERRETH-2]
Aqueous Silicates (clay)	10 ⁻⁴ -10 ⁻⁵	25°C-H ₂ O	[BARNEY]
Bottle Glass ^a	5 x 10 ⁻⁵	100°C-H ₂ O	[HEIMERL]
Borosilicate Glass	3 x 10 ⁻⁵	100°C-H ₂ O	[HEIMERL]
Lead Matrix ^a	2 x 10 ⁻⁵	100°C-H ₂ O	[VANGEEL-1]
Vitromet (63 vol % phosphate glass/ 37 vol % lead)	2 x 10 ⁻⁵	100°C-H ₂ O	[VANGEEL-1]
Phosphate Glass	1 x 10 ⁻⁵	100°C-H ₂ O	[VANGEEL-1]
Lead Matrix ^a	7 x 10 ⁻⁶	20°C-H ₂ O	[VANGEEL-1]
Glass (devitrified)	5 x 10 ⁻⁶	25°C-H ₂ O	[KELLEY]
Asphalt	4 x 10 ⁻⁶	25°C-H ₂ O	[MENDEL-2]
Zn Borosilicate Glass (devitrified)	2 x 10 ⁻⁶	25°C-H ₂ O	[MENDEL-3]
Borosilicate Glass (in-can melted)	1.3 x 10 ⁻⁶	25°C-H ₂ O	[BLAIR]
Borosilicate Glass	10 ⁻⁵ -10 ⁻⁷	25°C-H ₂ O	[VANGEEL-2]
Phosphate Glass	10 ⁻⁶ -10 ⁻⁷	25°C-H ₂ O	[MENDEL-2]
Titanates	5 x 10 ⁻⁷	25°C-H ₂ O	[DOSCH]
Alumina Phosphate Glass	5 x 10 ⁻⁷	25°C-H ₂ O	[PAIGE]
Phosphate Glass	5 x 10 ⁻⁷	20°C-H ₂ O	[VANGEEL-1]
Vitromet (63 vol % phosphate glass/ 37 vol % lead)	5 x 10 ⁻⁷	20°C-H ₂ O	[VANGEEL-1]
Zn Borosilicate Glass (as formed)	3 x 10 ⁻⁷	25°C-H ₂ O	[MENDEL-3]
Glass (as formed)	2 x 10 ⁻⁷	25°C-H ₂ O	[KELLEY]
Borosilicate Glass	10 ⁻⁴ -10 ⁻⁷	25°C-H ₂ O	[ERDA]
Silicate Glass (Canadian)	10 ⁻⁶ -10 ⁻⁷	25°C-H ₂ O	[MENDEL-2]
Sintered Glass Ceramics	10 ⁻⁵ -10 ⁻⁸	25°C-H ₂ O	[BERRETH-2]
Industrial Glass ^a	10 ⁻⁶ -10 ⁻⁷	25°C-H ₂ O	[MENDEL-2]
Industrial Glass ^a	10 ⁻⁵ -10 ⁻⁸	25°C-H ₂ O	[BERRETH-2]
Silicate Melts (fired clay)	10 ⁻⁶ -10 ⁻⁸	25°C-H ₂ O	[BARNEY]
Silicate Glass (USA)	2 x 10 ⁻⁷ - 6 x 10 ⁻⁸	25°C-H ₂ O	[MENDEL-2]

^aThese materials are listed for comparison purposes and contain no simulated waste.

3. Conclusions

Conversion of calcined high-level wastes (from fuel reprocessing) directly to a metal-matrix waste form significantly decreases its susceptibility to airborne dispersal but probably does not have a major effect on the leachability of the waste. A significant concentration of waste material in

the metal matrix (*i.e.*, >50 wt %) results in sufficient particle-particle contact so that the particles are no longer isolated from the environment by the metal matrix [BERRETH-2]. The leach rates of metal composites are expected to be significantly improved by decreasing the leachability of the dispersed waste forms prior to metal encapsulation.

II. THERMAL PROPERTIES OF WASTE FORMS

A. Reference Systems

In order to evaluate metal-matrix encapsulation of high-level waste, comparisons with other solids forms are required. Neither the final high-level waste form (*i.e.*, calcine, glass, ceramic, metal matrices) nor the final type of Federal repository (*e.g.*, salt, clay, granite, shale) has yet been specified. Thus many HLW forms and several types of repository sites are the subjects of current investigations. The discussions presented in this report are limited to properties of reference forms of high-level waste. These are calcine, glass, metal-encapsulated calcine, and metal-encapsulated glass beads. Reference properties, as they are currently known, will be assigned and used in subsequent calculations so that consistent conclusions can be made of the advantages and disadvantages of the various reference waste forms.

1. Waste Forms

a. Physical Properties

Calcine, produced by either fluidized-bed or spray techniques, and borosilicate glasses are the two principal forms of high-level waste. Glass is formed by additional processing or treatment of calcine. Typical ranges [ERDA] of values of fission product oxides content, final product volume, density, thermal conductivity, and other properties for a fluidized-bed calcine and a borosilicate glass are shown in Table 4. Reference values selected from these ranges are also shown and are assumed in all calculations requiring such data. A maximum 700°C temperature limit for calcine was assigned by assuming a calcine stabilization treatment of ~700°C [RINDFLEISCH]. A maximum temperature for glass in the range of 500-800°C is probably an acceptable upper limit [ERDA, MENDEL-5], but the maximum temperature for the reference glass was set at 700°C, primarily for calculational convenience. Glass that is encapsulated in metal is assumed to be in the form of beads having diameters of ~1-5 mm.

Metals for encapsulating calcine and glass waste forms will be limited to alloys of lead and aluminum. Lead alloys have lower melting points and thermal conductivities than aluminum alloys. The melting point of a 97.5 wt % Pb-2.5 wt % Sb alloy, 326°C [VANGEEL-1], and of an 88 wt % Al-12 wt % Si alloy [VANGEEL-3], 575°C, are assumed to be typical. To avoid molten phases in metal-encapsulated waste forms, maximum allowable (centerline) temperatures of 300 and 550°C are assigned (Table 4) to lead and aluminum alloys, respectively. Thermal conductivities of 10 W/m-°C for Pb composites and of 30 W/m-°C for Al composites, as previously summarized in Table 1, appear to be representative of experimental data [VANGEEL-3].

TABLE 4. Reference Waste Forms and Their Physical Properties

	Calcine ^a		Glass Monolith ^a		Metal-Encapsulated			
					Calcine		Glass Bead ^b	
	Ranges	Reference	Ranges	Reference	Pb Alloy ^c	Al Alloy ^c	Pb Alloy ^c	Al Alloy ^c
Fission Product Oxides	~100 wt %	100 wt %	20-35 wt %	30 wt %	70 vol %	70 vol %	70 vol %	70 vol %
Additives Content	---	---	80-65 wt %	70 wt %	30 vol %	30 vol %	30 vol %	30 vol %
Volume (m ³ /MTU) ^d	0.04	0.04	0.06-0.08	0.07	0.04 ^e	0.04 ^e	0.1	0.10 ^f
Density (kg/m ³) × 10 ⁻³	2.0-2.4	2	3.0-3.6	3	4.8 ^g	2.2 ^g	5.5 ^g	2.9 ^g
Thermal Conductivity (W/m-°C)	0.2-0.3	0.3	0.9-1.3	1	10	30	10	30
Assumed Maximum Centerline Temperature (°C), T _c	---	700	---	700	300	550	300	550

^aData based on [ERDA]. Ranges shown are for fluidized-bed calcine and a borosilicate glass.

^bGlass bead composites are assumed to be 70 vol % of the reference glass and 30 vol % pore or void space.

^cAlloys are assumed to be 97.5 wt % Pb and 2.5 wt % Sb with a melting point of 326°C [VANGEEL-1] and 88 wt % Al and 12 wt % Si with 575°C melting point [VANGEEL-3].

^dVolume is per metric ton of uranium (MTU) that is reprocessed.

^eThe metal phase is assumed to fill only the void spaces in the bulk calcine so that there is no volume increase for encapsulating calcine in a metal matrix.

^fA porosity of 30 vol % is assumed for a bed of glass beads in order to calculate the volume increase compared to the volume of reference glass (0.07 m³/MTU).

^gCalculated from the assumed fractions of metal and waste phases.

Preliminary data on metal-encapsulated waste forms have shown that the metal phase occupies, or fills, the original void spaces of bulk calcine or glass beads with little increase in the volume [BERRETH-2, VANGEEL-3]. Therefore, metal encapsulation is assumed not to increase the waste volume. In general, beds composed of granular or crystalline materials of a uniform size have porosities of ~ 0.30 - 0.45 [BROWN]. It is assumed that metal-encapsulated calcine or glass beads are 70 vol % waste and 30 vol % metal phase, which is consistent with experimental data [VANGEEL-3, BERRETH-2]. Thus, either calcine or calcine encapsulated in metal matrices has a volume of $0.040 \text{ m}^3/\text{MTU}$.^{*} Metal matrices of glass beads increase the waste volume compared to nonporous glass monoliths to $0.10 \text{ m}^3/\text{MTU}$ because of the assumed 0.30 porosity (Table 4) of a packed bed of beads which is occupied by metal phase. Densities based upon these porosity assumptions were calculated and are shown in Table 4 along with other properties of the reference waste forms.

As shown in Table 4, solid waste forms of either calcine or calcine encapsulated in metal occupy the smallest volume per metric ton of uranium reprocessed at $0.04 \text{ m}^3/\text{MTU}$. Glass monoliths occupy, for the same amount of uranium reprocessed, 1.75 times that volume. Metal encapsulation of glass beads produces the largest reference waste volume per unit of uranium reprocessed--2.5 times the volume for either calcine or metal-encapsulated calcine and 1.4 times the volume for glass monoliths. The waste volume increase for glass monoliths can be regarded as a dilution of the solidified waste due to the addition of glass-forming additives. Glass beads have an additional volume increase due to the porosity of a bed of glass beads.

b. Thermal Heat Generation Rates of Waste

Solidified HLW has a volumetric heat generation rate that depends upon the burnup of the spent fuel that was reprocessed, the age of the waste, and the form of the HLW. The volumetric process heat density (*i.e.*, kilowatts per metric ton of uranium reprocessed) of the HLW has been calculated for various times after reactor discharge, assuming that PWR enriched-uranium spent fuel with a burn-up of 25,000 MWd/MTU at 35 MW/MTU specific power had been reprocessed [KEE]. These results are shown in Table 5. The HLW was assumed to contain 0.5 wt % each of the plutonium and uranium and 0.1 wt % each of the iodine and bromine present in the spent fuel before reprocessing. All of the tritium, xenon, and krypton in spent fuel were assumed to have been removed from the HLW. The reference solidified waste forms production volumes that are given in Table 4 were used to convert the heat generation rate of watts per MTU to kW per m^3 . The latter heat generation rates are also included in Table 5.

A graphical representation of these data is also given in Fig. 11. This shows the relationship of the heat generation rate (in kilowatts) per canister of the reference waste forms as a function of the time since the waste was discharged from the reactor (or the age of the waste) for 30.5-cm (1-ft)-diameter cylindrical waste canisters filled to a height of 3.05 m (10 ft). This plot shows that canisters of the same volume containing the more concentrated waste forms (*i.e.*, either calcine or calcine encapsulated in a metal phase) have a higher heat generation rate and hence more heat to be dissipated at a given time after reactor discharge than do the more dilute

^{*} MTU is used to denote metric tons of uranium reprocessed.

TABLE 5. Heat Generation Rates of Radioactive High Level Wastes as a Function of Time After Reactor Discharge of Spent Fuel

Time, ^a years	HLW, ^b kW/MTU	Heat Generation Rates ^c (kW/m ³)		
		Calcine	Glass	Glass Beads
4.4 E-1	1.4 E+1	3.6 E+2	2.1 E+2	1.4 E+2
1.4 E0	5.4 E0	1.4 E+2	7.8 E+1	5.4 E+1
3.4 E0	2.0 E0	5.0 E+1	2.9 E+1	2.0 E+1
5.4 E0	1.2 E0	2.9 E+1	1.7 E+1	1.2 E+1
1.0 E+1	7.2 E-1	1.8 E+1	1.0 E+1	7.2 E0
3.0 E+1	4.0 E-1	1.0 E+1	5.7 E0	4.0 E0
1.0 E+2	7.4 E-2	1.9 E0	1.1 E0	7.4 E-1
3.0 E+2	6.7 E-2	1.7 E0	1.0 E0	6.7 E-1
1.0 E+3	1.4 E-3	3.6 E-2	2.1 E-2	1.4 E-1
3.0 E+3	1.4 E-3	3.6 E-2	2.0 E-2	1.4 E-2
1.0 E+4	1.4 E-3	3.5 E-2	2.0 E-2	1.4 E-2

^aTime measured from reactor discharge of spent fuel.
Read 4.4 E-1 as 4.4×10^{-1} .

^bThis is thermal decay heat per metric ton of uranium that is reprocessed. Spent fuel is from a PWR with a burnup of 25 000 MWd/MTU at a specific power of 35 MW/MTU [KEE].

^cThe production volumes of the reference waste forms given in Table 4 were used to establish a decay heat per unit volume prior to metal encapsulation.

waste forms. Hence, the net effect of dilution of the high-level waste is to shorten the time required for a specific volume of waste to decay to a given heat generation rate, but at the expense of increasing the total waste volume.

Figure 12 illustrates the effect of canister size (or volume) on the heat generation rates of either calcine or calcine encapsulated in a metal phase as a function of the age of the waste. As an example, assume it is desired to load canisters with either HLW calcine or metal-encapsulated calcine, so that each canister has exactly 5 kW of decay heat to be dissipated. From Fig. 12, the minimum time after discharge from a reactor is ~ 1.8 years for canisters with a diameter of 15.2 cm, ~ 7.4 years for a diameter of 30.5 cm, and ~ 54 years for a diameter of 61 cm.

Fig. 11. Thermal Heat Generation Rates of HLW Canisters Reference Waste Forms as a Function of Time After Reactor Discharge

The heat generation rate of HLW from spent fuel with burnups different from the assumed 25 000 MWd/MTU can be adjusted higher or lower. It should be noted that a different burnup can significantly alter the time axis of graphs like Figs. 11 and 12. A burnup of 33,000 MWd/MTU at 37.5 MW/MTU specific power yields a heat generation rate, compared with the reference burnup that is increased by factors of ~ 1.4 at 0.44 years after discharge and ~ 1.5 at 3, 30, and 100 years after discharge [BLOMEKE]. Increasing the total heat generation rate at a given time by these factors, for the example given above, has the following effects on the cooling time for a filled canister that is to have 5 kW of decay heat: for canisters with a diameter of 15.2 cm, the required time of ~ 1.8 years is increased to ~ 2.7 years; for 30.5 cm, ~ 7.4 years is increased to ~ 17 years; for 61 cm, ~ 54 years is increased to ~ 71 years.

Fig. 12. Heat Generation Rates of Canisters of Calcine or Metal-Encapsulated Calcine as a Function of Time After Reactor Discharge.

2. Waste Canisters

Design criteria for HLW canisters for a Federal repository have not yet been defined and are beyond the scope of this study. Solid right circular cylinders are assumed, although other shapes are still being considered [JANSEN-1, JANSEN-2, HOSKINS]. The material of construction is taken to be 304L stainless steel, although other candidate materials are being examined and may be better. Covering of a primary HLW canister with a secondary canister is not assumed. Canisters are assumed to be filled with waste forms to a height of 3.05 m (10 ft). This assumption also allows graphical data to be easily converted into kW/ft.

Three reference values of internal diameters for cylindrical canisters will be assumed: 15.2 cm (6 in.), 30.5 cm (12 in.), and 61 cm (24 in.). All canisters are assumed to be filled with reference HLW forms to a height of 3.048 m (10 ft). Such canisters have waste volumes of 0.055 m^3 (1.96 ft^3), 0.22 m^3 (7.85 ft^3), and 0.88 m^3 (31.4 ft^3), respectively. For the three canister sizes, Table 6 shows the number of canisters needed to contain the reference solidified HLW forms from the reprocessing of 1500 MTU.

TABLE 6. Number of Reference HLW Canisters for Waste Forms per 1500 MTU Reprocessed

HLW Canisters			
Diameter, cm	Volume, ^a m ³	Number ^b per 1500 MTU	Waste Form
15.2	0.055	1080	calcine, calcine-metal matrix
15.2	0.055	1890	glass monolith
15.2	0.055	2700	glass beads-metal matrix
30.5	0.22	270	calcine, calcine-metal matrix
30.5	0.22	473	glass monolith
30.5	0.22	675	glass beads-metal matrix
61	0.88	68	calcine, calcine-metal matrix
61	0.88	118	glass monolith
61	0.88	170	glass beads-metal matrix

^aA fill height of 3.048 m (10 ft) is assumed.

^bThe number of HLW canisters is calculated for the reprocessing of 1500 MTU, using the reference waste form production volumes of Table 4.

B. Thermal Analysis Applicable to HLW Canisters

Solidified high-level waste has a thermal heat generation rate due to decay of radioisotopes which can be modeled as uniformly distributed volumetric heat sources. Temperature distributions can be calculated for canisters of different sizes, using this assumption. Thermal analyses yielding the temperature distribution of waste canisters, aimed at identifying the maximum temperature within a HLW canister, are of interest in order to identify potentially excessive temperatures that could have detrimental effects on the waste form. Examples of effects that are desirable to minimize or to prevent are: 1) further denitration and volatilization of the components of the solidified HLW causing an increase in the internal pressure of a HLW canister, 2) increased glass devitrification, 3) glass softening, and 4) excessive internal or external corrosion of the primary HLW canister wall. Temperature distributions for HLW canisters isolated in water storage basins, air, or underground geologic formations are of immediate interest for waste management studies. This report is limited to the first two storage modes; the latter has been discussed for salt formations [CHEVERTON-1, CHEVERTON-2]. Thermal analyses of radioactive wastes in various containment situations have also been made previously [DEMIER-3, DEMIER-4, KASER-1, KASER-2, HOSKINS, MCELROY-2, MCELROY-3].

1. General Temperature Distributions--Solid HLW Cylinders

Simplifying assumptions of heat transfer properties have been made to facilitate calculations. Waste forms are assumed to be packaged and sealed in unfinned, cylindrical canisters for subsequent storage or isolation in

water basins, air, or underground geologic formations. Only steady-state temperature distributions have been considered. Axial heat losses and variations of thermal conductivity with temperature are neglected. No temperature gradient is assumed to exist in the canister wall, that is, the canister inside surface temperature is assumed to be equal to the outer surface temperature. It is further assumed that there is no thermal resistance between the solidified HLW form and the canister inner wall.

