**Quarterly Progress Report -
Research and Development
Activities - High-Level Waste
Immobilization Program:
April Through June 1979**

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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
HIGH-LEVEL WASTE IMMOBILIZATION PROGRAM:
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SUMMARY

Through the High-Level Waste Immobilization Program, the Pacific Northwest Laboratory is conducting research on the solidification of high-level radioactive waste. A major goal of this program is to develop solidified waste forms and reliable processes for their manufacture. This progress report describes the research and development activities for April through June of 1979.

- Test results are available on 21 out of a total of 65 glass compositions in a generic study of composition effects on waste glass properties. The effects of varying 11 glass components on such properties as Soxhlet leach rate, viscosity, electrical conductivity, and volatility have been fitted to partial quadratic approximation models.
- Preliminary results indicate the leaching behavior of a Cermet waste form prepared at Oak Ridge National Laboratory is similar to that of waste glass and supercal-cine.
- Scanning transmission electron microscopy has confirmed that supercal-cine contains up to 10 vol% glassy phase and that small fractions of Cs, Sr, and rare earth reside in the glassy phase.
- Two long-term runs were completed in the ceramic melter coupled directly to the full-scale spray calciner. In the first run the combined system operated for 239 continuous hours, reached a maximum glass production rate of 64 kg/h and produced 11,000 kg of simulated Savannah River Plant glass. In the second run, with the melter modified to have a higher current-carrying capacity, the combined system operated for 614 h, reached a maximum glass production rate of 85 kg/h, and produced 35,000 kg of glass.
- Two new ceramic melters were put into operation. A ceramic melter capable of being operated by completely remote means was installed in the High-Bay Engineering Laboratory of 324 Building. This melter, with a nominal melting capacity of 30 kg/h, features an airlift discharge system to eliminate sludge buildup problems. The second melter is capable of operating at temperatures approaching 1500°C and has a production capacity of about 6 kg glass/h.
- A preliminary test in the small spray calciner indicates that coal, which is present in some Savannah River Plant wastes, is only partially decomposed during spray calcination.

PREVIOUS REPORTS

Previous reports in this series were BNWL-1699, -1741, -1761, -1788, -1809, -1826, -1841, -1871, -1893, -1908, -1932, -1949, -1994, -2070, -2242, -2243, -2264, and PNL-2265-1, -2265-2, -2265-3, -2265-4, -2999-1, -2999-2, -2999-3, -2999-4, and -3050-1.

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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
HIGH-LEVEL WASTE IMMOBILIZATION PROGRAM
APRIL THROUGH JUNE 1979

INTRODUCTION

The High-Level Waste Immobilization Program (HLWIP)--formerly the Waste Fixation Program--is conducted by the Pacific Northwest Laboratory (PNL), operated by Battelle Memorial Institute for the Department of Energy (DOE). Under this program, PNL is conducting research to convert high-level radioactive waste to stable, nondispersible forms. Candidate waste forms include silicate glasses and various crystalline and multibarrier waste forms. The HLWIP is designed to be a means through which the government and users of the technology can cooperate to effectively handle nuclear waste. Objectives of the comprehensive program include: the development and characterization of waste forms; equipment and process development; and design, construction, and demonstration of full-scale process equipment. The following sections describe research and development activities in radioactive waste fixation for the past quarterly reporting period.

SECTION 1. WASTE FORM DEVELOPMENT

The purpose of this task is to develop solidified waste forms for containment of high-level radioactive waste produced by the commercial nuclear power and government defense programs. The waste forms must have properties that will increase safety and be compatible with all steps of nuclear waste management, including large-scale processing, interim surface storage, transportation, and deep geologic disposal.

GENERIC STUDY - L. A. Chick

The generic effects of composition on waste glass properties are being studied by systematically varying eleven glass components. We discussed the background of this study in the July-September 1978 HLWIP Quarterly (McElroy et al. 1979). The composition field under study is shown in Table 1. Testing is complete on 21 glass compositions. Forty-four more compositions are currently under study.