Under these assumptions, the temperature distribution for any radial position r (measured in meters from the centerline) within a cylindrical HLW canister containing uniformly dispersed volumetric heat sources is [KREITH]:

$$T(r) = T_s + \frac{q_v D^2}{16 k} \left(1 - \left(\frac{2r}{D} \right)^2 \right) \quad (3)$$

where $T(r)$ = temperature at any radial position within the canister ($^{\circ}\text{C}$)

T_s = temperature of the canister outer surface ($^{\circ}\text{C}$)

q_v = volumetric heat density (W/m^3)

D = canister internal diameter (m)

k = effective thermal conductivity of the waste form ($\text{W}/\text{m}-^{\circ}\text{C}$)

Only two temperatures of a HLW canister are of interest in this study. These are the maximum, which for cylindrical shapes is the centerline temperature, $T_c = T(0)$, and the minimum, or the outer canister surface temperature, $T_s = T(D/2)$. Maximum centerline temperature limits are given in Table 4 for each waste form. These are 700°C for calcine (to prevent further denitration with subsequent internal canister pressurization), 700°C for glass (to prevent excessive softening and devitrification), 300°C for lead alloys, and 550°C for aluminum alloys (to prevent melting of the metal phases). Maximum temperatures for the canister outer surface are of interest in designing heat removal systems for given canister heat loadings, preventing excessive corrosion rates, or in minimizing mechanisms (*e.g.*, sensitization of stainless steel) which can cause a premature breach of the canister. Allowable values of T_s are given in Section II.B.2.

The relationship between the temperatures of interest to this study for a solid cylindrical waste canister is [from Eq(3)]:

$$T_c = T_s + \frac{q_v D^2}{16 k} = T_s + \frac{Q}{4\pi L k} \quad (4)$$

where Q = total heat generation rate of the canister (*i.e.*, $Q = q_v \cdot \frac{\pi D^2 L}{4}$) (watts),
 L = fill height of the solid waste form in the canister (m).

The other quantities are as defined for Eq(3).

The maximum temperature, T_c , in a canister depends upon the surface temperature, the total heat generation rate (either $q_v D^2$ or Q/L) of the waste, and the thermal conductivity of the waste form. Equation 4 illustrates that if the HLW canister surface temperature is raised (*e.g.*, by switching from a water basin to air storage, using only natural convection cooling), the

centerline temperature rises correspondingly as long as the heat generation rate and thermal conductivity remain constant. Alternatively, the temperature difference, $T_c - T_s$, may be regarded as directly proportional to the heat generation rate and inversely proportional to the thermal conductivity. The canister surface temperature, T_s , is dependent upon the environment in which the HLW canister is placed and the total heat generation rate of the HLW canister. Relationships for surface temperatures, T_s , as functions of total heat generation rates in water basins and in air are explicitly developed in Section II.B.2.

It is instructive to examine Eq(4) in terms of four parameters: $(T_c - T_s)$, q_v , D , and k . Table 7 summarizes the results of assigning constant values to three of the four variables in order to identify the sensitivity of a single varied parameter. The data of Table 7 may not necessarily represent practical waste management options. Later sections will invoke additional criteria for waste forms and hence limit the range of the parameters.

First, Table 7 shows that for a constant heat density (q_v) and a constant canister diameter (D), the temperature difference from the centerline to the outer canister surface ($T_c - T_s$) changed as the effective thermal conductivity (k) is varied. Clearly, the larger the thermal conductivity, the lower is the temperature difference for a constant canister diameter.

For a constant heat density (q_v) and temperature difference ($T_c - T_s$), successively larger-diameter waste canisters can be used as the thermal conductivity of the waste form is increased. This has the effect of reducing the total number of HLW canisters since more waste is contained in each canister. However, the total heat generation rate per canister also increases; this must be considered before the canister is placed in an actual heat sink of air, water, or a geologic formation.

With a constant canister diameter and temperature difference ($T_c - T_s$), the use of increasingly large volumetric heat sources (q_v) is possible as k increases. Thus, solidified HLW can be put into canisters at shorter times after reactor discharge as the value of the thermal conductivity increases. This minimizes the storage capacity required for liquid HLW or spent fuel.

2. Surface Temperatures of HLW Canisters Stored in Water or Air

The temperature of the HLW canister outer surface, T_s , depends upon the heat flux passing through it, the environment or heat sink in which the HLW canister is placed, and the heat sink capacity (*i.e.*, the rate at which the sink can transport and dissipate heat). Our heat-transfer mechanism for water and air is assumed to be natural convection. For air, the additional heat-transfer mechanism of radiative cooling must be included. This section discusses surface temperature of HLW canisters in water and air as a function of total heat generation rates in a solid cylinder.

High-level waste canisters are assumed to be placed vertically in either water or air storage basins. Canisters are far enough apart so that the absence of any effect of neighboring canisters upon the heat transfer of a specific canister can be assumed. Variations in the surface temperature, T_s , as a function of canister length or waste fill height are neglected. Bulk air and water temperatures are assumed to be maintained constant at a temperature, T_∞ , by appropriately designed heat-exchange systems. Other assumptions are the same as those given in the first paragraph of Section II.B.1.

TABLE 7. Effect of Variation on Selected Parameters of $T_c - T_s = \frac{q_v D^2}{16 k}$ on Properties of High-Level Waste Canisters

Variables Held Constant	$T_c - T_s,$ °C	q_v		$k,$ W/m-°C	$D,$ cm	Canister Volume, ^b m ³	Total Canister Heat, ^b kW	No. of Canisters for 1500 MTU ^c
		kW/m ³	age ^a					
q_v, D	1667	8.5 E+1	~2y	0.3	30.5	0.22	19	270
	500	8.6 E+1	~2y	1	30.5	0.22	19	270
	50	8.6 E+1	~2y	10	30.5	0.22	19	270
	17	8.6 E+1	~2y	30	30.5	0.22	19	270
$q_v, T_c - T_s$	500	8.6 E+1	~2y	0.3	16.7	0.067	5.8	900
	500	8.6 E+1	~2y	1	30.5	0.22	19	270
	500	8.6 E+1	~2y	10	96.4	2.2	190	27
	500	8.6 E+1	~2y	30	167	6.7	580	9
$D, T_c - T_s$	500	2.6 E+1	~6y	0.3	30.5	0.22	5.8	270
	500	8.6 E+1	~2y	1	30.5	0.22	19	270
	500	8.6 E+1	<160d	10	30.5	0.22	190	270
	500	2.6 E+1	<160d	30	30.5	0.22	580	270

^a Age is established from corresponding heat density given in Table 5 for calcine.

^b Canister is assumed to be filled to a height of 3.05 m (10 ft) with HLW.

^c Number of HLW canisters calculated for wastes from reprocessing of 1500 MTU, assuming calcine (production volume of 0.04 m³/MTU) and the canister volume indicated.

For heat losses by natural convection in water or air, the HLW canister surface temperature, T_s , is related to the average (water or air) ambient temperature, T_∞ , by the relation [KREITH]:

$$T_s = T_\infty + \frac{Q_c}{Ah_{av}} \quad (5)$$

where h_{av} = *average* thermal surface convective heat transfer coefficient for water or air ($W/m^2-^\circ C$),

A = canister surface area available for cooling (m^2),

Q_c = total heat loss of canisters due to natural convection (W).

This expression for T_s is also implicitly dependent upon the length (or waste fill height) of the solid cylinders through the surface convective coefficient. Equation 5 provides an expression to calculate the surface temperature, T_s , as a function of the total heat losses due to natural convection if values of h_{av} and A are known.

For canisters in air and totally isolated from any nearby surrounding surfaces (*i.e.*, view factor assumed to be unity), radiation cooling must be assumed to occur in addition to natural convection cooling. The heat loss due to radiation cooling can be calculated from the following relationship [KREITH]:

$$Q_r = A \epsilon \sigma (T_s^4 - T_\infty^4) \quad (6)$$

where σ = the Stefan-Boltzmann constant ($W/m^2-^\circ K^4$),

ϵ = the dimensionless emissivity for grey surfaces,

A = canister surface area available for radiation (not including ends) (m^2),

Q_r = total heat loss due to radiation from canister (W).

The temperatures are as previously defined, except for the units which must be absolute or $^\circ K$ for Eq(6). The total heat loss, Q , for canisters in air is the sum of the natural convection losses, Q_c , and radiation losses, Q_r . For canisters in water cooling, $Q = Q_c$ since Q_r is negligible in comparison to Q_c .

Knowledge of the canister temperature, T_s , as a function of the total heat generation rate, $Q = Q_c + Q_r$, for either water or air cooling is of immediate interest. Natural convection heat losses are established from Eq(5), once values of T_∞ , A , and h_{av} are known. The *average* thermal surface convective heat transfer coefficient, h_{av} , is a function of the properties of the heat transfer fluid (*i.e.*, specific heat capacity, viscosity, density, thermal conductivity, and temperature coefficient of volume expansion), the length (or fill height of the waste) of the solid cylinder, and the temperature difference $T_s - T_\infty$. Temperature-dependent properties of water and air were evaluated for the mean (film) temperature $1/2 (T_s + T_\infty)$. Values of h_{av} were calculated from correlations for solid vertical cylinders in water or air [MCADAMS, KREITH]. Such values of h_{av} are shown in Table 8.

TABLE 8. Values of the Average Thermal Convective Heat Transfer Coefficient for 3.048-m-Long Vertical Cylinders in Air and Water at 100°F (38°C) Calculated from Correlations of [MCADAMS]

T_s		$h_{av} \left(\frac{\text{Btu}}{\text{hr} \cdot \text{ft}^2 \cdot ^\circ\text{F}} \right)^a$	
$^\circ\text{F}$	$^\circ\text{C}$	Water	Air
100	38	38	0.21
102	39	49	---
104	40	62	---
106	41	71	0.36
108	42	79	---
110	43	86	0.47
112	44	91	---
114	45	97	---
116	46	100	---
118	47	108	---
120	48	111	0.59
126	52	123	---
130	55	132	---
136	58	142	---
140	60	152	0.72
150	65	168	---
160	71	183	---
170	77	199	---
180	82	210	0.87
190	88	225	---
200	93	244	0.91
300	149	---	1.12
400	205	---	1.21
500	260	---	1.25
600	315	---	1.28
700	371	---	1.30
800	426	---	1.33
1000	538	---	1.33
1500	815	---	1.33

^aThe conversion factor to metric is $1 \frac{\text{W}}{\text{cm}^2 \cdot ^\circ\text{C}} = 1763 \frac{\text{Btu}}{\text{hr} \cdot \text{ft}^2 \cdot ^\circ\text{F}}$.

Since negligible radiation heat losses are assumed for water cooling, Eq(5) was evaluated to establish the relationship of T_s to Q . These data are plotted in Fig. 13 for canisters of three diameters and a bulk water storage temperature, T_∞ , of 38°C (100°F).

Fig. 13. HLW Canister Surface Temperature *vs.* Total Heat Generation Rate for Different Diameters: (1) Natural Convection in Air (Vertical) and Radiation Cooling ($\epsilon = 0.7$) (2) Natural Convection in Water.

Air cooling must include the contribution from radiation losses given by Eq(6) in addition to the natural convection losses of Eq(5). A relation of T_s *vs.* Q was calculated using these two equations by assigning a value of T_s and summing the two heat losses, after Eq(5) and Eq(6) for Q_c and Q_r were evaluated to establish a total heat generation rate, Q . Values of h_{av} in Table 8 and an emissivity of 0.7 were used. The relation of canister surface temperature to the total heat generation rate, Q , is shown in Fig. 13 for three canister diameters and a bulk air temperature, T_∞ , of 38°C (100°F).

Figure 13 clearly shows that for a given total heat generation rate Q , surface temperatures, T_s , of HLW canisters are much lower when water storage is employed. Increased surface areas for a larger-diameter canister result in a lower surface temperature for a given heat generation rate in a given storage medium (*i.e.*, water or air). Also, external fins can be used to increase the surface area and to lower the surface temperatures, but these were not considered here. Alternatively, larger-diameter canisters allow a larger total heat generation rate within a canister for the same surface

temperature (T_s). Curves for diameters of HLW canisters other than those plotted may be constructed from data in Fig. 13 by rescaling the values of Q in direct proportion to the diameter (*i.e.*, $Q_x = \frac{D_x}{D_{\text{graph}}} Q_{\text{graph}}$).

The maximum surface temperature for the HLW canister in either water or air storage basins has not been determined, not being within the scope of this study, but values have been assumed so that conclusions can be drawn. Stainless steel subjected to temperatures of 427-790°C (800-1450°F), can undergo sensitization (*i.e.*, chromium carbide precipitation in the grain boundaries). Subsequent water storage of sensitized canisters can lead to a higher failure probability [MECHAM] than for canisters of unsensitized metal. Thus, a surface temperature limit of $T_s \leq 400^\circ\text{C}$ for canisters stored in air is assumed. For water storage basins, maximum canister surface temperatures of 53°C (128°F) [MECHAM, ARH] and 60°C (140°F) [HOSKINS] have been used. Definitive data establishing a maximum surface temperature of the reference stainless steel canisters in water are lacking [MECHAM]. This report presents some conclusions for the limiting temperatures of $T_s \leq 53^\circ\text{C}$ and $T_s \leq 80^\circ\text{C}$ in water storage basins and of $T_s \leq 400^\circ\text{C}$ for air storage basins.

The data in Fig. 13 can be used to identify the maximum allowable heat generation rates, Q , for values of $T_s \leq 53^\circ\text{C}$ in water and $\leq 400^\circ\text{C}$ in air. The maximum total heat generation rates, Q , for water storage are ≤ 15 kW, ≤ 30 kW, and ≤ 60 kW for HLW canister diameters of 15.2 cm, 30.5 cm, and 61 cm, respectively; approximately the same total heat generation rates are allowed for air storage but with a surface temperature of $T_s \leq 400^\circ\text{C}$. Higher heat generation rates than these produce temperatures higher than those assumed, $\leq 53^\circ\text{C}$ (water) or $\leq 400^\circ\text{C}$ (air), as can be seen in Fig. 13.

The data in Fig. 13 can also be used to estimate the canister surface temperature change caused by moving a HLW canister from one cooling medium to the other. For example, the surface temperature of a 30.5-cm-diameter canister with a 30-kW total heat generation rate and a 53°C surface temperature in water would increase (by 347) to 400°C if moved into an air storage mode.

The shallow slope of the plot of T_s vs. Q for water storage in Fig. 13 implies that a slight increase in the allowable surface temperature, T_s , can result in a significant increase in the allowable heat generation. For canisters with the specified configuration, a canister surface temperature increase from 53 to 60°C would permit the allowable heat generation rate (Q) to nearly double. This illustrates the potential incentive for the highest possible allowable canister surface temperature in water storage since higher allowable heat generation rates allow canisters of these dimensions to be filled with shorter-cooled waste. The steeper slopes of the curves in Fig. 13 for air cooling means that there are significantly lower increases in allowable heat generation for comparable increases in the maximum T_s .

3. Maximum Allowable Total Heat Generation Rates of Solid HLW Cylinders in Water or Air

Equation 4 can be rewritten as:

$$k = \frac{Q}{4\pi L(T_c - T_s)} \quad (7)$$

This form can aid in estimating the thermal conductivity required of HLW forms for a given maximum allowable total heat generation rate. If values of T_c equal to the maximum temperature limits for the three reference waste forms of Table 4 are assumed, effective thermal conductivities can be calculated from Eq(7) by assuming values for T_s and Q . The previously derived relationships for T_s vs. Q (Fig. 13) for water and air can be used to establish values of T_s for a given total heat generation rate Q . The calculated thermal conductivities for such sets of T_c , T_s , and Q identify the maximum allowable heat generation rates in various media for a limiting waste centerline temperature. Results shown in Fig. 14 correspond to the locus of points satisfying Eq(7) for T_c values of 700, 550, and 300°C. The relation between the maximum allowable heat generation rate per canister, as limited by the maximum centerline temperature and the value of the thermal conductivity of the waste form required to satisfy a T_c criteria, is compactly represented in a generalized form by Fig. 14. For a given heat generation rate, values of k larger than those calculated from Eq(7) result in a $(T_c - T_s)$ smaller than assumed (*i.e.*, T_c lower than the maximum values used for Fig. 14). Smaller values of k correspond to greater values of T_c .

Fig. 14. Relation Between k and Q for Selected Maximum Values of T_c in Air and Water Cooling. Ambient air or water at 38°C (100°F). T_∞ dimensions are canister diameters. Fill height is 3.05 m (10 ft).

The data as shown in Fig. 14 have no restrictions on the magnitude of T_s . Values of T_s for a maximum allowable heat generation rate for any assumed value of Q can be obtained by referring to Fig. 13. The maximum allowable heat generation rates for an assumed value of T_s can be assigned in this way. The maximum allowable heat generation rates* corresponding to HLW canister surface temperatures of 53°C in water and 400°C in air are indicated in Fig. 14. Also indicated is the value of thermal conductivity assigned in Table 8 to the reference waste forms.

Figure 14 can be used to estimate the effects of changing the values for the parameters, Q , T_c , T_s , k of HLW canisters. For a canister with a 30-kW heat generation rate, a diameter of 30.5 cm (1 ft), *water* storage, and a value of $T_s \leq 53^\circ\text{C}$, limiting the centerline temperatures T_c to 700, 550, and 300°C results in the minimum values for the required thermal conductivity, k , of the HLW forms of 1.3, 1.6, and 3 W/m-°C, respectively. Heat generation rates greater than 30 kW for these three thermal conductivities raise the canister surface temperature T_s over the 53°C limit (Fig. 13). Lower thermal conductivities for each of the maximum T_c values yield higher centerline temperatures. Due to inadequate thermal conductivities, neither the reference calcine nor glass could be stored in water in a 30.5-cm-diameter canister with a 30-kW total heat generation rate and still satisfy the 700°C centerline temperature limit. In fact, the maximum heat generation rate of HLW canisters allowable for the reference calcine or glass waste forms to satisfy the assumed criteria of Eq(7) are obtained from Fig. 14 as 7.4 and 24.8 kW, respectively. Increases in the thermal conductivities of the reference calcine or glass by factors of 5 or 1.3, respectively, would be needed to increase the allowable heat generation rate to 30 kW, which is then limited by the wall temperature at $T_s \leq 53^\circ\text{C}$. Such modest increases in thermal conductivities may be achievable by alternatives such as a metal matrix for calcine or possibly internal fins with glass. It can be noted that a 5-kW heat generation rate (the assumed reference salt repository acceptance limit, Section III.A) of either calcine or glass easily satisfies the T_s and T_c criteria for a 30.5-cm-diameter canister in water storage.

The reference metal matrices have thermal conductivities in excess of those required for a 30-kW heat generation rate. The thermal conductivities of the aluminum alloy ($T_c \leq 550^\circ\text{C}$) and the lead alloy ($T_c \leq 300^\circ\text{C}$) show increases by factors of 19 (*i.e.*, 30/1.6) and 3.3 (*i.e.*, 10/3) over required values. Thus, metal matrices will have centerline temperatures well below their limiting values if the 30-kW heat generation rate or the 53°C outer surface temperature limit is satisfied.

Similar arguments as given above are applicable to *water* storage of 61-cm-diameter HLW canisters of metal matrices. These can have a higher heat generation rate of 60 kW that is limited by the 53°C wall temperature; this illustrates the advantage of the increased thermal conductivity of metal matrices. That is, HLW canisters with larger diameters are possible with the metal matrix concept so that more thermal benefits (higher heat loadings, larger volume per package) can be derived from packaging alternatives for metal encapsulation than for calcine or glass if high heat-generation-rate wastes (*i.e.*, short aging as in FDR fuel cycles) are available.