TABLE 1. Composition Field for Eleven-Component Generic Study

<u>Component</u>	<u>Low Value, mole%(a)</u>	<u>High Value, mole%(a)</u>	<u>Centroid Value, mole%</u>
<u>Formers</u>			
SiO ₂	42	58	49.03
B ₂ O ₃	6	12	8.82
Al ₂ O ₃	0	15	7.35
<u>Modifiers</u>			
CaO	0	14	6.86
MgO	0	8	3.92
Na ₂ O	11	16	13.24
<u>Intermediates</u>			
ZnO	0	6	2.94
TiO ₂	0	3	1.47
Cr ₂ O ₃	0	3	1.47
Fe ₂ O ₃	0	3	1.47
NiO	0	3	1.47

(a) The field was also limited by these restrictions:
total formers $\geq 55 \leq 75$ mole%; total modifiers $\geq 14 \leq 34$ mole%;
total intermediates $\geq 0 \leq 22$ mole%.

Effects of Components on Soxhlet Leach Rate

In this study we measured leach rates by the Soxhlet method. One-gram samples of crushed glass (-40+60 mesh) were placed in stainless-steel-mesh screens and weighed. They were then

subjected to 99°C refluxing distilled water for 24 hours. After drying at 110°C, samples were re-weighed and the percent weight loss was recorded.

A partial quadratic approximation model that expresses leach rate as a function of glass composition was fit to the data. The model can be used to predict Soxhlet leach rates for glasses other than those tested that lie within the composition field shown in Table 1. Such predictions were used to develop the plot shown in Figure 1. The composition of the glass that lies at the center of the composition field, referred to as the centroid composition, is shown in the right-hand column of Table 1. Its Soxhlet leach rate is about 3.7 wt%. Figure 1 shows the predicted leach rate when the centroid composition is changed by adding or subtracting increments of one component at a time. For example, when the level of Al_2O_3 is increased by 8 mole%, the leach rate falls from 3.7 wt% to about 1.6 wt%. To accommodate the increase in the Al_2O_3 , the other components are adjusted downward by amounts proportional to their levels in the centroid composition. The slopes of the component lines reveal their effects on Soxhlet leach rate. Addition of aluminum oxide decreases the leach rate. Chromium oxide is even more effective in decreasing the Soxhlet leach rate. The NiO , Na_2O , MgO , B_2O_3 , and CaO lines all have positive slopes, indicating that addition of these components to the glass increases leach rate. Conversely, removal of these components from the glass decreases the leach rate.

FIGURE 1. Effects of Components on Soxhlet Leach Rate

The reliability of the predictions was determined by calculating prediction error standard deviations at 1-mole% intervals for all components. These calculations were made possible by performing replications of leach tests on several glasses, and by comparison of measured leach rate for each test glass to that predicted by the model. Calculated errors are shown on the figure as bars. The size of the bars illustrates, for instance, that there is no significant difference between the effects of ZnO and TiO₂ on Soxhlet leach rate.

We expected that increases in the levels of Na₂O, MgO, CaO, or B₂O₃ would cause the leach rate to increase, since these oxides are known to weaken the glass structure by reducing the number of Si-O-Si bonds. The SiO₂ and Al₂O₃ have expected negative effects on leach rate, since they serve to strengthen the glass network. The reason for moderate negative effects of ZnO and TiO₂ are not understood, but have been verified in previous work on 76-375 glass (Ross 1978). The large positive effect of NiO and the large negative effects of Cr₂O₃ and Fe₂O₃ on Soxhlet leach rates are unexpected and are not well understood.

Effects of Components on Viscosity

Shear viscosity was measured on the 21 samples in platinum crucibles using a standard Brookfield viscometer mounted on an electric resistance-heated furnace. Data was plotted as log viscosity versus 1/T⁰K for the range of temperatures yielding measurable viscosities (N = ~5 to 3000 poise). The viscosity of each sample at 1250⁰C was determined from the resulting plots.

An approximation model of viscosity at 1250⁰C as a function of glass composition was constructed. We used this model to develop the component effects plot for viscosity shown in Figure 2. Reproducibility was better for the viscosity measurements than for the Soxlet

FIGURE 2. Effects of Components on Viscosity

leach measurements. The SiO_2 and Al_2O_3 lines have identical positive slopes, showing that viscosity increases as the concentration of these components increases. This tends to confirm the theory that Al_2O_3 enters the glass as a network former in this composition field. As expected, we found that B_2O_3 , MgO , CaO , and Na_2O show negative effects on viscosity because they disrupt Si-O-Si network bonds. Effects of Fe_2O_3 , ZnO , and TiO_2 are moderately negative on viscosity. Again, their role in affecting viscosity is not understood. The large position effects of NiO , and especially Cr_2O_3 on viscosity are the result of crystal formation. The Cr_2O_3 is not soluble in these glasses above ~1 mole% at 1250°C. Formation of chrome-containing crystals greatly increases the measured viscosity.