* Note that the maximum allowable heat generation rate for air with $T_s \leq 400^\circ\text{C}$ and for water with $T_s \leq 53^\circ\text{C}$ are approximately the same (Fig. 13).

For *air* storage of 30.5-cm-diameter HLW canisters with a 30-kW heat generation rate, the outer surface temperature limit is $\leq 400^{\circ}\text{C}$ (Fig. 13). Neither the reference calcine nor glass can meet this criterion; they do not have low enough centerline temperatures due to their low thermal conductivities (Fig. 14). For a 550°C centerline limit, the minimum value of thermal conductivity required is $\sim 5 \text{ W/m}\cdot^{\circ}\text{C}$, which is a factor of 6 below that of the reference aluminum-alloy metal matrix. The higher T_c of 550°C for aluminum alloys allows a full 30 kW (outer-surface-temperature limiting heat generation rate) in either air or water. In fact, the aluminum alloy, with thermal conductivity a factor of 6 greater than required at 30kW, would be able to accommodate a 50-kW heat generation rate (Fig. 14) if maximum canister surface temperature were of no concern. From Fig. 13, the HLW canister surface temperature in air for a 50-kW heat generation rate would be 500°C , or 100°C above the limit assumed for air cooling; the corresponding surface temperature with water cooling would be 58°C , 5°C over the assumed limit.

The 300°C centerline limit set for a lead-alloy matrix does not allow a 30-kW heat generation rate for air storage. From Fig. 14, the heat generation rate is limited to $\sim 13 \text{ kW}$ for a lead-alloy metal matrix with a thermal conductivity of $10 \text{ W/m}\cdot^{\circ}\text{C}$. An asymptotic limit of $\sim 16 \text{ kW}$ approached in Fig. 14 for a T_c of 300°C could only be met for an infinite value of the thermal conductivity. Thus, due to the relatively low T_c limit of 300°C *air* storage of a lead alloy allows only $\sim 43\%$ of the heat generation rate possible compared with the limit of the 30-kW heat generation rate for the same HLW canister placed in *water* storage.

III. ROLE OF THE METAL MATRIX AS AN ALTERNATIVE WASTE-MANAGEMENT STRATEGY

A. The Federal High-Level-Waste Repository Salt Formations and Maximum Allowable Heat Generation Rates

Since some isotopes in the high-level waste have half lives of greater than ~ 30 years, the management of high-level waste from reprocessed fuel is generally regarded as an isolation as well as a disposal problem. Current conceptual goals are to isolate solidified high-level waste in such a manner that there is an extremely low probability of the isotopes entering the human environment until the nuclides have decayed to innocuous levels. The time periods involved are of the order of 10^5 years. The current approach is to place the high-level waste in deep ($\sim 1000 \text{ m}$) geologic formations that have been stable for millions of years and have prospects of continuing to remain stable for additional millions of years. Such a concept would not require human surveillance, would be less affected by uncertain future surface conditions created by man or nature, and should keep the waste isolated for the time periods required.

Isolation in underground salt formations has received more study than in other geologic formations. Work has been summarized [BRADSHAW, BOCH], and some is still in progress [Y/OWI-8, SAND]. Salt formations, in comparison with other geologic formations, have relatively good thermal conduction properties to dissipate decay heat and can likely be mined at lower costs than can hard rock formations. Salt exhibits plastic flow under the lithostatic pressures associated with repository depths. Such a property would tend to mend any breach in the formation caused by earthquakes or other earth movements and would

reisolate the waste. Extensive salt formations are distributed over many locations in the United States. The use of several sites could reduce risks associated with transporting the high-level waste from a reprocessing plant to a waste repository by reducing transport distances. A primary disadvantage of a salt formation may be the high solubility of salt in water, although such formations have remained isolated from water for millions of years.

The Federal repository concept calls for transport of solidified high-level waste canisters to a mine in a salt formation and placing them in holes in suitable arrays that have been drilled into the tunnel floors. After back-filling of the holes with crushed salt, the plastic properties of salt, coupled with the thermal decay heat and lithostatic pressures, would lead to sealing of the area surrounding the high-level waste canisters.

Salt formations, which are limited to solid heat-conduction mechanisms for dissipating decay heat to the earth surface, have much less heat transport capabilities than do air- or water-basin surface storage with their natural convection mechanisms. In addition, the effects of large quantities of thermal decay heat upon a large salt formation with plastic flow characteristics must be carefully considered in order to prevent undesired phenomena that could terminate the desired waste isolation. As a result, lower maximum thermal heat generation rates per canister (or hole) will likely be required for a geologic formation compared to those allowed during air or water interim storage modes. The allowable heat generation per canister will be determined by the maximum desired salt temperatures and the disposal array employed.

Two undesirable phenomena, *i.e.*, migration of water of hydration and the sudden release of trapped "stream" pressure, are briefly reviewed as examples that can impose heat generation limits on canisters destined for the repository. In subsequent sections, the impact of these restrictions on the management of wastes as it relates to metal encapsulation is outlined.

In early salt-mine work [BRADSHAW, BOCH], it was observed that the average water content of salt was $\sim 1/2$ wt % and that this water can migrate toward a heat source, or against a temperature gradient. This implies that water in salt formations could enter holes containing buried high-level waste canisters. The quantity of water estimated to migrate during a 20-30 year period to a one-foot-diameter hole containing a high-level waste canister with an outer surface temperature of $\leq 250^{\circ}\text{C}$ is 2-10 liters [BOCH]. Higher outer-canister surface temperatures or salt temperatures (caused by higher heat generation rates per canister or smaller-diameter canisters with high heat fluxes) would result in more water migration.

Water migrating to the canister would be expected to reach the hot ($\sim 250^{\circ}\text{C}$) canister surface initially, but probably would move perhaps by evaporation) to a cooler zone, perhaps above the canister, and condense where the temperature and pressure conditions were proper. Water ultimately would condense upon the canister surface at some time. At this time, accelerated corrosion of the primary high-level waste canisters could occur. Water contacting a HLW canister could also potentially release radiation and thermal reaction products of water; possible consequences would be the formation of explosive gas mixtures and enhanced transport of fission products and/or noxious gases into tunnel areas of the repository still being filled [BOCH, BRADSHAW].

It was also observed in early salt repository work that a sudden release of trapped steam pressure could occur if salt that contained trapped water crystals or pockets of water got too hot [BOCH]. Accompanying this release was a fracturing of the salt, making the thermal conduction properties of salt low and hence increasing the thermal resistance and the temperature of the waste.

A parametric study has been made of a salt repository in which tunnel size, waste canister array and spacing, waste age, and power (decay heat) per canister were variables [CHEVERTON-1, CHEVERTON-2]. The objective of this analysis was to arrive at preliminary conclusions, consistent with some preliminary thermal criteria imposed upon the salt formation, on how to optimize the isolation of high-level waste canisters in a salt formation. Tentative thermal criteria developed in this parametric study were based upon maintaining acceptable extents of the undesired phenomena (water migration, plastic flow, trapped steam releases, *etc.*) that are accelerated by increasing temperature. The temperature limitations assumed for salt formations are that no more than 1 vol % of the salt in the entire formation is allowed to reach a temperature of 250°C and no more than 25 vol % is allowed to reach a maximum temperature of 200°C, based upon the unit cells assumed for the storage area [CHEVERTON-1]. These thermal criteria form the basis for limiting the maximum allowable heat generation rates per high-level waste container, or per hole, in the underground repository. Other thermal criteria are also developed for the maximum temperatures of the high-level waste (to maintain stability), on the overlying shale and/or clay layers (to maintain their integrity), on the earth surface temperature above the repository, and on any nearby underground aquifers. It was generally found that the centerline temperatures of high-level waste canisters containing calcine limited the allowable heat generation rate. However, criteria invoked upon the maximum permissible temperatures within the salt formation are such that even if the centerline temperature is no longer limiting as a result of improved properties of solidified waste (*i.e.*, metal encapsulation, internal fins, glass), only slightly (approximately 20-50%) higher heat generation rates per canister, or per hole, are allowable [CHEVERTON-1]. Details of these complex relationships can be found in published reports [CHEVERTON-1, CHEVERTON-2]. The results lead to the conclusion that any major net advantages of increasing the thermal conductivity of waste are likely to be gained during interim storage rather than in the salt repository.

For the present work, it has been assumed that a Federal repository will accept waste in the form of calcine, glass, calcine-metal matrices, or glass beads-metal matrices. The maximum allowable heat generation rate at the time of receipt at a repository is assumed to be equal to or less than 5 kW per canister. Discussions are based on a ≤ 5 kW per canister limit, but the decay heat limit is actually a per-hole limit. Thus, four canisters of 1.25 kW per canister placed in one hole can also satisfy this criterion, but this is not explicitly considered in this study. A heat generation rate limit of ≤ 5 kW per canister is preliminary but probably is within a factor of two of what might be ultimately set as a salt repository limit. This assumption is required to provide conclusions about the interim storage time requirements of the different high-level waste forms. Also, note that the real limit is imposed by the maximum temperature allowable for the salt rather than by a heat generation per canister. Clearly, waste management alternatives exist wherein large-

diameter canisters (to decrease the wall heat flux) and higher heat generation rates per canister could exist. However, this would likely involve repository alternatives where canisters are initially buried further apart than in the reference study [CHEVERTON-1] to satisfy the maximum allowable salt temperature. For example, after suitable decay periods, tunnels could be reentered and additional canisters placed between the original canisters such that the maximum salt temperature criteria is not violated. Such schemes are not considered further here.

B. Thermal Analysis Related to High-Level Radioactive Waste Management Options

1. General Introduction

A current Federal Regulation* requires that the inventory of liquid high-level waste be limited to that produced within 5 years of its generation and that the waste be solidified and transported to a repository within 10 years after separation of fission products from the irradiated fuel. No specific solid form is required, only that it be stable and thermally, chemically, and radiolytically inert.

Reprocessing of spent LWR fuel within one-half year of reactor discharge is often proposed but is not actually required. Long cooling of spent fuel reduces the decay heat to be managed as well as the activity of some of the troublesome shorter-lived radioisotopes (*e.g.*, ^{131}I , ^{106}Ru). Because of the large current inventory and the absence of fuel reprocessing, spent fuel from LWRs may never be reprocessed after cooling times as short as 1/2 year. In contrast, rapid reprocessing of LMFBR fuel is motivated by the need to rapidly recycle the plutonium and hence shorten the "double time." This report assumes that one-half year is the shortest cooling time for reprocessing wastes of interest.

To manage the thermal heat dissipation of high-level waste, storage of spent fuel elements (assemblies) can be an important waste management option. The storage of spent fuel assemblies in water basins with secondary heat exchangers provides shielding and is a suitable method to dissipate decay heat. The spent oxidic fuel is rather inert, water insoluble, and in a stable form [KATAYAMA-2]. Ion exchange resins in the storage-pool-water purification systems provide a method of collecting any soluble elements in the pool water. Storage of spent fuel elements is a rather simple operation that has been routinely carried out for many years in nuclear technology without a major release of radionuclides to the environment.

Once fuel is reprocessed, there are two alternatives, or a combination thereof, for managing the thermal decay heat: 1) High-level waste may be directly solidified after reprocessing if the storage environment can adequately dissipate the decay heat of the solid waste form without exceeding maximum temperature limitations. 2) The high-level waste can be retained as solutions stored in large double-lined tanks and the decay heat dissipated through cooling coils.

*Title 10, *Code of Federal Regulations (CFR)*, Part 50, Appendix F.

Various combinations of fuel and waste storage are possible. Spent fuel assemblies could be stored until the decay heat reached a point where the high-level waste from the reprocessed fuel could be directly solidified and placed in canisters having a 5-kW heat generation rate. Such canisters could then be immediately transported to a salt repository. This strategy would minimize requirements for the storage of high-level liquid waste and for the interim storage of high-level waste canisters. However, storage space requirements for spent fuel would be large. Alternatively, the storage time and space for spent fuel assemblies can be reduced by using smaller high-level waste canisters in order to satisfy the ≤ 5 kW limitation. This, however, would result in an increased number of high-level waste canisters for a given volume of waste. In still another option, waste canisters filled with short-cooled wastes can be stored, with cooling, at the reprocessing plant until radionuclide decay has reduced the heat generation rates to ≤ 5 kW per canister and canisters would be acceptable for geological isolation.

The next subsections discuss primarily waste management operations associated with the proper dissipation of thermal decay heat. A criterion that will be always assumed is the ≤ 5 kW heat generation rate for a canister transported to a repository. Additional criteria for maximum waste-form centerline and canister surface temperatures are introduced as required. The requirements for leach rates, mechanical strengths, radiation, and chemical stabilities of waste forms are discussed very little in these sections.

2. Reference Waste Forms and Reference Canisters

a. Introduction

At a reprocessing plant, one of two temperatures (T_c or T_s) limits the allowable total heat generation rate of canisters at the time of initial filling with solidified HLW. Maximum temperatures will be defined for the canister surface (T_s) and for the center of the solidified HLW (T_c) canister to minimize detrimental effects (*i.e.*, thermal degradation, devitrification, melting, and corrosion). Figures 13 and 14 show the maximum allowable heat generation rates for values of T_s and T_c for HLW canisters in water and air storage environments. After HLW canisters are filled, the total heat generation rates decrease with time due to decay of radionuclides. This effect is illustrated in Figs. 11 and 12. Waste management operations will likely have the general objective of initially loading a HLW canister such that either T_s or T_c is near its maximum value at the time of filling. This allows solidified HLW to be packaged as soon as possible after reactor discharge while producing a maximum heat generation rate per canister; if a HLW canister were loaded to less than the maximum T_s or T_c value, this would not fully utilize the selected canister size and interim storage mode. Management based on the use of these temperature limits 1) probably minimizes the quantity of either water-basin storage for spent fuel assemblies (prior to reprocessing) or high-level liquid waste storage after reprocessing, and 2) is consistent with a goal of solidifying and packaging HLW as soon as possible after reprocessing.

A second, and more limiting, condition on the maximum heat generation rate of HLW canisters is imposed by the Federal repository. The maximum allowable heat generation rate, which is assumed in order to avoid detrimental effects to the waste forms and to the geologic formation housing

the repository, is discussed in detail in Section III.A. However, the maximum heat generation rate for a HLW canister that is to be isolated in a Federal repository is assumed to be 5 kW (Section III.A). A 5-kW heat generation rate per canister yields temperatures of T_s and T_c for either water or air storage environments below prescribed maximum values. Thus, the Federal repository imposes the limit on heat generation rates of HLW canisters.

In summary, HLW canisters are initially filled so that either T_s or T_c is at the maximum allowed value. The canisters are then stored in either water or air environments. Here, the values of T_s or T_c decrease as the heat generation rate decreases due to the decay of radionuclides. The canisters must be stored until the total heat generation rate reaches the Federal repository limit of 5 kW. Canisters generating 5 kW each can be transported to a Federal repository for final isolation.

It is convenient to define three time intervals in the management of high-level waste. These correspond to the limiting conditions imposed upon the maximum allowable heat generation rates of HLW canisters. The time intervals are designated "to fill," "interim," and "to repository." The time that must elapse from reactor discharge of spent fuel to the time that a HLW canister can be filled while satisfying the indicated T_s and T_c criteria is defined as the storage time "to fill." Spent fuel can be stored during the entire "to fill" storage time period so that upon reprocessing there can be direct solidification and filling of the HLW canister (*i.e.*, no high-level liquid waste storage). Alternatively, the time period can be divided into intervals of spent fuel storage and storage of high-level liquid waste, such that the total storage time is the "to fill" period. In all cases, HLW canisters are assumed not to be filled prior to the elapse of the "to fill" decay time. The time interval after HLW canisters are filled until the total heat generation rate of a HLW canister has decayed to the 5 kW assumed acceptable for a Federal repository is designated as the "interim" storage time. During the "interim" storage time, HLW canisters are assumed to be stored in water and/or air. The time designated "to repository" is defined as the minimum time, measured from reactor discharge, that must pass before the total heat generation rate of the solidified HLW contained in a canister has reached 5 kW. This is the assumed maximum heat generation rate per canister acceptable for a salt repository (Section III.A). During this required storage time period, storage may be as spent fuel elements, high-level liquid wastes, or solidified HLW in canisters in water or air or any combination thereof. For example, if desired, the entire storage time "to repository" may be passed by storing spent fuel elements, thereby eliminating most high-level liquid storage and interim water or air storage, until the fuel is reprocessed and the waste directly solidified into HLW canisters with a heat generation rate of 5 kW per canister. Such canisters could be immediately placed in the repository. This terminology is illustrated on the next page.

The following subsections examine some waste management operations for various reference waste forms and storage modes. Where possible, comparisons of different waste-management storage alternatives are given. The discussions are a direct application of the results given in Section II.

b. Reference Calcine in Water or Air Storage

Table 9 summarizes the maximum allowable heat generation rates of HLW canisters filled with the reference calcine (Section II.A). These data show that for either water or air storage environments, the maximum allowable heat generation rate ($Q^{\max}$) at the time of the initial filling (labeled $Q_{\text{fill}}^{\max}$) is limited by the maximum centerline temperature (T_c) of 700°C . This limitation is a direct consequence of the relatively low thermal conductivity of calcine. Also shown are the three storage time intervals (measured starting with reactor discharge of the fuel) as defined above.

The data in Table 9 show that water storage of a 30.5-cm-diameter canister, filled initially with calcined waste that liberates 7.425 kW heat ($Q^{\max}$), results in a 43°C outer wall temperature (T_s) and a 700°C centerline temperature (T_c). The earliest time after reactor discharge that the canister could be filled with the reference calcine waste is given in the column "to fill" as 5.2 years. This can also be obtained from Figs. 11 or 12 where the heat generation rates of HLW canisters for the reference waste forms are given as a function of time after reactor discharge. To satisfy the 700°C T_c limiting condition on the maximum allowable total heat generation rate,

TABLE 9. Comparison of Maximum Total Heat Generation Rate of Reference Calcine in Reference Canisters Stored in Water or Air (3.05-m fill height assumed)

$Q_{\text{fill}}^{\text{max}}$ kW	Storage Mode	T_c^a °C	T_s^a °C	D, cm	Storage Time ^b		
					"to Fill," years	"Interim," years	"to Repository," years
7.40	water	700 ^c	46	15.2	1.2	0.6	1.8
7.425	water	700 ^c	43	30.5	5.2	2.2	7.4
7.45	water	700 ^c	41	61	39	15	54
5.4	air	700 ^c	230	15.2	1.6	0.2	1.8
6.1	air	700 ^c	170	30.5	6	1.4	7.4
6.6	air	700 ^c	130	61	41	13	54

^aCalculated from Eq(4), (5), (6), and (7). A thermal conductivity value of 0.3 W/m-°C was used. These are the values at the time of HLW canister filling which correspond to the time "to fill."

^bStorage times are as defined in text.

^cThis temperature limits the maximum permissible heat generation rate from the canister.

spent fuel assemblies and/or liquid high level waste must be stored for a total of 5.2 years after reactor discharge. After the canister is filled, an "interim" water storage period of 2.2 years is required in which time the heat generation rate decays to 5 kW per HLW canister. The column "to repository" shows that the 5-kW-per-canister limit is reached 7.4 years after reactor discharge.

For air storage of a 30.5-cm-diameter HLW canister, the initial heat generation rate is limited to 6.1 kW due to the 700°C centerline temperature limit. This is 18% less than for water storage. The outer surface temperature T_s is 170°C at the time of filling. Six years must elapse before a HLW canister can be filled with the reference calcine in order to satisfy the $T_c \leq 700^\circ\text{C}$ criterion. The air "interim" storage time, 1.4 years, is shorter than that for water due to the increase in the "to fill" storage time. However, the same 7.4 years must elapse before the repository heat generation rate criterion of 5 kW is satisfied.

The effects of changes in HLW canister diameter, volume, and outer surface area can also be estimated from the data of Table 9. Smaller canister diameters result in smaller waste volume per canister and hence generate more HLW canisters per waste volume (see Table 6) but allow the "to fill" storage time to be shortened to either 1.2 years (water) or 1.6 years (air). The "interim" storage period until the salt repository limit is satisfied is also shorter. Use of larger diameter canisters decreases the total number of HLW canisters for a given waste volume of fuel processed.

However, the "to fill" storage time period is increased significantly. The required ~40 years storage of spent fuel elements and/or high-level liquid waste for 61-cm-diameter canisters is almost independent of water or air storage mode. The shortest time in which 61-cm-diameter canisters filled with calcine satisfy the 5-kW repository criteria (*i.e.*, "to repository") is 54 years. Thus, smaller-diameter HLW canisters for calcine may be useful if the goal is to shorten the "to fill" and "interim" storage times while simultaneously increasing the total number of canisters. Large-diameter HLW canisters of calcine may be of less value due to the lengthy "to fill" storage periods required.

It can be noted that the HLW canister outer surface temperature, T_s , can be obtained from Fig. 13 for any time for which the total heat generation rate (obtainable from Figs. 11 or 12) is known. For example, the temperatures at times when the 5-kW repository limit is reached are 40°C (61 cm), 42°C (30.5 cm), and 44°C (15.2 cm) for water storage and are 110°C (61 cm), 155°C (30.5 cm), and 230°C (15.2 cm) for air storage. These data also provide a method for estimating the temperature change as a result of switching between water and air storage.

c. Reference Glass Monoliths in Water or Air Storage

The maximum allowable heat generation rates per HLW canister of the reference glass (Section II.A) at the initial filling time (*i.e.*, "to fill") are shown in Table 10. The heat generation rates of all canisters, except water storage of a 15.2-cm-diameter canister, are limited by the 700°C maximum allowable centerline temperature (T_c) of the reference glass. The one exception is assumed to be limited by a 53°C outer surface temperature (T_s), which is a direct result of the relatively small surface area of a 15.2-cm-diameter canister. The area could be increased by the use of external fins. Very little increase in the allowable heat generation rates is observed as the diameter is increased when the centerline temperature is limiting.

The diameter influences the time that must pass before a HLW canister can be filled as well as the time required for the 5-kW heat generation rate repository limit to be satisfied. The larger diameters require longer storage time intervals. Even though the heat generation rate of HLW decreases approximately as the inverse of time since reactor discharge, the actual rate of decrease is reduced below the expected value at long decay times since the effective half-life of the waste increases with the loss of the shorter-lived components in the waste (see Fig. 11). This effect can be observed by comparing the water storage of a 30.5-cm-diameter and 61-cm-diameter HLW canister in Table 10. Both are initially filled with waste having a 25-kW heat generation rate, but at different times after reactor discharge. The "interim" storage time for waste that has been cooled 3.2 years before reaching 25 kW is 7.9 times the "interim" storage time for waste cooled only 0.7 years prior to filling.

The data in Table 10 show that if a goal is to solidify HLW at <1 year after discharge and to transport the HLW to a repository at ≤4.2 years after discharge, glass monoliths of ≤30.5-cm diameter may be used. Larger diameters decrease the number of HLW canisters but increase 1) the "interim" storage time requirements and 2) the earliest times they can be filled. This results in rather long storage times prior to final isolation.

TABLE 10. Comparison of Maximum Total Heat Generation Rate of Reference Glass Monoliths in Reference Canisters Stored in Water or Air (3.05-m-fill height assumed)

$Q_{\text{fill}}^{\text{max}}$ (kW) ^a	Storage Mode	T_c ^a °C	T_s ^a °C	D, cm	Storage Time ^b		
					"to Fill," years	"Interim," years	"to Repository," years
15	water	445	53	15.2	≤0.5 ^d	~0.5	1
25	water	700 ^c	49	30.5	0.7	3.5	4.2
25	water	700 ^c	45	61	3.2	27.8	31
13	air	700 ^c	360	15.2	≤0.5 ^d	~0.5	1
16	air	700 ^c	290	30.5	1.2	3	4.2
18	air	700 ^c	230	61	4	27	31

^aCalculated from Eqs.(4), (5), (6), and (7). A thermal conductivity value of 1 W/m-°C was used. These are the values at the time of HLW canister filling which correspond to the time "to fill."

^bStorage times are as defined in text.

^cThis temperature limits the maximum permissible heat generation rate from the canister.

^dTimes shorter than 0.5 year may be possible based on the thermal analysis; however, shorter times will probably not be of interest due to additional handling and chemical separation problems likely to be encountered with shorter-cooled fuel.

d. Some Comparisons of Reference Calcine and Glass in Water or Air Storage

The data in Tables 9 and 10 can be used to make a general comparison of the reference calcine and glass. Glass increases the thermal conductivity while diluting the waste (or increasing the total waste volume). For water storage of 30.5-cm-diameter HLW canisters, calcine requires a longer "to fill" storage period for the waste (*i.e.*, 5.2 years *vs.* 0.7 years) than glass. In both cases, the 700°C centerline temperature limits the heat generation rate at the filling. For decay to the 5-kW repository heat generation rate limit, almost twice as long (7.4 years *vs.* 4.2 years) is required for calcine as for glass. Glass has a longer "interim" storage period but can be transported to a repository sooner than calcine. Since glass effectively dilutes the waste, the number of HLW canisters required for a given total volume of liquid HLW is 75% greater for glass (Table 6) than for calcine. The same general trend is seen upon comparison of air storage of glass and calcine.

e. Reference Low-Melting (Lead Alloy) Metal Matrix of Calcine or Glass Beads in Water or Air Storage

Shown in Table 11 are the storage times required for different maximum-allowable initial heat generation rates and storage modes of calcine or glass beads encapsulated in the reference lead alloy (Section II.A). The effect of a maximum 53°C outer surface temperature, T_s , for water storage is evident by comparison of the 0.6-year fill time for a 30.5-cm diameter canister with encapsulated glass beads to 1 year for encapsulated calcine. The dilution effect of glass beads (waste volume is increased by a factor of 2.5 compared with the calcine-metal matrix) allows the "interim" storage time to be decreased to 2.4 years for glass beads encapsulated in lead compared with the 6.4 years required for a calcine-metal matrix. Encapsulated glass beads can be transported to a repository 3 years after reactor discharge compared with 7.4 years for calcine-metal matrices. However, the total number of HLW canisters for glass beads-metal matrices is 2.5 times the number for calcine-metal matrices (Table 6) for a given waste volume. Time periods for 61-cm-diameter canisters are longer than is permitted by the current Federal regulation which requires repository isolation within 10 years of reprocessing.

The effect of allowing the centerline temperature of 300°C to limit the heat generation rate is also evident from data for water and air storage. However this requires that the previous criterion of $T_s \leq 53^{\circ}\text{C}$ be raised to $T_s \leq 80^{\circ}\text{C}$ for water storage. The melting point of the reference lead alloy is $\sim 326^{\circ}\text{C}$. For water storage, this requires that the maximum allowable outer surface temperature (T_s) limit be taken as $\leq 80^{\circ}\text{C}$ for the three diameters selected. Under these conditions, HLW canisters ≤ 30.5 cm in diameter of either calcine-metal matrices or glass beads-metal matrices can be filled at times ~ 0.5 years after discharge. When these results (*i.e.*, T_c limiting) are compared to the case where a 53°C wall temperature is limiting, the time that must elapse to reach the 5-kW repository heat limit remains the same but a shortening of the "to fill" storage time for encapsulated calcine is realized for diameters of 30.5 and 61 cm.

Results for air storage and a 300°C centerline limiting condition are given in the bottom portion of Table 11. The "to fill" storage time for 30.5-cm-diameter canisters is 3 years for encapsulated calcine and 1 year for glass beads encapsulated in a metal matrix. Both these "to fill" time requirements are longer than for water storage. This is a result of the heat-sink capacities of air being lower than those of water.

If a waste management objective is to fill a 30.5-cm-diameter HLW canister with encapsulated glass beads or calcine at times ≤ 1 year after reactor discharge, subject to limits of both $T_c \leq 300^{\circ}\text{C}$ and $T_s \leq 53^{\circ}\text{C}$, the data of Table 11 show that for matrices of calcine, only water "interim" storage is allowed, but either water or air storage of encapsulated glass beads satisfies the imposed criteria. Encapsulated calcine requires a longer "interim" storage period of 6.4 years due to its being a more concentrated waste form. Metal matrices of glass beads require only ~ 2 years of "interim" storage prior to transport to a repository although the number of such canisters is 2.5 times greater (Section II.A). Allowing the water-storage canister-wall temperature to be raised to $T_s \leq 80^{\circ}\text{C}$ shifts the limiting temperature to the 300°C centerline limit.

TABLE 11. Comparison of Maximum Total Heat Generation Rate of Reference Canisters Containing Calcine or Glass Beads in a Matrix of a Lead Alloy Stored in Water or Air

$Q_{\text{fill}}^{\text{max}}$ kW ^a	Waste Form	Storage Mode	T_c , °C	T_s , °C	D, cm	Storage Time ^b		
						"to Fill," years	"Interim," years	"to Repository," years
15	calcine	water	92	53 ^c	15.2	≤0.5 ^d	1.3	1.8
15	beads	water	92	53 ^c	15.2	≤0.5 ^d	---	0.5
30	calcine	water	131	53 ^c	30.5	1	6.4	7.4
30	beads	water	131	53 ^c	30.5	0.6	2.4	3
60	calcine	water	210	53 ^c	61	2.2	51.8	54
60	beads	water	210	53 ^c	61	0.8	17.2	18
84	calcine	water	300 ^c	80 ^e	15.2	≤0.5 ^d	1.3	1.8
84	beads	water	300 ^c	80 ^e	15.2	≤0.5 ^d	---	0.5
89	calcine	water	300 ^c	67 ^e	30.5	≤0.5 ^d	6.9	7.4
89	beads	water	300 ^c	67 ^e	30.5	≤0.5 ^d	2.5	3
93	calcine	water	300 ^c	57 ^e	61	1.5	52.5	54
93	beads	water	300 ^c	57 ^e	61	0.7	17.3	18
7.4	calcine	air	300 ^c	280	15.2	1.2	0.6	1.8
7.4	beads	air	300 ^c	280	15.2	0.5	---	0.5
13	calcine	air	300 ^c	265	30.5	3	4.4	7.4
13	beads	air	300 ^c	265	30.5	1	2	3
23	calcine	air	300 ^c	240	61	6	48	54
23	beads	air	300 ^c	240	61	2.5	15.5	18

^aCalculated from Eqs(4), (5), (6), and (7). A thermal conductivity value of 10 W/m-°C was used. These are the values at the time of HLW canister filling, which corresponds to the time "to fill."

^bStorage times are as defined in text.

^cThis temperature limits the maximum heat generation rate from the canister.

^dTimes less than 0.5 year may be possible based on the thermal analysis; however, shorter times will probably not be of interest due to additional problems in handling and chemical separation with short-cooled fuel.

^eThe previous limit of $T_s \leq 53^\circ\text{C}$ is increased to $\leq 80^\circ\text{C}$ so that the center-line temperature T_c becomes the limiting temperature.

f. Reference High-Melting (Aluminum Alloy) Metal Matrix of Calcine or Glass Beads in Water or Air Storage

The centerline temperature with an aluminum alloy is not a limiting condition because of its higher thermal conductivity and higher melting point. The result is that waste forms encapsulated in alloys similar to aluminum will be limited by the canister outer surface temperature. Water and air storage of metal matrices of an aluminum alloy limited by the HLW canister outer surface temperatures of $T_s \leq 53^\circ\text{C}$ and $T_s \leq 80^\circ\text{C}$ were examined. Results are shown in Table 12 for encapsulated calcine and glass beads.

The results for the allowable heat generation rate, "to fill," "interim," and "to repository" storage times for either a maximum surface temperature T_s of 53°C in water or 400°C in air are essentially identical. These values also are identical to those for lead-encapsulated waste forms subject to the limit of $T_s \leq 53^\circ\text{C}$ in water storage (Table 11).

The effect of increasing the maximum allowed outer surface temperature for water storage to $\leq 80^\circ\text{C}$ (as was done for the lead-alloy discussion) was also examined. Air storage of HLW canisters with outer surface temperatures greater than 400°C were not considered due to the potential for sensitization of stainless steel. If the limit of T_s is increased from 53 to 80°C in water storage, HLW canisters with diameters up to 61 cm containing either encapsulated calcine or glass beads can be filled as early as 0.5 year after reactor discharge (Table 12). The time to decay to the 5-kW repository limit ("to repository") if the T_s is 80°C initially remains the same as for a lower outer canister surface temperature limit. Thus, if shorter "to fill" times are desired, as perhaps will be the case for wastes from FBR fuel, there may be some incentive to establish the highest possible maximum limit for canister surface temperature in water.

g. Some Comparisons of Calcine and Glass Beads Encapsulated in Reference Alloys of Lead and Aluminum in Water or Air Storage

Based on the data given in Tables 11 and 12, identical maximum heat generation rates and storage times ("to fill," "interim," and "to repository") are allowed for water storage of lead-alloy matrices and for either water or air storage of aluminum-alloy matrices of calcine or glass beads when surface temperature limits of 53°C for water and 400°C for air are assumed. Air storage of lead-alloy matrices require longer storage times by a factor of ~ 3 prior to filling than either of the above cases in order to satisfy the T_c limit. This longer "to fill" time decreases the in-air "interim" storage time requirements since this is an older waste. The time required to achieve the repository 5-kW limit remains the same regardless of the type of matrix alloy or storage media. The "to repository" storage time varies only with the canister diameter (or volume). Thus, the effect of different melting points and thermal conductivities is to change the lengths of the "to fill" and "interim" storage times but not their sum.

Allowable canister surface temperatures of $\leq 80^\circ\text{C}$ for water storage of the aluminum-alloy matrices allow canisters of ≤ 61 -cm diameter to be filled at 0.5 year. Water storage of the (lead alloy) calcine metal-matrix does not allow "to fill" times shorter than 1.5 year for a 61-cm-diameter

TABLE 12. Comparison of Maximum Total Heat-Generation Rate of Reference Canisters Containing Calcine or Glass Beads in a Matrix of an Aluminum Alloy Stored in Water or Air

$Q_{\text{fill}}^{\text{max}}$ kW ^a	Waste Form	Storage Mode	T_c^a °C	T_s^a °C	D, cm	Storage Time ^b		
						"to Fill," years	"Interim," years	"to Repository," years
15	calcine	water; air	66; 413	53; ^c 400 ^e	15.2	≤0.5 ^d	1.3	1.8
15	beads	water; air	66; 413	53; ^c 400 ^c	15.2	≤0.5 ^d	---	0.5
30	calcine	water; air	79; 426	53; ^c 400 ^c	30.5	1	6.4	7.4
30	beads	water; air	79; 426	53; ^c 400 ^c	30.5	0.6	2.4	3
60	calcine	water; air	105; 452	53; ^c 400 ^c	61	2.2	51.8	54
60	beads	water; air	105; 452	53; ^c 400 ^c	61	0.8	17.2	18
84	calcine	water	153	80 ^{c,e}	15.2	≤0.5 ^d	1.3	1.8
84	beads	water	153	80 ^{c,e}	15.2	≤0.5 ^d	---	0.5
168	calcine	water	226	80 ^{c,e}	30.5	≤0.5 ^d	6.9	7.4
168	beads	water	226	80 ^{c,e}	30.5	≤0.5 ^d	2.5	3
336	calcine	water	372	80 ^{c,e}	61	0.5	53.5	54
336	beads	water	372	80 ^{c,e}	61	0.5	17.5	18

^aCalculated from Eqs(4), (5), (6), and (7). A thermal conductivity value of 30 W/m-°C was used. These are the values at the time of HLW canister filling, which corresponds to the time "to fill."

^bStorage times are as described in text.

^cThis temperature limits the maximum heat generation rate from the canister.

^dTimes less than 0.5 year may be possible based on the thermal analysis; however, shorter times will probably not be of interest due to additional problems in handling and chemical separation with short-cooled fuel.

^eThe limit of $T_s \leq 80^\circ\text{C}$ was used in order to fill 61-cm-diameter canisters at 0.5 year. This also corresponds to the limiting case for a 15.2-cm canister and a lead alloy where $T_c = 300^\circ\text{C}$ and $T_s = 80^\circ\text{C}$.

canister because of the 300°C centerline limiting temperature. Canisters of lead-encapsulated glass beads can be filled at 0.7 year. Increasing the allowable canister surface-temperature limit for the lead-alloy matrices introduces no further advantages due to the $T_c \leq 300^\circ\text{C}$ criterion. However, HLW canisters of <30.5-cm diameter with lead-encapsulated calcine or glass beads can be filled at times of 0.5 year (Table 11). Thus, water storage of lead-alloy matrices restricted to diameters ≤ 30.5 cm offers advantages similar to those for the higher-melting aluminum alloys.

h. Some Comparisons of Calcine with Metal Matrices of Calcine or Glass Beads in Water or Air Storage

The data in Tables 9, 11, and 12 show that, for canisters of a given diameter, the "to repository" time and the number of HLW canisters containing either calcine or calcine-metal matrices each remain constant. The "to repository" time for glass beads-metal matrices is always shorter because of the effective dilution (*i.e.*, glass additives and bead pores that are filled with metal) of waste, but this is accompanied by a corresponding increase in the number of waste canisters. The main differences evident in the above tables are the storage times when HLW canisters can be filled (*i.e.*, the "to fill" storage time) and thus the length of required "interim" storage periods to achieve the repository limit of a 5-kW heat generation rate for each canister.

Air storage of 30.5-cm-diameter canisters containing only calcine requires a "to fill" storage time (as spent fuel and/or high-level liquid waste) of 6 years prior to being packaged, and an additional 1.4 years of "interim" storage. Calcine-lead alloy composites require a "to fill" time of 3 years with 4.4 years of "interim" storage. Calcine/aluminum-alloy composites require a 1-year "to fill" storage time with 6.4 years of "interim" storage. For all three cases, 7.4 years must elapse prior to deposition in the repository. (The number of HLW canisters per waste volume is the same for all these examples.)

Similar HLW canisters of glass bead/lead-alloy composites require only 1 year of cooling (*i.e.*, "to fill" storage time) prior to filling of a HLW canister and 2 years of "interim" storage. These canisters are acceptable for isolation in a repository 3 years after reactor discharge, compared with 7.4 years for the calcine or metal encapsulated calcine waste. Aluminum-alloy/glass-bead composites decrease the "to fill" storage or cooling time to 0.6 year and require 2.4 years of "interim" storage.