Effects of Components on Electrical Conductivity

Electrical conductivity of the sample melts was measured at 1000 hertz at 6 volts in conjunction with the viscosity testing. The platinum viscosity spindle and the platinum crucible served as electrodes. The data was modeled and the resulting component effects plot is shown in Figure 3.

Error bars are fairly large in this plot; nevertheless, the effects of the conducting components are significant. Two modes of electrical conduction are represented in these glasses. Being small and relatively mobile, Na^+ actually moves through the melt and causes ionic conduction. Viscosity plays an important role in ionic conduction. Reduction of viscosity results in increased conductivity by decreasing the resistance to movement of Na^+ .

FIGURE 3. Effects of Components on Electrical Conductivity

Although iron is introduced to the batches as Fe_2O_3 , it is present in the glasses in both the ferric and ferrous valence states--thus facilitating electronic conduction. The Fe^{+2} and Fe^{+3} ions provide jump sites for electrons within the melt. The large positive effect slopes for Na_2O and Fe_2O_3 confirm their roles as conducting components. The possible presence of Cr^{+2} and Cr^{+3} may contribute to electronic conduction; however, the addition of Cr_2O_3 also increases the viscosity, which reduces ionic conduction of sodium. The result is the relatively flat component effect slope for Cr_2O_3 on conductivity. All other components have varying negative conductivity effects.

Effects of Components on Volatility

Volatility of the glasses was measured by heating a 2-g sample for 3 h at 1300°C in flowing air. Our results are reported as total mg lost. The effects plot constructed from the resulting model is shown in Figure 4. The error bars are relatively small. Based on previous work at PNL (Gray 1976), sodium and boron are the two components expected to be volatilized from these melts in the largest amounts. This is consistent with Figure 4, which shows Na_2O and B_2O_3 to have the greatest positive effects on volatility.

FIGURE 4. Effects of Components on Volatility

Understanding the effects of other components is related to the correlation between viscosity and volatility illustrated in Figure 5. Here the measured volatility loss (in mg) is plotted against the viscosity at 1300°C for the 21 glasses tested (four replicated measurements are included, yielding a total of 25 data points). A strong correlation between the two properties is evident. Thus, any component that reduces viscosity when added to the glass would be expected to increase volatility. Since Na_2O and B_2O_3 lower viscosity and are also volatile species, their positive effects on volatility are probably increased. Calcium oxide also has a negative effect on viscosity, which explains its moderate positive effect on volatility. By the same reasoning, MgO , which reduces viscosity, would be expected to increase volatility. Its negative effect on volatility is, thus, not understood. The strong positive effects of Cr_2O_3 , SiO_2 , and Al_2O_3 on viscosity explain their negative effects on volatility. All other components have little or no effect on volatility.

FIGURE 5. Correlation of Viscosity with Volatility in Generic-Study Glasses

Future Work on the Generic Study

As mentioned previously, we are now testing 44 more glasses. Properties that will be included in the study but are not reported here are thermal expansion, phase behavior, and leaching behavior by solution analysis. An attempt will be made in future analyses to separate the effects of crystal formation from those caused by components in the vitreous glasses.

After completion of the current study of eleven components, a study involving approximately 25 components will be undertaken.

ANCIENT MATERIALS DATA AS A BASIS FOR WASTE FORM INTEGRITY PROJECTIONS - M. F. Kaplan (The Analytic Sciences Corporation, Reading, Massachusetts)

A compilation of relevant information on ancient glass, glass-like materials and ceramics is being made to assist in predicting the durability of nuclear waste forms. Although many differences will exist, particularly in temperature and radiation conditions, it is believed that the known long-term behavior of these man-made materials can provide valuable insights into the factors affecting waste form durability in the environment. The initial investigation has emphasized glass; similar investigations of glass-like and ceramic materials will follow.