Thus, if the objective is to use air storage for a 30.5-cm-diameter HLW canister to be filled less than 1 year after reactor discharge, either glass beads encapsulated in the low-melting lead alloy, followed by 2 years of interim storage, or calcine encapsulated in an aluminum alloy, followed by 6.4 years of "interim" storage, may be used. Since canisters cannot be filled with calcine until 6 years after discharge, calcine does not meet the assumed objective.

i. Some Comparisons of Glass with Metal Matrices of Calcine or Glass Beads in Water or Air Storage

Data in Tables 10, 11, and 12 can be used to compare glass monoliths with metal matrices of calcine or glass beads. In general, the heat generation rates of glass monoliths are limited by a 700°C centerline

temperature. Glass beads encapsulated in metal matrices are limited by either the canister outer-surface temperature or by the 300°C centerline temperature of the lead-alloy matrix. In either case, the much lower temperatures for metal-encapsulated glass beads probably help minimize glass devitrification (Section III.C). Glass monoliths, a more concentrated waste form than glass beads, require longer "to fill" and "to repository" storage times than do encapsulated glass beads. This is due to the increased dilution of the HLW caused by the void fraction of a column of spherical glass beads encapsulated in a metal matrix. A larger number of HLW canisters (~43% more) is required for encapsulated glass beads than for glass monoliths (Table 6) due to the dilution. Metal-encapsulated calcine is a more concentrated waste form with a smaller number of canisters but the longest "to repository" storage times. Depending upon the alloy and the maximum allowed values of T_s or T_c , encapsulated calcine can have longer or shorter "to fill" times than glass monoliths but not shorter "to fill" times than encapsulated glass beads.

These relationships can be illustrated for 30.5-cm-diameter canisters, stored in water with the restriction of $T_s \leq 53^\circ\text{C}$. Glass monoliths can be filled at 0.7 year, compared with 0.6 year for glass beads encapsulated in lead and 1 year for calcine encapsulated in lead. Aluminum alloys allow the same "to fill" times as do lead alloys. Raising the limit of T_s to $\leq 67^\circ\text{C}$ allows "to fill" storage times as short as 0.5 year for either glass beads or calcine encapsulated in either lead or aluminum alloys. This is shorter than the 0.7 year allowed for the 700°C centerline-limited glass monoliths. At the time of the initial filling, the lead alloy is centerline-limited at 300°C and the aluminum alloy is surface-temperature limited at 53°C. The time between the canister initial filling and decay to 5 kW (*i.e.*, "to repository") is 3 years for the encapsulated glass beads, 4.2 years for glass monoliths, and 7.4 years for encapsulated calcine. The "interim" storage periods are the differences between the "to repository" and "to fill" storage times and hence are somewhat dependent upon the outer canister surface temperature and the metal-matrix alloy selected.

3. Relationships of Maximum Allowable Canister Diameter and Age of Reference Waste Forms

For a selected "interim" storage environment and a given canister size, either T_s or T_c generally limits the maximum allowable heat-generation rate for waste at the time of the initial HLW canister filling. Increasing the time (*i.e.*, "to fill" time) interval after reactor discharge (*i.e.*, aging HLW waste), prior to filling a HLW canister, decreases the volumetric heat-generation rate of solidified HLW (Table 5 or Figs. 11 and 12). This fact allows successively larger-size HLW canisters to be employed with increasing age of solidified HLW if canisters are loaded so that their maximum heat generation rate satisfies maximum T_c and T_s criteria. The rate of decrease in the thermal power of HLW rapidly decreases during the first 5-10 years after reactor discharge; then the rate of decrease slows. For example, Table 5 shows a decay factor of ~20 in the first ten years but a factor of only ~10 during the succeeding ninety. This effect is more important when it is a waste-management objective to have the heat generation rates of HLW canisters decay to a prescribed lower limit within a required period of time. An example might be the requirement for a salt repository that ≤ 5 kW per canister be satisfied within a certain time period (*e.g.*, within 10 years of reprocessing, according to current Federal regulations).

A smaller number of larger-diameter HLW canisters is required for a given total volume of solidified HLW. The number of canisters will be most important for waste management handling operations involving interim storage, transportation to a repository, and final storage operations at a repository. A smaller number of canisters should reduce the magnitude of operations (*i.e.*, weld closures, canister inspections, *etc.*), transportation shipments, and inventory controls, and hence reduce waste-management costs. However, as the physical size of canisters is arbitrarily increased in order to minimize their number, the complexity of handling equipment and the magnitude of risks in the event of a canister breach increase. Ultimately, a balance of these types of coupled relationships and other criteria will probably define optimum canister sizes. Currently, no HLW canister design criteria are available. This section discusses for the reference waste forms some relationships between the maximum allowable canister diameter at the initial filling, the number of canisters per 1500 MTU, the interim storage time required (or aging) for HLW canisters to decay to ≤ 5 kW per package (the assumed salt repository acceptance criteria), and the time that solidified HLW has been out of a reactor (age of the waste).

Shown in Fig. 15 is a parameterization of the maximum allowable canister diameter for bulk calcine, glass monoliths, and calcine encapsulated in either an aluminum or a lead alloy *vs.* the earliest time after reactor discharge that these solidified HLW forms can be packaged. These data satisfy T_s and T_c criteria for either water or air environments. Assumed temperature criteria for Fig. 15 are $T_s \leq 80^\circ\text{C}$ for water, $T_s \leq 400^\circ\text{C}$ for air, $T_c \leq 700^\circ\text{C}$ for either calcine or glass, $T_c \leq 550^\circ\text{C}$ for waste encapsulated in aluminum and $T_c \leq 300^\circ\text{C}$ for lead. Canisters are assumed to be filled to a height of 3.05 m (10 ft).

Fig. 15. Maximum HLW Canister Diameter *vs.* Minimum Time After Discharge of Spent Fuel that Canisters May be Filled, Limited by Surface or Centerline Temperature. $T_c \leq 700^\circ\text{C}$ for glass, calcine; $T_c \leq 300^\circ\text{C}$ for Pb; ≤ 550 for Al. Water: $T_s \leq 80^\circ\text{C}$, $T_\infty = 38^\circ\text{C}$. Air: $T_s \leq 400^\circ\text{C}$, $T_\infty = 38^\circ\text{C}$.

The data of Fig. 15 illustrate the effect of delaying the time before filling a HLW canister (by increasing the "to fill" time) or HLW age through increased spent fuel storage and/or liquid HLW storage in order to employ larger-diameter canisters. The most sensitive effect occurs for aluminum-alloy metal matrices and the least sensitive for calcine. For example, for bulk calcine aged ~ 2 years, ~ 18 -cm-diameter canisters can be filled if water storage is used; for calcine aged ~ 10 years, ~ 42 -cm-diameter canisters could be employed. Thus, the number of HLW canisters of calcine for a given volume of solidified HLW could be reduced by a factor >5 by increasing by a factor of 5 the time, *i.e.*, "to fill" time.

The differences for water and air storage (Fig. 15) merit some comment. Maximum diameters for either calcine or glass monoliths do not differ significantly for water and air storage. For canister diameters $\lesssim 61$ cm and "to fill" times of $\lesssim 2$ years after discharge, there are only modest differences between water and air storage of calcine encapsulated in aluminum. However, a significant difference exists between water and air storage for lead-alloy metal matrices. A lowering of the maximum allowable diameter for air storage of lead alloys is caused by the relatively low centerline temperature criterion of $T_c \lesssim 300^\circ\text{C}$. This T_c is even lower than the $T_s \lesssim 400^\circ\text{C}$ canister surface temperature criterion for air storage. Thus, for a given diameter, the increased aging requirements from using air storage rather than water storage are greater for calcine encapsulated in lead alloys than for the other waste forms. In fact, air storage of calcine encapsulated in lead alloys requires a smaller-diameter canister and hence more canisters than does either water or air storage of glass monoliths. The incentive for using water storage for HLW canisters of lead-alloy matrices is illustrated by this example.

The minimum number of HLW canisters required to contain solidified HLW from the reprocessing of a given volume of spent fuel at various times after reactor discharge is also of interest. Such data for water storage are shown in Fig. 16. These data assume 1) that there is no restriction upon the canister diameter and 2) that the waste volume is from the reprocessing of 1500 MTU. A canister fill height of 3.05 m is assumed, and the appropriate T_s and T_c criteria defined for Fig. 15 are also satisfied. Figure 16 illustrates that metal encapsulation can reduce the number of HLW canisters and allow filling at times closer to reactor discharge (*i.e.*, shorter "to fill" times or less aging of spent fuel or high level liquid waste are required). This trend results primarily from an increase in the thermal conductivity of the waste form provided by metal encapsulation. It is important to recognize that canisters would have large and unrealistic or impractical physical sizes if the number of canisters is arbitrarily reduced.

As an example, compare (using Fig. 15 and 16) the diameters and "to fill" times if 100 HLW canisters are assumed to contain the solidified waste from 1500 MTU. This situation requires ~ 50 -cm-diameter (by 3.05-m fill height) HLW canisters for calcine and for calcine encapsulated in either aluminum or lead alloys and ~ 66 -cm-diameter canisters for glass monoliths. The "to fill"

* Arguments for the selection of $T_s \lesssim 80^\circ\text{C}$ for water storage have been given in Sections III.B.2.e, III.B.2.f, and III.B.2.g.

Fig. 16. Minimum Number of Canisters for Solidified HLW from 1500 MTU vs. the Minimum Time After Discharge Before Filling. $T_c < 700^\circ\text{C}$ for calcine or glass; $\leq 300^\circ\text{C}$ for Pb; $\leq 550^\circ\text{C}$ for Al. Water storage, $T_s \leq 80^\circ\text{C}$.

times are ~ 0.5 year for calcine encapsulated in aluminum, ~ 1.5 years for calcine encapsulated in lead, ~ 3.8 years for glass monoliths, and ~ 24 years for bulk calcine. The high thermal conductivity of aluminum coupled with a relatively high melting point or T_c criteria allows the shortest canister "to fill" times for 100 canisters. Lead-encapsulated calcine offers an improvement in shortening the "to fill" times over glass monoliths or calcine, but is somewhat limited by the $T_c \leq 300^\circ\text{C}$ criterion compared with the higher-melting aluminum alloy. The poor thermal conductivity of bulk calcine would require the most "to fill" time, ~ 24 years, if only 100 HLW canisters were employed. Glass monoliths, because of the dilution of the HLW with glass-forming additives, require a larger canister diameter for a given HLW volume. The thermal conductivity of glass monoliths is between that of calcine and that of metal-encapsulated calcine; hence, the "to fill" or aging requirements are also intermediate.

4. Conditions Required of Reference Waste Forms for Shipment to Salt Repository at Ten Years After Discharge

a. Introduction

With the current Federal regulations, which require disposal of HLW at a Federal repository within ten years of generation, there is interest in discussing "to fill" times and canister sizes utilizing water and air interim storage that are within this ten-year time interval. This section discusses waste canister sizes for the reference waste forms that can be filled at ≤ 10 years after discharge and will have no greater than a 5-kW heat generation rate at 10 years after discharge. The shortest "to fill" time is assumed to be 0.5 year after reactor discharge. Canisters are assumed to be filled to a height of 3.05 m. Temperature criteria required are $T_s \leq 80^\circ\text{C}$ for water interim storage, $T_s \leq 400^\circ\text{C}$ for air interim storage, $T_c \leq 700^\circ\text{C}$ for calcine and glass monoliths, $T_c \leq 550^\circ\text{C}$ for aluminum alloys, and $T_c \leq 300^\circ\text{C}$ for lead alloys. Under these conditions, the "to fill" and "interim" storage time intervals are derived. Some comparisons of the increased thermal heat transfer benefits of the different waste forms are given in order to identify the advantages of metal encapsulation.

Table 13 shows the maximum-allowable-diameter canister for each reference waste form that has a 5-kW heat generation rate 10 years after discharge (based on Table 5). Larger-diameter canisters than these require more than 10 years after discharge to decay to 5 kW. Smaller diameters would decay to 5 kW prior to 10 years after discharge. The "to fill" times satisfying the assumed temperature criteria (Table 4) were calculated using data of Section II. "Interim" storage times are the time increments, 10 years minus the derived "to fill" times. The effect of increased thermal conductivity is best illustrated for water storage by comparing the 6-year "to fill" time for calcine with any of the metal-encapsulated waste forms. The same trend, less pronounced, exists for air storage. It should be noted that the same number of canisters for a given volume of waste (*i.e.*, 217 canisters per 1500 MTU) is required for any of the reference waste forms. However, canister diameters (volumes) differ in order to allow for the volume increase caused by dilution effects (*i.e.*, glass additives, glass bead porosity) of glass.

b. Conclusions

Calcine, as directly produced and put into HLW canisters, minimizes the number of additional solidification process steps. However, rather long "to fill" waiting periods must be imposed in order to avoid exceeding the limiting centerline temperatures. Such time delays may be achieved by storing spent fuel and/or high-level liquid waste or any combination of these. The alternative is to institute further process steps to produce glass monoliths or metal-encapsulated waste forms in order to shorten the "to fill" time intervals while also improving the dispersibility properties of the waste forms. These latter properties may play a large role in the degree of the public's acceptance of any waste management practice.

TABLE 13. "To Fill" and "Interim" Storage Times for Canisters Shipped at 10 Years with a Heat Generation Rate of 5 kW per Canister

Waste Form	Canister Diameter, ^a cm	Storage Time ^b			
		Water		Air	
		"To Fill," years	"Interim," years	"To Fill," years	"Interim," years
Calcine	34	6 ^c	4	7.4 ^c	2.6
Glass Monolith	45	2 ^c	8	3 ^c	7
Glass Beads-Pb Alloy	54	0.5 ^{c,d}	9.5	2.4 ^c	7.6
Calcine-Pb Alloy	34	0.5 ^{c,d}	9.5	3.2 ^c	6.8
Glass Beads-Al Alloy	54	0.5 ^d	9.5	0.7 ^e	9.3
Calcine-Al Alloy	34	0.5 ^d	9.5	1.7 ^e	8.3

^aThis is largest-diameter HLW canister that can be filled with the assumed HLW waste form within 10 years of reactor discharge and have a 5-kW heat generation rate per canister (3.05-m fill assumed) at 10 years after reactor discharge. Canisters each contain the high-level waste from reprocessing of 6.9 MTU.

^bThe maximum "interim" storage time is 9.5 years. Solidified HLW is assumed to not be generated within 0.5 year after reactor discharge; it is shipped to a Federal repository 10 years after reactor discharge.

^cShorter "to fill" times are prohibited by maximum centerline criteria.

^dFuel is assumed to not be reprocessed at times less than 0.5 year after reactor discharge.

^eShorter "to fill" times are prohibited by maximum canister surface-temperature limits of $\leq 400^{\circ}\text{C}$ in air.

Table 13 identifies conditions under which metal encapsulation of HLW offers advantages (based on thermal criteria) over calcine and glass monoliths. Water basin-storage of HLW metal-matrix canisters offers significantly shorter "to fill" times than calcine or glass monoliths. This can be advantageous in minimizing liquid high-level waste storage requirements or in shortening the time period in which fuel can be reprocessed with immediate solidification of high-level waste.

Lead alloys provide the same net advantage that aluminum alloys offer for water storage in regards to shortening the "to fill" storage time. However, a $\leq 80^{\circ}\text{C}$ outer-surface temperature criterion of a HLW canister in water "interim" storage was employed as well as a $\leq 300^{\circ}\text{C}$ centerline temperature limit of lead alloys, and acceptance of these criteria for the length of "interim" storage periods assumed may need more examination. Lead, because of its lower melting point, should be adaptable to a lower-temperature encapsulation process than aluminum and thus may be a more desirable choice to industry for an alloy in future encapsulation schemes if water "interim" storage is employed.

Only if aluminum alloys are used does air storage and metal encapsulation of pelletized or stabilized calcine or glass beads offer net advantages over calcine and glass monoliths. In fact, the relatively low $\leq 300^{\circ}\text{C}$ centerline limit imposed for calcine/lead-alloy matrices requires approximately the same "to fill" period as glass monoliths and so there is no net benefit, and perhaps a slight time penalty, for encapsulation in lead.

5. Overview of the Thermal Analysis

Interpretation of data on the use of a metal matrix for encapsulation of solid high-level waste is complicated by the many variables and their lack of independence. In order to provide a final overview of the results of some of these calculations, some data for glass monoliths, calcine, metal-encapsulated glass beads, and metal-encapsulated calcine have been reassembled into five scenarios. These represent potential answers to a question likely to be posed by a potential plant manager: What are the options and their consequences of minimizing the number of HLW canisters? The five examples selected do not cover all possible situations but can serve as a guide for many typical examples. For comparison purposes, the use of internal fins with canisters of glass monoliths and calcine has also been estimated. This was done by assuming that thermal conductivity would increase by a factor of two (consistent with PNL's fin design, which roughly allows a doubling of the allowable heat generation rate) and no volume increase (roughly 5% is lost) due to the fins [CHIKALLA].

The scenarios considered are as follows:

Scenario 1

Solidified HLW is shipped 10 years after reactor discharge from the reprocessing plant to a repository that requires a maximum heat generation rate of 5 kW per canister. It is assumed that 38°C water-basin storage is used for heat dissipation and shielding at the reprocessing plant for the entire "interim" storage period. Solidification and filling of canisters can take place any time before 10 years (the "to fill" time). What is the number of such (≤ 5 kW) canisters (3.05-m fill height is assumed) that must be transported to the repository from the reprocessing of 1500 MTU, what is their heat generation rate, and what is the minimum time after reactor discharge that the canisters can be filled?* In this example, the canister diameter is held constant at 34 cm, and the "to fill" time and number of canisters are varied. Results are given in Table 14.

Comments on Scenario 1

All of these waste-management alternatives produce canisters for transport at 10 years with a ≤ 5 kW heat generation rate. Also given is the maximum allowable heat generation rate ($Q_{\text{fill}}^{\text{max}}$) at the earliest time the HLW canisters can be filled ("to fill" time) without exceeding the maximum centerline temperature ($\leq 700^{\circ}\text{C}$ for calcine and glass monoliths; $\leq 300^{\circ}\text{C}$ for lead metal matrices; $\leq 550^{\circ}\text{C}$ for aluminum metal matrices) or outer-canister surface

* Additional constraints, possibly limiting, are the centerline temperature of the canister, or the wall temperature during interim storage. These are listed in the subsequent discussion.

TABLE 14. Data for Scenario 1

Waste Form	Storage Times			D, cm	Q_{ship}^c kW	No. of Canisters per 1500 MTU
	$Q_{fill}^{max\ a}$ kW	"To Fill," years	"Interim," ^b years			
Calcine	7.4	6	4	34	5	217
Calcine (internal fins)	~15	~2.2	~7.8	34	5	217
Glass Monolith (no fins)	25	~1	~9	34	2.9	380
Glass (internal fins)	~50	~0.5	~9.5	34	2.9	380
(Pb or Al) Metal-Matrix/ Calcine	90	0.5	9.5	34	5	217
(Pb or Al) Metal-Matrix/ Glass Beads	90	0.5	9.5	34	2	543

^aMaximum heat generation rate of canister at time of filling.