Glass first appears in the Near East about 1450 B.C. Earlier examples in the form of beads and small glazed objects occur sporadically, but free-standing glass objects become established only at this time. The history of ancient glass can be divided into roughly fourteen periods from its beginning to the 16th century A.D., when it begins to develop into a modern industry. These periods are determined by the styles and manufacturing areas of glass. Glass production may decline in some of these periods, but it never entirely ceases. The geographic areas covered include the Near East and Europe. Glass was a very minor art in the Far East; the earliest examples may be imports from the West, and the material has not received much study.

The chemical composition of ancient glasses fall into three broad categories: lead, potassium and sodium. Lead glasses occur primarily in the Far East and most samples have lead-carbonate, lead-phosphate and lead-sulfate as corrosion products.

Glass can weather by several mechanisms:

- "Weeping" - Objects stored under museum conditions collect atmospheric moisture in droplets on their surface.
- Crizzling - Formation of a network of hair-thin cracks over the surface of the glass; in severe cases, glass may lose its transparency.
- Weathering Crusts - Opaque deposits accompanied by destruction of silica matrix; deposits include gypsum and syngenite.
- Pits, Type I - Isolated pits filled with opaque weathering products.

- Pits, Type II - Isolated pits in which the traces of weathering layers can still be seen.
- Weathering Layers - Often iridescent, these layers mark the original surface of the glass and can often be removed mechanically to reveal unaltered glass.

The first four mechanisms appear to be found only in potassium glasses, while the last two are restricted to sodium glasses. Chemical analyses indicate that weeping and crizzling occur when the glass has insufficient amounts of network stabilizers for good durability. The proportions of network formers, looseners and stabilizers also appear to affect whether potassium-based medieval stained glass windows will corrode in isolated pits or form crusts of gypsum or syngenite; the latter is due to an excess of calcium.

Very little work has been done to correlate the composition of sodium glasses with weathering because they are so durable. In fact, the compositions of sodium and potassium glasses are so different that they weather by different mechanisms. Sodium glasses, when buried in the earth for extended periods of time, have the sodium and potassium completely leached away from the surface. Large amounts of magnesium, calcium and phosphorous also leave. What remains is primarily a hydrated silica layer, though materials such as lead-antimonate have been identified in completely weathered glass. Not only does one layer form, but a whole series of layers builds up, creating an iridescent effect of diffracting light between them. There are numerous examples where the original surface of the glass is still intact. For example, total silica network dissolution (i.e., corrosion) does not typically occur in sodium glasses.

CERAMIC MATERIALS - H. T. Fullam

Several series of tests are under way to evaluate ceramic materials as a potential over-pack for the primary metallic waste canister. The tests are designed to evaluate the relative resistances of a number of ceramic materials to attack by simulated geologic repository environments. The tests include: 1) static hydrothermal leach tests done in sealed gold ampules at 150° and 250°C in demineralized water, a synthetic Hanford groundwater, and a synthetic WIPP brine solution; 2) static leach tests at 100°C in demineralized water; 3) dynamic leach tests at 90° and 250°C in flowing demineralized water; and 4) dry tests in which ceramic specimens are packed in crushed basalt or salt in sealed silica ampules and held at 375°C for three to six months.

We are evaluating a total of 16 ceramic materials in two series of tests--each series involving eight materials. Initial results from the first series of tests show that leach rates between the materials vary greatly, with the degree of variation depending upon the test conditions. For example, Table 2 shows variations in leach rates between materials of up to four orders of magnitude for tests carried out in flowing demineralized water at 250°C. Variations in leach rates approaching three orders of magnitude were observed in the static tests. As expected, the leach rates increased with temperature, decreased with increasing exposure time, and were much greater in the dynamic tests than in the static tests. In

TABLE 2. The Leach Rate of Ceramic Materials in Flowing Demineralized Water^(a) at 250°C

Material Tested	Total Exposure, h	Specimen Wgt Loss, mg/cm ² (b)	Average Leach Rate, g/cm ² -d(c)
99.8% Al ₂ O ₃	168	0.96	1.4 x 10 ⁻⁴
	504	2.54	1.2 x 10 ⁻⁴
99% Al ₂ O ₃	168	1.72	2.5 x 10 ⁻⁴
	504	3.92	1.9 x 10 ⁻⁴
ZrO ₂	168	2.12	3.0 x 10 ⁻⁴
	504	3.41	1.6 x 10 ⁻⁴
Mullite (2Al ₂ O ₃ ·SiO ₂)	168	9.51	1.4 x 10 ⁻³
	504	34.27	1.6 x 10 ⁻³
Graphite	168	0.014	2.0 x 10 ⁻⁶ (d)
	504	0.120	5.7 x 10 ⁻⁶ (d)
Vitreous Silica	168	4.85	6.9 x 10 ⁻⁴
	504	11.22	5.3 x 10 ⁻⁴
Pyroceram 9617 ^(e)	168	72.74	1.0 x 10 ⁻²
	504	201.48	9.6 x 10 ⁻³
Marcor Glass	168	46.42	6.6 x 10 ⁻³
Ceramic ^(e)	504	113.80	5.4 x 10 ⁻³

(a) 1.7-gal autoclave; water flow = 0.5 gal/h.

(b) Based on geometric surface area of test specimen.

(c) Based on the geometric surface area of the specimen.

(d) The graphite used has an actual surface area (BET) of 2800 cm²/g; the leach rate based on the actual surface area would be 1.9 x 10⁻⁹ and 5.5 x 10⁻⁹ g/cm²-d for the 168-h and 504-h tests, respectively.

(e) Corning Glass Works product.

general, the leach rates were greatest in the demineralized water and lowest in the WIPP brine solution. The relative leach rates for the materials tested are as follows:

- Demineralized water at 250°C - static tests
99.8 Al₂O₃<ZrO₂<99 Al₂O₃<Graphite<Silica<Mullite<Pyroceram<Marcor
- Demineralized water at 150°C - static tests
99.8 Al₂O₃<Graphite<99 Al₂O₃<Mullite<Silica<ZrO₂<Pyroceram, Marcor
- Hanford Groundwater at 250°C - static tests
99.8 Al₂O₃<Graphite<99 Al₂O₃<Mullite<Pyroceram<ZrO₂<Silica, Marcor
- Hanford Groundwater at 150°C - static tests
99.8 Al₂O₃<ZrO₂<Graphite<99 Al₂O₃<Mullite<Pyroceram<Silica<Marcor
- WIPP Brine at 250°C - static tests
Graphite<99.8 Al₂O₃<99 Al₂O₃<ZrO₂<Mullite<Silica<Pyroceram<Marcor
- WIPP Brine at 150°C - static tests
Graphite<ZrO₂<99.8 Al₂O₃<99 Al₂O₃<Mullite<Silica<Pyroceram<Marcor
- Flowing Demineralized Water at 250°C - dynamic tests
Graphite<99.8 Al₂O₃<99 Al₂O₃<ZrO₂<Silica<Mullite<Marcor<Pyroceram

The eight materials to be evaluated in the second series to tests are TiO₂, CaTiO₃, CaZrO₃, BaTiO₃, BaZrO₃, CaTiSiO₅ (sphene), ZrSiO₄, and basalt.

LONG-TERM DURABILITY OF METALS IN NATURAL ENVIRONMENTS - A. B. Johnson, Jr. and B. Francis

Assessments of metal behavior over centuries and even millenia are important in some nuclear waste management concepts. Several metals including archeological artifacts, metal meteorites, and native metals have in fact demonstrated excellent durability, in selected environments, from antiquity. Although the behavior of these materials does not relate directly to nuclear waste management, it represents potentially useful information from several standpoints, including:

- baseline data on metal durability
- insights into factors that contribute to metal durability
- comparisons with extrapolations of laboratory data on modern materials.

Superimposed upon the baseline information must come evaluations of radiation effects and elevated temperatures. Even so, it appears useful to assess the durability of ancient materials for the reasons indicated above, and a program has been instituted to conduct such a review.

Archeological Materials

Ancient metallurgists fashioned implements and artwork from gold, silver, copper, lead, tin, and iron in various alloys and combinations. The durabilities have varied with environment and material, but there are examples of each material that are well preserved for at least one thousand years, and some artifacts have survived for times estimated at 5000 to 6000 years. Corrosion measurements are available for selected artifacts that provide estimates of corrosion rates. These can be used to at least partially validate extrapolations of modern corrosion measurements.