^bTime between filling of canister and shipment to repository; storage is in water.

^cHeat generation rate of canister at shipment time (sum of "to fill" and "interim" time increments).

temperature ($\leq 80^{\circ}\text{C}$ for water basins; $\leq 400^{\circ}\text{C}$ for air basins). It should be noted that the sum of the "to fill" time and "interim" storage time is the time (i.e., 10 years) of shipment to a repository. During the time before HLW canisters can be filled, 1) spent fuel assemblies may be stored until reprocessing and the HLW directly solidified or 2) spent fuel assemblies may be stored until reprocessing after which liquid HLW may be stored until solidification. Often the option of eliminating liquid HLW storage by increasing the spent-fuel storage time so that immediate solidification can take place after processing does not receive enough explicit consideration, especially since there is an increasing supply of "aged" spent fuel.

Under these conditions, the use of calcine or calcine encapsulated in metal results in the minimum number of canisters. Unencapsulated calcine requires the longest storage time (as spent fuel and/or liquid HLW) before canisters can be filled (6 years); metal matrices of calcine offer the shortest at 0.5 year. Glass monoliths require ~ 1 -year HLW "age" before canisters can be filled and require an increase in the number of canisters due to the dilution of the solidified HLW. Internal fins in glass canisters can shorten the "to fill" or "aging" time to ~ 0.5 year, but this does not change the number of canisters. Metal matrices of glass beads can shorten the time in which canisters can be filled to 0.5 year but increase the number of canisters by a factor of ~ 2.5 compared to calcine. Internal fins in canisters containing calcine shorten the time after discharge that canisters can be filled from 6 to ~ 2.2 years. Notice that glass monoliths and glass beads encapsulated in metal produce canisters having heat generation rates significantly lower than 5 kW. This could result in the burial of more than one canister per repository hole, thus mitigating some of the extra costs associated with the increased number of canisters per unit of spent fuel reprocessed.

Scenario 2

All conditions of Scenario 1 are assumed to be the same except that (1) the number of canisters is held constant (at the minimum possible for calcine of $0.040 \text{ m}^3/\text{MTU}$; glass monoliths $0.070 \text{ m}^3/\text{MTU}$; glass beads $0.10 \text{ m}^3/\text{MTU}$) and (2) the canister diameter and the time of canister filling are varied. Results are shown in Table 15.

Comments on Scenario 2

All canisters are ready for the repository at 10 years with a 5-kW heat generation rate. The major difference between this scenario and Scenario 1 is that the number of canisters with 5-kW heat generation rates at 10 years after reactor discharge is the same. However, achieving this requires a penalty for the glass monolith forms. The penalty is an increase in the minimum time that must pass (either as spent fuel and/or liquid HLW storage) before HLW canisters can be filled. Glass monoliths in canisters with internal fins may have a negligible increase compared to Scenario 1. Metal matrices of glass beads can be filled at 0.5 year while the number of canisters (larger in diameter) is a minimum at 217. Thus with only moderate increases in the minimum "to fill" time, a larger-diameter HLW canister can be made (Scenario 1 vs. Scenario 2) so that the number of canisters is the same for all waste-treatment alternatives.

TABLE 15. Data for Scenario 2

Waste Form	Storage Times			D, cm	Q_{ship}^c kW	No. of Canisters per 1500 MTU
	$Q_{fill}^{max\ a}$ kW	"To Fill," years	"Interim," ^b years			
Calcine	7.4	6	4	34	5	2.7
Calcine (internal fins)	~15	~2.2	~7.8	34	5	217
Glass Monoliths (no fins)	25	2	8	45	5	217
Glass (internal fins)	~50	~0.6	~9.4	34	5	217
(Pb or Al) Metal-Matrix/ Calcine	90	0.5	9.5	54	5	217
(Pb or Al) Metal-Matrix/ Glass Beads	90	0.5	9.5	34	5	217

^aMaximum heat generation rate of canister at time of filling.

^bTime between filling of canister and shipment to repository; water storage is assumed.

^cHeat generation rate of canister at shipment time (sum of "to fill" and "interim" time increments).

Scenario 3

The objective is the same as for Scenario 1 (*i.e.*, to ship at 10 years after reactor discharge with a ≤ 5 kW heat generation rate per HLW canister) but 38°C *air* storage is assumed rather than 38°C water storage. What is the number of such (≤ 5 kW) canisters that must be transported at 10 years, what is their heat generation rate, and what is the shortest time after reactor discharge that the canisters can be filled? The canister diameter is held constant at 34 cm, and the "to fill" time and number of canisters are varied. Results are shown in Table 16.

Comments on Scenario 3

The same number of canisters results as for Scenario 1. The major difference between this and Scenario 1 is that the minimum "to fill" time is generally increased (because of lower maximum allowable heat generation rates $Q_{\text{fill}}^{\text{max}}$ at the initial filling); an exception is air storage of aluminum metal-matrix/glass beads which remains the same. An advantage of the higher melting point of aluminum over lead metal matrices is reflected in the greater minimum time for filling of canisters with lead metal matrices than with aluminum metal matrices. Thus, lead metal matrices/calcine lose some advantage (in "to fill" time) with air storage but still produce a smaller number of canisters than do glass monoliths. Canisters of glass monoliths and metal-encapsulated glass beads have significantly lower than 5-kW heat generation rates 10 years after discharge.

Scenario 4

This scenario (38°C air storage; ≤ 5 kW per canister at 10 years after discharge) has the same assumptions as Scenario 3 except that the number of canisters is held constant and the canister diameter and "to fill" time are varied. Results are shown in Table 17.

Comments on Scenario 4

There are differences in minimum "to fill" times and HLW canister size. Lead metal matrices (due to the relatively low 300°C centerline limit) show a slight disadvantage in minimum "to fill" time when compared with glass monoliths (with or without internal fins) and aluminum metal matrices.

Scenario 5

The diameter of HLW canister is not of concern in this case and solidification can take place at any time less than 7 years after reactor discharge. Interim storage of filled canisters at the reprocessing plant in water basins is assumed. What is the number of canisters per 1500 MTU, how long must canisters be stored to decay to 5-kW heat generation rates per package, and what is the minimum time in which they can be filled? Results are shown in Table 18.

TABLE 16. Data for Scenario 3

Waste Form	Storage Time			D, cm	Q _{ship} , ^c kW	No. of Canisters per 1500 MTU
	Q _{fill} ^{max a} kW	"to Fill," years	"Interim," ^b years			
Calcine	6.2	7.4	2.6	34	5	217
Calcine (internal fins)	13	3.1	6.9	34	5	217
Glass Monoliths (no fins)	16	1.8	8.2	34	2.9	380
Glass (internal fins)	26	1	9	34	2.9	380
Pb Metal-Matrix/ Calcine	15	3.2	6.8	34	5	217
Al Metal-Matrix/ Calcine	33	1.7	8.3	34	5	217
Pb Metal-Matrix/ Glass Beads	15	1.3	8.7	34	2	543
Al Metal-Matrix/ Glass Beads	33	0.5	9.5	34	2	543

^aMaximum heat generation rate of 34-cm-diameter canister at time of filling.

^bTime between filling of canister and shipment to repository; air storage is assumed.

^cHeat generation rate of canisters at shipment time (sum of "to fill" and "interim" time increments).

TABLE 17. Data for Scenario 4

Waste Form	Q_{fill}^{max} ^a kW	Storage Time		D, cm	Q_{ship}^c kW	No. of Canisters per 1500 MTU ^c
		"to Fill," years	"Interim," years			
Calcine	6.2	7.4	2.6	34	5	217
Calcine (internal fins)	13	3.1	6.9	34	5	217
Glass Monoliths (no fins)	17	3	7	45	5	217
Glass (internal fins)	28	1.5	8.5	45	5	217
Pb Metal-Matrix / Calcine	15	3.2	6.8	34	5	217
Al Metal-Matrix / Calcine	33	1.7	7.3	34	5	217
Pb Metal-Matrix / Glass Beads	21	2.4	7.6	54	5	217
Al Metal-Matrix / Glass Beads	53	0.7	9.3	54	5	217

^aMaximum heat generation rate of canister at time of filling.

^bTime between filling of canister and shipment to repository; air storage is assumed.

^cHeat generation rate of canisters at shipment time (sum of "to fill" and "interim" time increments).

TABLE 18. Data for Scenario 5

Waste Form	Storage Time			No. of Canisters ^b per 1500 MTU
	"to Fill," years	"Interim," ^a years	D, cm	
Calcine	5	2.4	30.5	270
	1.2	0.6	15	1078
Glass Monoliths (no fins)	~7	59	91.5	53
	~3.2	28	61	118
	~0.7	3.5	30.5	471
Glass (internal fins)	~2	29	61	118
	0.5	3.7	30.5	471
Pb Metal-Matrix/ Calcine	~7	106	122	17
	~4	80	91.5	30
	~2	52	61	67
	0.5	6.9	30.5	270
Al Metal-Matrix/ Calcine	1.5	111.5	122	17
	~1	83	91.5	30
	0.5	53.5	61	67
Pb Metal-Matrix/ Glass Beads	2.5	69.5	122	43
	1.7	44.3	91.5	75
	0.7	17.3	61	168
	0.5	2.5	30.5	675
Al Metal-Matrix/ Glass Beads	0.6	~71	122	43
	0.5	~45	91.5	75
	0.5	~17	61	168
	0.5	~2.5	30.5	675

^aTime between filling of canister and shipment to repository; water storage is assumed.

^bCanisters have a 5-kW heat generation rate at the time of shipment to a repository; shipment time is the sum of the "to fill" and "interim" storage increments.

Comments on Scenario 5

The time that must pass before HLW canisters can be shipped with a 5-kW heat generation rate is the sum of the "to fill" time and the "interim" storage time. As one extreme example, all the wastes from the reprocessing of 1500 MTU, if aged to 1.5 years, could be contained in 17 canisters as aluminum metal-matrix/calcine. However, these 122-cm (4-ft) diameter x 3.05-m (10-ft)-long canisters would have to be held in "interim" storage for 111.5

years and could not be shipped to a repository requiring 25 kW heat generation rates per canister until 113 years after reactor discharge. If the size were reduced to 61-cm (2-ft) diameter x 3.05-m (10-ft) long, the time before shipment (at 5 kW per canister) would be reduced to 54 years but the number of canisters would be increased to 67.

The results of this scenario illustrate the increase in "interim" storage time required to achieve a 5 kW per canister maximum heat generation rate if the number of canisters for transport is arbitrarily reduced by increasing their diameter. Increased handling difficulties are a problem with large diameters but were not considered here. This also illustrates the importance of selecting as large as possible a heat generation rate per canister for a HLW repository in order to reduce the number of canisters that must be shipped and to reduce the interim storage time periods.

C. Comparison of Glass Monoliths to Glass Beads Dispersed in a Metal Matrix

1. Introduction

Glass beads approximately 1-10 mm in diameter encapsulated in a metal matrix offer advantages compared with large glass monoliths. Comparison of the heat transfer differences are given in Section III.B.2.i. However, whether metal encapsulated glass beads or glass monoliths are employed in waste management, a high temperature ($\geq 1050^{\circ}\text{C}$) glass vitrification process would be required. Typical glass-monolith fabrication concepts require either pouring softened glass into a preheated HLW canister or a direct "in-canister melting" process [BLAIR]. Both processes subject the canister walls to temperatures $\geq 1050^{\circ}\text{C}$ for a period of time, and the softened glass causes some, but probably negligible, corrosion of the interior prior to cooling [MANESS]. Corrosion rates of ~ 0.1 in./month at 1050°C have been reported [MENDEL-3] for stainless steel canisters.

Stainless-steel canister materials can become sensitized (i.e., by chromium carbide precipitation in the grain boundaries) at temperatures of $427-790^{\circ}\text{C}$ ($800-1450^{\circ}\text{F}$). The rate of sensitization is a time- and temperature-dependent process that is not fully understood [MECHAM]. Sensitized HLW canisters of glass monoliths are more susceptible to failure by stress corrosion cracking because, after fabrication, canisters are left with an induced tensile stress and the glass monolith is in compression. This is a result of the coefficient of expansion of stainless steel being twice that of glass. Failures due to this mechanism in actual HLW canisters containing glass monoliths have been reported [KATAYAMA-1]. Use of container materials other than stainless steel (e.g., black iron, brass, etc.) may remove the sensitization problem, but canisters are still likely to be stressed.

Encapsulation of glass beads in a low-melting alloy such as lead can eliminate or reduce the stressed-canister failure mechanism. For example, casting of glass beads dispersed in a lead matrix requires maintaining the canister wall temperature at $\leq 400^{\circ}\text{C}$. Further, metal alloys would tend to shrink slightly away from the canister wall during solidification, eliminating "stressing" of a canister. This may be a very important aspect for long-term storage of waste canisters. The resulting thermal contact resistance should present no unsolvable problems, yet needs some examination.

Canisters of large glass monoliths require long periods to be cooled from fabrication temperatures ($>1000^{\circ}\text{C}$) to equilibrium temperatures because of their low thermal conductivity and their susceptibility to thermal shock. Rapid rates of cooling can produce excessive cracking of large glass monoliths, and hence larger surface areas of the HLW form [ROSS-3]. Surface area increases by factors as large as ten for glass monoliths have been proposed for normal handling and processing conditions [MENDEL-3]. A wide range of cooling rates of $\sim 20\text{--}500^{\circ}\text{C}/\text{hour}$ have been used for 30.5-cm-diameter glass monoliths [ROSS-3]. Such rates have increased the surface area by factors as large as 15. Cooling rates of $\sim 2^{\circ}\text{C}/\text{hour}$ are required to avoid any cracking. Thus, to cool a glass monolith from 500°C with minimal cracking can require ~ 250 hours. Alternatively, glass beads of 1-5-mm diameter can be cooled to room temperature within a minute with no cracking [HEIMERL, VANGEEL-1]. The increased thermal conductivity due to the presence of the metal phase for glass beads encapsulated in metal would allow very short cooling times for lead/glass bead composites. Such a property should be desirable for an industrial process.

Data [MENDEL-5] show that the leach rate and porosity of glass monoliths increase somewhat with storage temperatures greater than 500°C , as shown in Fig. 17. Increased crystallization (i.e., devitrification) of glass produces phases of water-soluble cesium and strontium molybdates that increase the leach rate of glass if cracking and/or water contact occurs. Segregation of these phases, or other somewhat insoluble constituents (e.g., CeO_2), during the glass-softening process can also cause localized "hot" spots due to the radioactive decay. This has the potential of locally raising the temperature and causing even further devitrification. Thus, techniques that lower the maximum temperatures of glass should help to maintain a good leach resistance. Metal encapsulation of glass beads, coupled with water-basin "interim" storage, could maintain the temperature of the glass at values near the wall temperature of the canister, well below 500°C , and probably enhance the long-term predictability of leach rates and surface areas.

Porosity is associated with microcracking of a glass monolith and is due to the formation of zinc silicate phases in the glass network. The cracking is caused by the different thermal expansion coefficients of the zinc silicate phase and the glass [MENDEL-5]. Figure 17 shows increasing porosity, or a depletion of zinc, at storage temperatures above 500°C . This phenomenon is another mechanism for increasing the surface area of glass monoliths with increasing glass temperatures. Proper "interim" storage of metal-encapsulated glass beads should eliminate this degradation mechanism.

The properties or attributes discussed above have resulted from the increased thermal conductivity provided by the metal matrix. Metals are somewhat ductile, while glass is brittle. Impact tests [SMITH] of glass monoliths have determined the extent of fracturing for some scenarios. Fracturing can contribute to increased dispersibility risks because of an increased surface area and the generation of airborne particles ($<10\text{ }\mu\text{m}$). The glass-monolith impact tests did not indicate a significant increase in surface areas or generation of airborne particles. However, similar impacts tests with metal encapsulated glass beads should, when performed, allow the ductile matrix to absorb some of the mechanical energy and reduce the risks of dispersion by fracturing even further. Such a property may be particularly appealing to the public although technically the probability of breaching the primary shipping cask and canister is so low that the increased product attributes may be rather small.

Fig. 17. Physical and Chemical Changes Due to Devitrification (2 months storage at temperature) [MENDEL-5].

2. Conclusions

Glass beads dispersed in a metal phase have a much lower temperature gradient than glass monoliths due to the increased thermal conductivity. With water or air storage, the centerline temperature of glass beads dispersed in a metal matrix can be reduced to within ~50°C of the outer-wall temperature for ~2-year-old waste in a 30.5-cm-diameter canister (*e.g.*, Tables 11 and 12). Water storage of glass beads encapsulated in lead can serve to maintain a glass waste form well below 400°C and should significantly reduce the magnitude of the detrimental effects of increasing leachability, porosity, and phase separation. The surrounding ductile metal phase should help reduce fracturing of the waste form during mechanical impacts. Metal-matrix encapsulation of glass beads may help 1) maintain a predictable surface area of the waste form for safety analyses and 2) minimize dispersal from mechanical impacts and perhaps leaching/corrosion.

IV. CONCEPTUAL PROCESSES

A. Introduction

In order to illustrate the application of data on the development of metal-matrix encapsulation to the management of high-level waste, it is instructive to formulate a conceptual process outline based on existing information in the literature. Areas in which information important to process feasibility and execution are missing, including data related to the safety and economics of the proposed process, can be identified by this means. Figure 18 summarizes the general sequence of process steps that are required to transform high-level liquid waste (HLLW) into a metal-encapsulated solid form and to isolate the waste in a geologic formation. Solid waste forms that are included are either agglomerated, sintered, stabilized calcine or glass beads. Techniques for metal encapsulation include casting and powder metallurgical fabrication. These processes and operations have been discussed in this review to various degrees of detail; some of their attributes and weaknesses have been identified.

Fig. 18. Flowsheet for Metal Encapsulation of High-Level Waste. (The reference process follows the solid lines).

A solid line in Fig. 18 denotes a reference path for which a conceptual encapsulation flow sheet will be discussed in more detail. The dashed paths (*i.e.*, a powder metallurgical encapsulation process) may provide equally attractive routes to an acceptable HLW form. However, the pressing need to demonstrate a waste-management technology requires a timely narrowing of options to those believed to be in the most developed stages and to those that show the least technologic difficulties in implementation. Casting of solid metal is currently believed to be the leading candidate for an encapsulation process that can be demonstrated with a lesser effort and on a more rapid time schedule than the other options for metal encapsulation. Further, if reliable

agglomeration techniques can be developed, sintered, stabilized calcine can be made at a modest ($\sim 800^{\circ}\text{C}$) temperature without any liquid phases. Note that vitrification required for glass beads fabrication requires liquid phases at temperatures above 1000°C , perhaps with anticipated corrosion problems. Thus, the former route may be a more desirable process eventually for industrial application than vitrification. Nevertheless, metal-encapsulated glass beads retain the advantages of glass which is the currently favored waste management alternative, but avoid many of the detrimental effects of monolithic glass. Hence, encapsulated glass beads may become an even more acceptable solid waste form than glass monoliths. The choice of a final waste form may ultimately be made in part on the basis of the operational details of the processes (e.g., temperatures, volatility, corrosion, process reliability, off-gas handling) and factors that minimize secondary waste streams, rather than entirely on the attributes of the solid products since all three forms appear to be technically acceptable. Metal encapsulated glass beads are not discussed further as a reference process in this section.