Metal Meteorites

Approximately 530 metal meteorites have been identified--some of which have known or estimated terrestrial ages. Current documentation includes:

- approximately 35 meteorites that were observed when they fell to earth (with ages ranging from 10 to 240 yr);
- approximately ten large metal meteorites that formed craters with ages between ~500 and >100,000 yr (geologic dating of the crater establishes an approximate terrestrial age for the meteorite);
- a few metal meteorites dated by radio-counting--a difficult and seldom used method for metal meteorite dating;
- meteorites and artifacts made from meteoritic iron that have been studied extensively.

The metal meteorites are principally iron-nickel alloys; a large majority have nickel concentrations of between 5 and 11 wt%. The degree of metal meteorite degradation can be gauged by the presence or absence of the surface oxide (fusion crust) and the heat-altered metal (α_2) layer. Of 480 iron meteorites assessed, 146 had both the fusion crust and α_2 layers and 230 had α_2 zones. Thus, over half experienced very little corrosion.

Native Metals

Several metals occur in nature, including gold, silver, and copper. A large native copper deposit in the upper Michigan peninsula has been studied extensively. The deposit occurs in Pre-Cambrian rocks ($\sim 2\frac{1}{2}$ billion yr old), though the deposit itself may be more recent. Copper boulders from the deposit were transported up to two hundred miles from their original location by glaciers during the Pleistocene ice age ($2\frac{1}{2}$ million to $\sim 20,000$ yr ago). Striations that developed on the copper surfaces during transport are still evident, attesting to minimal weathering over at least twenty millenia.

LEACH-TESTING OF THE OAK RIDGE NATIONAL LABORATORY CERMET - J. H. Westsik, Jr.

The chemical durability of the Oak Ridge National Laboratory (ORNL) Cermet waste form was evaluated using the Soxhlet, pH-4, pH-9, IAEA, and autoclave leach tests. The thick discs provided by W. S. Aaron were doped with ^{137}Cs and ^{106}Ru at ORNL. Leach rates were then determined using these isotopes and weight-loss measurements. The results are shown in Table 3.

The Cermet is defined as a continuous iron-nickel metal phase containing small particles of waste oxides (Aaron et al. 1978). In preparing the Cermet, many of the fission products including ruthenium are reduced to their metallic states. Cesium is incorporated in a pollucite phase within the metal matrix. The disc we received for leach-testing had mirror surfaces with some slight imperfections--apparently from the waste oxides. The discs leached at room temperature retained their shiny surfaces after the test. There was a galvanic reaction between the Cermet and the stainless-steel baskets used to hold the sample in the pH-4, pH-9, and IAEA leach tests. Rust-colored patches found on both the samples and the baskets

TABLE 3. Results of Leach Tests on ORNL Cermet

Leach Test	Conditions	Weight Loss	Leach Rate g/cm ² -d	
			Cs	Ru
Soxhlet	72 h @ 99°C Distilled H ₂ O	7.1×10^{-6}	7.2×10^{-5}	(a)
pH-4	31 h @ 25°C Acetate buffer	7.4×10^{-4}	4.6×10^{-4}	1.0×10^{-5}
pH-9	31 h @ 25°C Ammonium- Hydroxide buffer	1.6×10^{-5}	2.4×10^{-4}	1.7×10^{-6}
IAEA	146 d @ 25°C Deionized H ₂ O	4.1×10^{-6}	4.3×10^{-6} (average over 146 d)	(a)
Autoclave	7 d @ 350°C Deionized H ₂ O	1.5×10^{-5}	1.5×10^{-2}	(a)
Autoclave	7 d @ 350°C Saturated NaCl	Gained weight	3.9×10^{-2}	(a)

(a) Not detected.

resulted from this galvanic reaction. These samples are being studied by ORNL to determine the changes in the Cermet. The two samples exposed to hydrothermal conditions in a Hastelloy autoclave had dull gray surfaces at the end of the test, but they did not show any rust coloring. The gray finish is probably a thin oxide coating.

The leach rate data do not show any surprises. Ruthenium is less mobile than is cesium, and was not detected in the leach solutions from most of the tests. Cesium releases increased with increasing temperature. Cermet leach rates based on cesium behavior went from 4×10^{-6} g/cm²-d at 25°C to 7×10^{-5} g/cm²-d at 99°C to 1.5×10^{-2} g/cm²-d at 350°C. This corresponds to an activation energy of 1 kcal/mole. Releases of cesium at a given temperature increase as the ionic strength of the solution increases. The pH-4 and pH-9 test results support this conclusion when compared with the IAEA test and the two autoclave test results. Because of the galvanic reactions and the oxide film formation, the leach rates based on weight loss probably do not reveal much about the leaching behavior of the Cermet.

Although more study is needed, the preliminary conclusion is that the Cermet shows a leaching behavior similar to that of glass and supercalcines.

THE PENNSYLVANIA STATE UNIVERSITY SUPERCALCINE INVESTIGATIONS - G. J. McCarthy, Program Leader

Specimens were prepared from sintered supercalcine for scanning transmission electron microscopy (STEM) by grinding and then argon-ion thinning. They were mounted on copper grids. The instrument, located at the Rockwell Science Center^(a) was a Philips EM-400 with a STEM attachment operated at 120 kV. The electron probe diameter used for these analyses was 200 Å, so that sampling of multiple crystals and excitation of x-rays from neighboring crystals was minimized.

Table 4 summarizes the elemental chemistry obtained to date from the STEM characterization. Partitioning of waste ions between the proposed supercalcine crystalline phases was observed. For example, the apatite structure (A_{ss}) phase contains minor substitutions of Zr and Fe. A phase was identified in the matrix of the SPC-4+U specimen that was not one of those originally proposed. This crystalline phase contains Si, Al, Ba, Sr, Fe, Na and Ca. The intensities of the characteristic x-ray energies are similar to those that would be observed from a celsian (feldspar) phase, $(Ba, Sr, Na, Ca)(Al, Fe)_2Si_2O_8$, but further work to include electron diffraction will be required to confirm this assignment. As indicated in Table 4, all of the other synthetic mineral phases in current supercalcine-ceramics [P (pollucite), M_{ss} (monazite), T_{ss} (ZrO₂-rich fluorite) and Sp_{ss} (spinel)] except $(Fe_2O_3)_{ss}$ have been observed in one or both of the specimens. An additional matrix phase that has Al as its dominant cation, possibly corundum (α -Al₂O₃), was found in PSU-SPC-2+U.

The largest crystals found from STEM analyses are on the order of a few μ m in cross section. A general statement based on the limited studies to date is that in these supercalcine-ceramics, crystal or grain sizes vary from about 0.05 μ m (500 Å) to 10 μ m, with the median at about 0.2 μ m.

(a) STEM studies were conducted by D. E. Clarke, Rockwell Science Center, Thousand Oaks, CA

TABLE 4. Elemental Chemistry of Supercalcine-Ceramic Phases

Phase	[Structural] Type	PSU-SPC-2+U	SPU-4+U
A _{ss}	[Apatite]	Si, RE, Ca, Sr, Zr (Gd>Nd>Pr>La>Ce>Y) (a)	Si, RE, Ca, Sr, Zr, Fe (Gd>Nd) (b) [crystal a]
F _{ss}	[Fluorite]	U, RE, Zr (Gd>Ce>Nd>Sm, Y) (a)	U, RE, Zr (Gd>Ce>Nd) (b) [crystal b]
M _{ss}	[Monazite]	RE, P (Gd>Nd>La, Pr) (a)	
T _{ss}	[Fluorite-related]	Zr, RE, U	
S _{ss}	[Scheelite]	Mo, Ca, Sr, Ba	Mo, Sr, Ca, Ba, Nd [crystal c]
P	[Pollucite]		Si, Cs, Al, Rb, Fe
Sp _{ss}	[Spinel]	Fe, Ni, Cr	
Matrix		1. Si>Fe>Al 2. Al	1. Si, Al, Ba, Sr, Na Fe, Ca [crystal d] 2. Si>>Al, Fe minor Na, Mg, Ag, Ca, Sr, Ba, Cd, Cs, Nd, Gd [region e]

(a) Rare earth (RE) distribution was examined semi-quantitatively

(b) Rare earth (RE) analyses incomplete

These studies have confirmed that sintered supercalcine has intergranular noncrystalline phases that could constitute up to about 10 vol% or 6 wt% of the specimen. It has been expected that a glassy phase was present from x-ray diffractograms and from an apparent liquid-phase sintering mechanism. The glass is predominantly SiO₂, Al₂O₃ and Fe₂O₃, but it has small amounts of elements of concern such as Cs, Sr and rare earth (RE) (as possible models for the actinides). While aluminosilicates are among the most durable glasses, their durabilities could be considerably lower than those of the crystalline synthetic mineral hosts for these elements. Thus, the leachability of sintered supercalcine with respect to, for example, Cs might lie between that of crystalline pollucite and Cs in an aluminosilicate glass. Based again upon preliminary evidence, the partitioning of Cs and Sr between the crystalline phases and glass would appear to fall between 10:1 and 200:1, and of REs (and potentially actinides) between 100:1 and 1000:1.