B. Conceptual Flowsheet for Waste Encapsulation by Casting

1. Introduction

A conceptual flowsheet for the encapsulation of solid HLW in a metal matrix is shown in Fig. 19. The reference path (solid lines of Fig. 18) employs agglomerated, sintered, stabilized calcine that is ultimately encapsulated in a metal matrix by casting. The process explicitly leaves a protective envelope of pure metal surrounding the outermost HLW granules. The envelope serves to reduce the risk of waste dispersion into the environment as a result of aqueous leaching or mechanical impacts coupled with a canister breach. Sintering of the calcine during the agglomeration-stabilization portion of the process, prior to metal encapsulation, serves to reduce risks of dispersion of radionuclides by volatility in any accident scenarios resulting in fires, at least in fires whose temperatures do not exceed those at which the waste was sintered. The protective metal envelope is believed to be amenable to widespread technical, industrial, and public acceptance.

The process steps in the reference flowsheet of Fig. 19 are briefly summarized below. Examination of these process steps in more detail will provide an estimate of the flow rates and volumes and partially identify existing technology, process parameters and assumptions. Solids transfer operations are not detailed in this report but they certainly pose some uncertainties that will require either modifications or development of techniques as used in other existing waste-management operations (i.e., transfer of solids from calciners to storage bins at INEL or transfers from the spray calciner to the in-can vitrification units at PNL).

2. Waste Characterization

For discussion purposes, the basic flow rate of Fig. 19 assumes that wastes from a 5 MTHM/day reprocessing plant are treated. The total daily liquid volume of waste from the reprocessing of 5 MTHM is taken as ~ 4200 L,*

*Combination of intermediate and high level waste types simplifies waste management schemes. Early calciner development problems with wastes having a large sodium ion content (i.e., primarily due to ILLW wastes from Na_2CO_3 solvent scrubs) are believed soluble by work demonstrated at INEL [FREEBY-1, FREEBY-2], and PNL [BJORKLUND-1, BONNER].

Fig. 19. Waste Solidification Flow Rate for 5 MTHM/Day Reprocessing Plant (LWR Fuel).

prior to calcination [FREEBY-1]. For fuel processed 1.4 years after reactor discharge, the total radioactivity content of the wastes would be of the order of 10^6 Ci/day [KEE] and the total heat generation rate would be ~ 27 kW/day (Table 5).

3. Calcine, with Stabilization Option

The entire daily liquid HLW product is assumed to be solidified at $\sim 550^\circ\text{C}$ into a reference bulk calcine totaling $\sim 0.2 \text{ m}^3$ per day or $\sim 400 \text{ kg}$ (Table 4). No explicit choice is made in this study between a spray calciner [BONNER] and a fluidized-bed calciner [FREEBY-1, BJORKLUND-1]. Details of these calciners are also discussed elsewhere [ERDA]. A conceptual design for a 5 MTHM/day (~ 2 -ft-ID) commercial waste fluidized-bed calciner is in progress [VALENTINE]. The flowsheet may assume that residual nitrates and water levels are reduced to $<0.02 \text{ wt } \%$ nitrates and $<0.006 \text{ wt } \%$ water by a fluidized-bed drying technique at 600 – 700°C [RINDFLEISCH]. Insignificant ruthenium and cesium releases have been observed during drying at fluidizing velocities of 0.2 – 0.5 ft/sec . Studies of the results of a loss of fluidizing velocity on a rise in bed temperature due to waste-heat generation in a calciner or drying chamber having a diameter of $<2.5 \text{ ft}$ have shown that very rapid responses restoring fluidization are not required to avoid detrimental effects (*i.e.*, bed agglomeration or volatilization of fission products) [SCHINDLER]. In fact, a

secondary, redundant, fluidizing air supply of modest size and with response times of $\sim 1/2$ hour for 1-year-aged waste or 3 hours for 5-year-aged waste should be adequate to prevent detrimental effects [SCHINDLER]. A final flow sheet may not require separate stabilization process steps after calcination, depending on additives or binders employed in subsequent steps as the sintering process can be used to achieve stabilization prior to canister filling and sealing.

4. Blend*

After calcination, ~ 10 wt % additives, (*e.g.*, metakaolin and H_3PO_4 , HNO_3 as used by [SAMSEL-1], or the INEL flux used by [SAMSEL-2], or glass frit [ROSS-2]) that serve to chemically fix, after sintering, the more leachable and toxic longer-lived radionuclides (^{137}Cs , ^{90}Sr), are blended with the solidified, powdered, calcined HLW. This study does not attempt to identify specific blending equipment. However, equipment sizes are small since ~ 20 kg/hour would have to be blended if a continuous plant operation was assumed. Even larger but arbitrary batches (*i.e.*, 440 kg/batch) should be readily achievable. When blending equipment is selected, problems of dust control and specific heat evolution (~ 0.06 kW/kg for 1.4-year-cooled fuel) will have to be addressed. Dusting problems may be surmountable with filter blowback and recycle techniques already developed for calciners [BJORKLUND-2].

5. Agglomerate*

Premixed solids (*i.e.*, calcine and additives) are transferred to an agglomeration device where wet binders (*e.g.*, water or H_3PO_4 - HNO_3 in 3:1 volume ratio as used at INEL [SAMSEL-1]) are added to the premixed solids to increase the calcine powder-particle-size distribution sufficiently into granules (*e.g.*, 1-5 mm) which allow successful encapsulation in metal. Techniques using a disc pelletizer (agglomerator) have been partially developed and support this process step [ROSS-2, SAMSEL-1]. The device has been run at its minimum production rate of ~ 20 kg/hour and is of sufficient size for plant-scale operations, if reliability and adaptation to remote maintenance can be demonstrated [ROSS-2]. To ensure continuous formation of a good product, quality control inspections of the green granules could be instituted. Granules not meeting composition criteria could be cycled back to the blending stage, perhaps after a single crushing operation, for composition adjustments and another cycle. Problem areas needing careful examination during development are volumetric heat generation rates of the calcine, dust control, remote maintenance, and corrosion if H_3PO_4 were used as an additive-binder. Alternatives to the disc pelletizer, perhaps simple automated press and dye machines for pelletizing, may also be found desirable.

6. Sinter

The agglomerated waste granules are then sintered at $\sim 800^\circ C$ to chemically fix select radionuclides with the additives and to remove volatiles (*e.g.*, residual binders and/or water, nitrates, *etc.*). The sintering furnace is assumed to have a resistance heater with positive atmosphere flow to an

* In practice, the blend and agglomeration steps may be a combined operation, especially if wet binders are employed to coat the component before it is blended with the other.

off-gas system. The off-gas system might consist of an absorbent trap, followed by a series of filters and scrubbers, ending with gas recycle to the calciner. Periodically, the absorbent is blended into the waste stream for disposal. As an example of the importance of driving off excessive volatiles, it was calculated [RINDFLEISCH] that a 30.5-cm-diameter canister filled to a 3.05-m height (i.e., no gas plenum was assumed) with calcine containing 0.5 wt % NO_3 and 0.1 wt % H_2O could generate an internal pressure of $>6.2 \times 10^6$ Pa (>900 psi) at 150°C . The granular waste form after sintering should exhibit a leach rate comparable to that of glass, a significantly increased particle-size distribution compared to calcine and a mechanical strength significantly greater than that of calcine [SAMSEL-1, SAMSEL-2]. The heat evolution rate of the granules (>0.06 kW/kg for 1.5-year aged waste) may be high enough to require provisions for cooling of the waste when an environment of low thermal conductivity (i.e., prior to metal encapsulation) is present. The granules should have sufficient strength and size for transport to the next process—encapsulation.

7. Casting

Agglomerated, sintered waste granules are encapsulated in a metal matrix by a casting process, probably in an inert atmosphere to minimize any metal oxidation seams. The encapsulation technique should be designed to provide a protective envelope of pure metal surrounding the outermost waste granules of at least 1 cm. In the concept shown in Fig. 19, sintered waste granules are placed in an enclosed wire mesh basket, smaller in height and diameter than the outer canister. With one concept, the filled basket is placed in a canister of molten metal. The mesh retains or separates the waste granules from the walls of the canister and allows the molten metal to penetrate the waste in order to produce the final waste form.

This multistep description is used only for purposes of illustrating the protective envelope concept and is similar to the ANL casting experiments [ANL-77-36, ANL-78-11] described in Section 1.C.1. Modifications of the INEL and Eurochemic casting techniques should be achievable and could be used instead. Still another alternative might be to precast the metal envelope and to insert the wire mesh outside the hot cell. In the cell, granules are added, then molten metal to make the top envelope before the final canister weld is performed. For any of these methods, problem areas may exist in achieving full penetration of the metal into the bed of granules. Methods have not been developed that establish when uniform penetration has been achieved.

Lead has been shown in the reference flowsheet as the matrix metal. For several reasons, however, alloys of lead may prove to be more advantageous. Stainless steel is often suggested as the canister metal but other metals (i.e., black iron, brass, etc.) may also be of advantage. Substitution of glass beads for the sintered, stabilized calcine granules in Fig. 19 (at the expense of increasing the total volume by a factor of two) could form the basis of a conceptual flowsheet if vitrified wastes were desired rather than sintered waste granules.

8. Product Characterization

The flowsheet assumes that two canisters (rather than one canister having twice their length) are produced each day, even though this would double the number of (remote) welds. If desired, one canister could be employed. A protective envelope of 1 cm that extends beyond the outermost waste granules (*i.e.*, sides, top, and bottom) is assumed in estimating the quantity of lead required.

The conceptual flowsheet shown in Fig. 19 requires ~ 1200 kg per day of lead (\$678 at \$0.25/lb) or per 5 MTU reprocessed. On a yearly basis, this is 369,600 kg (814,833 lb or 407.4 short tons) or $\sim 0.03\%$ of the total U. S. consumption in 1969 [BROBST] for a 1500 MTU/year reprocessing plant. If one assumes the figure of 45.6 MTU/GW year [ERDA], this corresponds to 11,236 kg of lead per/GW year (24,771 lb/GW year) or \$6,193/GW year (if lead is assumed to cost \$0.25 per lb). If the cost of electricity is \$0.01/kW hour, a GW year is worth $\$87.6 \times 10^6$. The cost of lead is thus 0.007% of the cost of producing the electricity. The two biggest consumers of lead in the U.S. are batteries at 41.9% and gasoline at 19.6% [BROBST]. The 369,600 kg of lead is equivalent to $\sim 0.15\%$ of the lead used in gasoline. Hence, reductions in the use of lead in gasoline, as is being proposed in current clean air standards, would provide many times the amount of lead required for metal-matrix encapsulation of HLW.

The lead corrosion rate at 25°C was measured [AZIM] to be 2.3×10^{-5} g/cm²·day in Egyptian tap water and 2.1×10^{-5} g/cm²·day in 1M NaCl solution. If lead is assumed to have a corrosion rate (*i.e.*, leach rate) of 10^{-5} g/cm²·day, ~ 3100 years of corrosion of a 1-cm-lead protective envelope (Fig. 19) would be required before the first waste particles would be exposed for leaching. This illustrates the arguments for slowing the release of radionuclides via leaching as a large fraction of the more long-lived isotopes such as ¹³⁷Cs and ⁹⁰Sr will have decayed during the time required to corrode the outer, protective lead layer. Increasing the thickness of the protective barrier delays even further the time before the waste is exposed. If the leach rate of the agglomerated, sintered calcine can be also reduced to a similar 10^{-5} g/cm²·day, $\geq 10^4$ years would be required to leach (or corrode) an entire 32-cm-diameter HLW cylinder to a "zero" diameter. Note that the above discussions give no credit to the time that is likely to pass before the waste form is ever contacted by water.

9. Conclusions

There are sufficient data available to produce a reasonable flowsheet based upon existing or developing technology for which a conceptual plant design, acceptable to industry, could be performed. Technology (*i.e.*, calcination, off-gas handling, blending, agglomeration, sintering, materials transfer) has either been developed for other nuclear applications or else could be taken from current industrial practices in order to provide the major design bases. Materials cost and lifetimes for the flowsheet appear to be reasonable. It may be desirable to consider metal alloys other than lead.

V. CONCLUSIONS

Metal-matrix encapsulation of solidified high-level radioactive waste from commercial power reactors can probably serve as an excellent waste-management option that may be superior to the use of glass. The metal-matrix concept has the potential of becoming a desirable waste-management method, meeting technical, industrial, and public acceptance criteria. Further work to demonstrate the feasibility of metal encapsulation as a technical alternative should continue.

Two of the most important advantages gained with this concept are (1) more certainty in the predictability of the long-term dispersibility properties (*i.e.*, leach rates, surface areas, mechanical strengths) and (2) more flexibility in plant operations with respect to canister sizes and the minimum required cooling times of high-level waste from spent fuel prior to solidifying and packaging, especially if "interim" storage of solidified metal-encapsulated HLW in water is utilized. This latter advantage may become very significant for wastes from short-cooled high-burn-up spent fuel from FBRs where large amounts of liquid HLW storage are not desirable. Another potential advantage is that high-temperature ($>1000^{\circ}\text{C}$) liquid phases that are required in the production of glass can be eliminated if HLW is instead converted to a relatively nonleachable, agglomerated, sintered calcine that is then encapsulated by casting it into a low-melting metal matrix. The latter process should have minimal corrosion and off-gas problems compared with those experienced in the production of glass, and hence potentially will reduce secondary waste streams and thus may offer some significant process attributes for industrial application.

Metal-matrix encapsulation is concluded to have enough potential so that it should be pursued further as either as a "back-up" for glass vitrification processes for HLW from all types of reactors (*e.g.*, including LWRs) or as the primary solidification method for HLW wastes from FBRs.

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APPENDIX

SURVEY OF POWDER METALLURGICAL FABRICATION TECHNIQUES
APPLICABLE TO SOLIDIFIED HIGH-LEVEL RADIOACTIVE WASTE*

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I. BACKGROUND

A. Introduction

Powder metallurgy is a very well developed industrial technology and offers metal and cermet (*i.e.*, metal and metal oxide) fabrication techniques that produce specimens from a wide range of particle-size distributions. Such methods may allow the use of calcine as directly produced (including the calcine fines fraction that cannot be directly dispersed with casting encapsulation techniques unless agglomerated) to fabricate metal-matrix-encapsulated waste forms (*i.e.*, cermets). However, two important differences from conventional powder metallurgical processes will be the intense radiation and internal heat generation associated with the radioactive waste forms. The radiation will require the use of "hot cells" (*i.e.*, cells for entirely remote operation and maintenance of equipment). The internal heat generation rates may require restrictions upon the time periods and/or upon the volumes of wastes or mixtures of wastes and metal powders that may be stored or handled. Thus, major modifications of existing industrial powder metallurgy technology will be required. For these reasons, potential powder metallurgical techniques have been surveyed. The objective was to identify methods that may be applicable to the remote fabrication of metal-encapsulated calcine or glass beads. To accomplish this, a set of tentative criteria was developed to serve as a guideline for selection of processes, and a list was made of possible candidate metals or alloys. Suitable powder metallurgy fabrication techniques were then identified.

B. Tentative Process Criteria

Powder fabrication procedures for cermets of continuous metal matrices containing high-level waste in the form of either calcine or glass beads should be designed to utilize about 30-70 vol % metal. They must to some extent meet the requirements given below:

- (1) Simple, reliable, and economic fabrication procedures are required.
- (2) The procedures must be amenable to totally remote operation and maintenance of equipment.
- (3) Fabrication and utilization of calcine or glass beads with various ranges of internal heat generation rates must be considered (*i.e.*, up to 360 kW/m^3 for 0.5-year aged waste).
- (4) To minimize excessive volatility, devitrification, or materials problems, fabrication temperatures probably should not exceed about $700\text{--}800^\circ\text{C}$ for either calcine powder or glass beads.
- (5) The thermal conductivity of the calcine-metal cermet must be greatly improved over that of the calcine (or glass beads), thus allowing storage of waste that has been aged for a shorter period or of larger canisters without the occurrence of centerline overheating.
- (6) The fabricated bodies must be more resistant to loss of radionuclides by leaching or corrosion than the unencapsulated waste forms themselves.

- (7) The fabricated product should have strength and impact resistance greater than that of calcine or glass beads so as to minimize dispersal and to facilitate handling.
- (8) Of secondary importance, the cermet product should be capable of reconstitution (or retrieval and refabrication) in the event superior methods of containment or isolation procedures are developed later.

C. Selection of Metal or Alloys for Matrices

The matrix metal must be relatively conductive, inexpensive, and resistant to corrosion by the atmosphere and by water. Metals such as aluminum and copper are of immediate interest. Iron, nickel, and stainless steels are also likely candidates, having a fairly good balance of cost, thermal conductivity, corrosion resistance, and refractory characteristics. Magnesium is also highly conductive, but it is pyrophoric. Silver is too expensive. Other metals melt at too high or too low a temperature, have poor thermal conductivities, or are rather expensive.

In general, the selected base metals will be alloyed with small amounts of other elements because of excessive degradation of their properties (i.e., melting points, thermal conductivities, *etc.*) with excessive dilution. For example, the addition of ~5 wt % silicon to aluminum reduces its thermal conductivity by a factor of about two and also lowers its melting point; this aluminum-silicon alloy may still be acceptable. Small amounts of silicon (<1%) may be useful for liquid-phase sintering and may give a good balance of properties. Alloying of copper and iron reduces their thermal conductivities.

The following metals and alloys [METALS-1, METALS-2, SUMP] are considered the most attractive for cermet matrices, based on qualitative consideration of thermal conductivity, cost, corrosion resistance, and fabrication and operating temperatures:

- (1) Aluminum,
- (2) Aluminum alloys,
- (3) Austenitic stainless steel,
- (4) Brasses,
- (5) Bronzes,
- (6) Copper,
- (7) Copper-silver (*i.e.*, small amounts of silver for liquid-phase sintering),
- (8) Ferritic stainless steel,
- (9) Iron and mild steel,
- (10) Nickel
- (11) Nickel alloys.

II. A SURVEY OF FABRICATION PROCESSES

The fabrication procedures to be used should produce a somewhat impervious material which will not undergo excessive leaching of activity from the dispersed waste particles. This and other requirements such as thermal conductivity and strength can be met by a number of fabrication techniques such as cold pressing and sintering, hot pressing, and extrusion, or modifications and combinations of these and other techniques [JONES].

A. Sintering Processes

Sintering processes are the most used powder metallurgy fabrication processes. A number of sintering processes considered in this evaluation are discussed below. The size of product varies, depending upon the particular process. One can fabricate small blocks or small rods by cold pressing and sintering, small rods by cold extrusion and sintering, and very large blocks by molding and sintering or by vibratory compaction and sintering.

1. Cold Pressing and Sintering

A flowsheet for cold pressing and sintering is given in Fig. 20. This process is most likely to be used when small parts (up to a few inches in cross section) are to be processed and fairly high density is required. Densities of about 95% of theoretical can usually be obtained in metals; at this density there is little or no open porosity in the product. The limiting density in a cermet will generally depend on its composition.

Cold pressing can be done either by pressing in a die or by cold hydrostatic pressing in a rubber mold. When a die is used, wall friction limits the length of good compaction to at most a few inches. Lengths of a few feet can be cold pressed by hydrostatic means. Compaction by hydrostatic pressing is more isotropic and can be somewhat greater than compaction obtained by pressing in a die [JONES].

High densities can sometimes be best obtained along with accelerated sintering rates by the use of liquid-phase sintering [JONES]. This method of sintering utilizes a small amount of metal which melts at a lower temperature than does the matrix metal, or which alloys with the matrix metal to melt at a lower temperature. The molten metal becomes distributed along grain boundaries and results in accelerated diffusion, enhancing the rate of sintering and increasing the density. There is not a problem with settling or segregation when liquid-phase sintering is properly done. An important feature of cold pressing and sintering is the proper use of a binder [JONES]. Normally, a small amount of binder (e.g., camphor) is added to the ceramic (i.e., calcine) powder and thoroughly mixed so that each particle is coated with the binder. The coated ceramic is then blended with the metal component. Here, it is desirable to use metallic particles considerably finer than the ceramic particles. When optimized, blending results in each ceramic particle being coated with a layer of metallic particles. After the pressing and sintering operations, the structure tends to have a continuous metal matrix and little interparticle contact of the ceramic phase. This is much more effective than random mixing of particles of the two phases [GURLAND].

Fig. 20. Cold Pressing and Sintering Flow-sheet. (A 125-ton mechanical press appears to be adequate for the cold-pressing operation, if one ton of material is processed per day.)

The sinterability of a cermet, of course, depends not only on the characteristics of the metal but also on the composition and the condition of the calcine or ceramic phase. A modification of the cold pressing and sintering process might incorporate what is termed mechanical alloying [BENJAMIN]. In this process, high-energy ball milling is used to obtain intimately mixed dispersions of a ceramic phase within a metal matrix. This is a relatively new process. Although it is more expensive than the normal method of preparing powders, it may provide a product having unique characteristics in its ability to resist leaching. A mechanically alloyed powder would be mixed with a binder, cold pressed, and sintered in the normal manner.

Automatic cold-pressing machines are available commercially and, along with a sintering furnace, are capable of turning out a large number of pressed shapes in one day [DOUGHERTY]. A mechanical press may be more desirable because of its rapid pressing cycle. If desirable for improved containment (to lower leach rates) or for minimizing contamination of work areas, it is possible to automatically manufacture thin-wall cans, load them with powder, cold press, cap and close the cans, and sinter. This might be applicable for either aluminum- or copper-containing cermets. An alternative procedure would be to can the cold pressed and sintered blocks; this would be an additional containment capability preceding transfer to a larger HLW canister.

Some bench-scale cold pressing and sintering encapsulation work has been done at INEL (see Section I.B. and I.C.). This work involved blending simulated (nonradioactive) calcine powder and metals, cold pressing (40,000 psi), and sintering. Products were tested for thermal conductivities, leach rates, and strengths. Also PNL has reported some cold pressing ($\sim 1\frac{1}{4}$ -in. diameter) and sintering studies [ROSS].

The advantages of cold pressing and sintering are low cost, high density and impervious structure (especially with liquid-phase sintering), suitability for remote operation, and (probably) fewer problems with the internal heat of the calcine.

The primary disadvantage is that more handling is required in loading large canisters with the relatively small sintered blocks. Another disadvantage is the possible need for a heat-transfer agent, because of the multiple thermal contact resistances present when a canister is loaded with small blocks or rods. This problem could be reduced by pouring molten lead around the sintered blocks. There must be further examination of limitations that would exist during handling (prior to sintering) if wastes from short-cooled fuel (*i.e.*, with high heat generation rates) are used.

2. Cold Extrusion and Sintering

Cold extrusion and sintering is somewhat similar to cold pressing and sintering [JONES]. In this case, a plasticizer is generally used along with the binder, calcine, metal, and possibly a lubricant to form a paste which is extruded wet onto a tray, dried, and sintered. Rods having a maximum diameter of ~ 2 in. can be produced in this manner. See Fig. 21 for a flow-sheet of this process. The advantages are similar to those of cold pressing and sintering and in addition there is less handling of the product due to the long length of the rods made. Also, there is less anisotropy of distribution of phases by this method than with cold pressing.

Fig. 21. Cold Extrusion and Sintering Flowsheet.

The principal disadvantage is that a lower density is achieved. The maximum density attainable by this process is usually 80-85% of theoretical. Also, self-heating may interfere with maintaining a plastic body during extrusion. If higher densities are required, infiltration of liquid metal into the pores can be done to obtain adequate resistance to penetration by corrosive agents.

Infiltration is a process that is widely used in powder metallurgy. What is required in this case is an alloy that melts at a slightly lower temperature than does the matrix metal and which wets it. For example, for infiltration of aluminum-calcine cermets, molten aluminum-silicon alloy which melts below the melting point of aluminum might be used. Infiltration would be facilitated by evacuating the cermet, immersing it in molten aluminum-silicon alloy, and then introducing pressure (probably atmospheric) to accomplish complete filling of the pores.

Another infiltration technique is to introduce a liquid compound or a solution such as water glass (*i.e.*, sodium silicate) into the pores in the manner described above and then to heat to drive off the contained water, leaving the pores sealed. At present, it is not clear whether a sealant of this type has adequate thermal behavior properties to be useful with commercial HLW treatments.

Some cold extrusions (1/2-in.-diameter column) and sinterings of mixtures of simulated nonradioactive waste sludge and a glass frit were done at PNL. It was found unnecessary to add binders and plasticizers. Sintering caused cracking of the extruded products, but this problem is believed solvable [ROSS].

3. Molding and Sintering

Molding and sintering is similar to cold pressing and sintering in the preparation and blending of powders, but consists of pouring blended powders into a large mold with a diameter as large as 2 ft and a length of perhaps 2 ft, accompanied by tamping (to achieve some densification) and sintering [JONES]. It is not considered possible to get high density in large sections by molding and sintering alone, even at high temperatures. Thus, infiltration of pores by liquid metal might be useful. A flowsheet for this process is shown in Fig. 22. This method's principal advantages are low cost and a large size that is suitable for remote loading in canisters. Its principal disadvantages are its poor microstructure (as a result of tamping) and a low density, possibly requiring infiltration. If processing is by this method, self-heating prior to sintering could be a problem, depending on the age of the calcine or glass beads.

4. Vibratory Compaction and Sintering

It is well known that by a proper selection of particle size, vibratory compaction of a mixture of large and a small particle can yield densities of about 80% of theoretical [AYER-1, AYER-2, AYER-3]. This process might be applied to achieve a fairly dense large body (up to 2 ft in diameter or larger) as in molding, followed by sintering to achieve a more acceptable density. This type of process has been thoroughly examined by both theoretical and practical means and is adaptable to a large-body [AYER-4] fabrication process. A flowsheet of this process is given in Fig. 23.

Fig. 22. Molding and Sintering Flowsheet.

Fig. 23. Vibratory Compaction and Sintering Flowsheet.

In this application, the calcine would be the large particles and the metal would be the small particles. Selection or possible tailoring of various particle sizes would be required for best results, *i.e.*, the calcine would be separated into a number of size fractions and matched with appropriate smaller sizes of metal particles. This may require manufacture of suitable calcine powders, especially if a large amount of fines is to be utilized. Liquid-phase sintering may be used in this process.

Vibratory compaction is being examined at PNL (cold bench-scale) [SUMP]. The concept involves first loading the simulated waste forms (*i.e.*, Al_2O_3 or glass beads) into a canister and then the metal powder, assisted by vibratory compaction. Such packed canisters (of ~30-65% theoretical density) would be sealed and their contents sintered. Experiments to date have employed simulated waste forms of rather large size so that metal powder

sizes have probably not yet been critical. More dense (and better) structures will be achieved by careful matching of particle sizes as development work proceeds [SUMP].

The principal advantages are the isotropic distribution of calcine and metal, relatively good microstructures, and bodies of large size (up to 2 ft in diameter) suitable for loading into canisters. The principal disadvantages are the extensive handling and processing required to prepare powders having the right packing characteristics and the accompanying relatively high costs for the extra process steps. Depending on the sinterability, liquid-metal infiltration of pores might still be required to establish an impervious structure. Self-heating may be a significant problem in processing by this method, depending on the age of the calcine used.

B. Pressing

There are a number of processes for fabrication of cermets which fall in the category of pressing, such as hot pressing, hot isostatic pressing, and press forging [WILKINSON, HOLDEN, CUNNINGHAM, MEINERS, CONAWAY, HANLON, KIZER]. These processes are applicable to fabrication of bodies having a range of sizes. Pressing usually requires containment via a sealed metal jacket to contain the powders. Hot pressing of large bodies requires a very large press to achieve adequate densification. For example, a 500-ton press used to press a 2-ft-diameter body would exert a maximum pressure of about 2210 psi. At higher pressures, such as 10,000 psi, a 500-ton press could handle bodies up to 11 in. in diameter. The use of higher-capacity presses is feasible, but probably not desirable because of their size and slower operation. Also, pressing has the length limitation of 1 ft. Thus pressing operations may have size limitations imposed.

Frequently, separation of a die from a hot-pressed body by machining is required due to reaction of the pressed body with the die at high temperatures. It may be possible to develop a die that could be disassembled and which would use a coating to prevent welding of the pressed body and dies, especially at the lower temperatures at which aluminum and copper would be handled. Use of a die liner which would bond to the pressed body and not require removal might be feasible. Also, an inert atmosphere or coatings or cans might be necessary to prevent undue oxidation of the pressed material.

Hot vacuum pressing using an automatic compacting press and graphite dies to produce cermets (2-in. OD by 0.2-in. thick) of incinerator ash and of PuO_2 have been examined at Mounds Laboratory, using a semiremote operation [RICHARDSON]. This was the only report found on radioactive (low gamma levels) cermet production, using powder metallurgy techniques.

Press forging involves canning of the powder and pressing, a step at a time along the length of the can in a die. By turning the can and repeating the procedure, successively smaller sizes are handled until the desired shape and density are achieved. A starting billet-size limit of 12-in. square (or round) could be desirable, resulting in a final size of 6 to 8-in. square. Continuity of the metal phase would not be so good as in the product of isostatic pressing. Because of the superiority of the hot isostatic pressing process, it is the only pressing method discussed in more detail below.

1. Hot Isostatic Pressing

The hot isostatic pressing (H.I.P.) technique for powders consists of loading powder into a sealed can and pressing at high pressures (up to 30,000 psi) and temperatures ($>1200^{\circ}\text{C}$) in a helium-filled autoclave [WILKINSON, MEINERS, CONAWAY, HANLON, KIZER]. Before loading, the powder is processed in a manner similar to other powder metallurgy procedures. Facilities for isostatic pressing are available in sizes up to 4 ft in diameter and 10 ft in length [CONAWAY, KIZER]. A flowsheet for this process is given in Fig. 24.

The chief advantage of H.I.P. is that densification occurs isotropically and powder distributions previously achieved by blending, *etc.* are not broken up. Full densification of canned powders in diameters up to two feet has been achieved [MEINERS]. Leaching of material produced by this process should be minimal, since the calcine-metal matrix composite can be fully densified. Some densification of the calcine itself may take place during the pressing. Another advantage of H.I.P. is its moderate cost in dealing with fabrication of large bodies. For example, more than four tons of material can be pressed in a single run if the original density is 4 g/cm^3 and the pressing is 2 ft in diameter by 10-ft long. This volume would correspond to the wastes from the reprocessing of ~ 22 metric tons of spent fuel. It is felt that this process is amenable to remote operation [MEINERS, CONAWAY, HANLON].

Perhaps the greatest disadvantage (which applies to all fabrication methods for large bodies) will be the limitation in handling imposed by the self-heating rate of the HLW prior to sintering. For example, calcine wastes (a density of 2.2 g/cm^3 is assumed) of ages 1, 3, and 5 years have adiabatic heating rates of ~ 630 , ~ 225 , and $\sim 125^{\circ}\text{F/hour}$ [SCHINDLER]. This indicates that a limited time may be available for handling. Also, safety during operation in a hot cell of a hot pressurized autoclave needs to be analyzed. Full background on design information is readily available [CONAWAY, HANLON].

C. Extrusion

The extrusion processes that are considered here are hot extrusion, hot hydrostatic extrusion, and high-velocity or impact extrusion. These processes are capable of producing high densities and are perhaps most applicable for small-(2-3 in.) to medium-(4-6 in.) sized bars when used remotely.

Hot extrusion as discussed here consists of canning either blended powders or blended and cold-pressed powders and then extruding the canned material under pressure through a die at elevated temperature [JONES, WILKINSON].

High-velocity extrusion has been used successfully in densifying refractory metals and oxide powders [WILKINSON]. However, it is not especially suited to control of microstructures as required here. Rather, the calcine particles would be broken up by the relatively severe high-rate deformation, although overall density might be acceptable. If hard, dense calcine powders were available, this method might be somewhat more useful.

Fig. 24. Hot Isostatic Pressing Flowsheet.

1. Hot Extrusion and Hot Hydrostatic Extrusion

Hot extrusion of a canned batch of blended or blended and cold pressed powders has both advantages and disadvantages [LOEWENSTEIN-1, LOEWENSTEIN-2, HUNT, LUP1, ANDERSON, MONTAGUE, PLOETZ]. It is capable of producing dense structures, but there is a tendency during extrusion of damaging the ceramic particles and of actual formation of stringers of the ceramic phase. This is normally lessened by designing the container for streamlined flow.

Still more effective is the use of hot hydrostatic extrusion where a liquid is maintained between (1) the extrusion can or billet and (2) the extrusion cavity walls up to the point of contact with the extrusion die. This eliminates wall-billet friction and results in a smoother flow and a superior microstructure. This is usually done at a lower temperature than straight hot extrusion and depends on the temperature limitation of the hydrostatic liquid. The flowsheet for hot hydrostatic extrusion is the same as for hot extrusion (Fig. 25).

Hot extrusion can be combined with hot pressing or with cold pressing and sintering, but this will be more expensive. The combination of hot pressing and extrusion is more common. It is usually done by blocking the die in the extrusion cavity and hot pressing the billet with the extrusion ram. The die is then opened, and hot extrusion is carried out to complete the process.

The advantages of hot extrusion are that a dense structure is feasible, although less ideal than is possible by hot isostatic pressing, and, like H.I.P., hot extrusion might be expected to achieve some densification of the calcine phase. The actual results depend on the extrusion ratio, with high density favored by high extrusion ratios and with good microstructural distributions favored by low extrusion ratios.

An extrusion press handling one ton of product per day would make about 160 ft of 3-in.-diameter bar (if the density is about 4 g/cm^3) or 360 ft of 2-in. bar. Such lengths of bar would require considerable handling, *etc.* Straightening would be required. Machining or otherwise removing the can would be optional. Sawing into lengths and/or sawing off ends would be required. It is estimated that extrusion ratios of about 5 to 1 would be adequate for densification of billets to greater than 95% of theoretical to form bars. If so, a 200-ton press would probably be adequate.

D. Other Processes

Other potential powder metallurgy processes were considered for use with high level waste-containing cermets and were discarded as not suitable. Among these are such processes as swaging, hot rolling, impact forging, explosive compaction, and drawing [WILKINSON]. The reasons are described briefly below:

- (1) Swaging is most suitable for fabrication of relatively small cylindrical rods rather than hexagonal or square-cross-section pieces. The resulting microstructures would be less than ideal, since some longitudinal elongation of calcine particles would occur. If used, this is perhaps most applicable at low calcine concentrations.

Fig. 25. Hot Extrusion Flowsheet. (Can removal would be optional in the sectioning operation.)

- (2) Remote hot rolling is feasible, but it would require considerable development of large, special equipment for handling and processing. The cermet microstructures produced by rolling also are not as good as those attainable by the methods discussed in detail above. If used, hot rolling would produce very dense material.
- (3) Impact forging is not considered practical for either remote operation or forming of satisfactory microstructures. It would not be feasible for high calcine concentrations.
- (4) Explosive compaction of these cermets may be feasible but not considered to be practical for the production of large quantities of material [WILKINSON]. Its effects on microstructures may be unsatisfactory, especially at high calcine contents when weak friable calcine particles are used.
- (5) High-calcine-content cermets cannot be fabricated by drawing because of the low ductility and low tensile strength of these materials.

III. SUMMARY OF FEASIBLE FABRICATION PROCEDURES

Selection of the most suitable fabrication procedures will probably depend to a large extent on the age of the waste in calcine or glass beads, *i.e.*, the radiation level and associated internal-heat generation rate. If short-cooled waste is being processed, relatively small bodies would be produced--probably by cold pressing and sintering. It is believed that liquid-phase sintering is desirable in this case. Such procedures may be convertible to production and are usually more economic than other powder metallurgical procedures. This procedure does not require canning and decanning, but a protective atmosphere may be required during fabrication, especially during sintering. Also, the small bodies produced will probably require placing a heat-transfer medium (*e.g.*, lead) in the canister after the above procedure is completed. The process is quite suitable to remote operation but would need development.

If cermets to be processed contain longer-aged waste (*i.e.*, have lower internal-heat generation rates), perhaps the best results can be obtained by hot isostatic pressing of very large bodies, although cold pressing and sintering is also competitive here. Hot isostatic pressing provides the best microstructure control. It is particularly attractive because the calcine as well as the metal matrix can be fully densified. Hot isostatic pressing is believed to be suitable to remote operation, but would require very large, expensive autoclaves and associated handling equipment. Other procedures for the fabrication of large bodies, such as hot pressing, would require very large presses and thus would have somewhat the same problem. It is felt that (1) molding and sintering or (2) vibratory compaction and sintering each has some potential, but may require considerable processing of powders, which would offset its basic low cost. The microstructures produced by these methods are marginal at best, and infiltration would probably be required to reduce the residual porosity.

Another process which deserves some examination is hot extrusion. This process has the capability of densifying the calcine along with the matrix metal. Its best application is in the manufacture or processing of intermediate sizes of cermet bars. The microstructural control would be best if

hot hydrostatic extrusion were used, but straight hot extrusion may be adequate. It is felt that the best application of extrusion is to produce intermediate sizes of bars, say about 3-in. cross section. The bars can be hexagonal, square, or round.

IV. CONCLUSIONS

A series of studies is required to further evaluate powder metallurgy techniques for the fabrication of high-level radioactive waste composites. The results must be compared with results of casting-encapsulation methods under development at INEL and Eurochemic. Such an evaluation requires data that allows comparison of properties of both types of waste composites (i.e., composites prepared by casting and powder metallurgy). Studies are lacking that address the feasibility of using selected powder metallurgy techniques in hot cells, including the remote maintenance of equipment.

Powder metallurgy offers several attractive fabrication routes. However, the requirement of conservation of resources and a need to develop a workable waste-treatment process in a reasonable time may not allow the luxury of developing two or more metal-encapsulation fabrication techniques. If so, casting encapsulation appears inherently more developed and to offer sufficient potential so that no further examination of powder metallurgy techniques is recommended at this time.

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