SECTION 2. PROCESS DEVELOPMENT

The purpose of this task is to develop or improve processes for converting liquid high-level radioactive waste into solidified waste forms. Processes for producing glass as a first-generation waste form are well along in their development; process improvements are still being made, however. Processes for other waste forms must be developed through the sequence of conceptual equipment design, construction, pilot-plant testing, and process integration and demonstration.

LIQUID-FED CERAMIC MELTER - J. L. Buel

Analysis of much of the data gathered during the 5-d powder-fed run in the liquid-fed ceramic melter (LFCM) during December, 1978 has been completed. The run was performed using Savannah River Plant's simulated composite waste and glass former 411. The feed material was a premixed, powdered mixture of synthetic calcine and glass formers. The glass formers were added in the form of minerals, as opposed to a premelted frit.

The primary purpose of the run was to determine the maximum continuous capacity attainable with this feed in the LFCM. We were also interested in determining the amount of crystalline material formed during the run.

During the 5-d run, 5000 kg of Savannah River Plant (SRP) glass was produced, filling three 0.61-m-dia x 2.9-m-tall canisters. Including all down time, the average glass production rate was 42 kg/h. The capacity was limited by a phenomenon called "foaming," which is the formation of a voluminous glass filled with gaseous bubbles. It was found that foaming could be avoided by maintaining the production rate at or below 51 kg glass/h. Figure 6 illustrates the melter behavior when this melting rate was exceeded.

The reason stable cold-cap operation could be maintained at 51 kg/h or less was that the cold cap did not reach the wall and gases could escape at the periphery of the cold cap. This production rate was converged upon by repeated reductions of feed rates until stable behavior was attained, as is shown in Figure 7. In many cases, foaming was prolonged by reducing the feed rate after foaming had developed. This did not allow the cold cap to recover until the feeding operation was shut down.

Figure 8 shows some of the temperatures at certain vertical depths of the melter. High glass temperatures of $>1200^{\circ}\text{C}$ were attained consistently during stable cold cap operation. Foaming could be detected easily by a sudden drop in temperature near the cold cap.

Figure 9 shows that the power requirements during stable operation were between 60 and 70 kW. The power increases during foaming were necessary because of the loss of the insulative value of the stable cold cap.

The reduction of resistance is clearly shown in Figure 10, as the conductive Savannah River Laboratory glass displaced the previous glass composition. The spikes in resistance are results of the occasional foaming behavior that temporarily reduced bulk-glass temperatures and increased resistance.

FIGURE 6. Sequence of Cold Cap Behavior During Foaming

FIGURE 7. Feed Rate vs. Time

FIGURE 8. Glass Temperature vs. Time

FIGURE 9. Power vs. Time

FIGURE 10. Glass Resistance vs. Time

Subsequently, a short run was made in which the glass formers were added as premelted frit. In 8 h, 753 kg of glass having the same composition as in the longer run were produced without foaming at an average production rate of 92 kg/h. Even though past experience has generally shown more stable cold-cap operation when minerals were used as the glass formers, this run showed improved behavior with premelted frit. The premelted frit reduced gas generation during melting.

No crystalline sludge accumulated on the floor of the melter during these runs.

CALCINE-FED CERAMIC MELTER - R. D. Dierks and J. E. Jenkins

Following the modification and reassembly of the calcine-fed ceramic melter (CFCM), a 418-kg startup charge of a blend of simulated SRP composite waste calcine and 411 frit was added to the ceramic melter tank before the tank's lid was secured. Thirteen silicon-carbide heating elements (inserted through the lid of the melting cavity into the vapor space over the startup charge) were used to raise the temperature of the charge uniformly over a 4-d period to 950°C. At 950°C, electrical conduction between the submerged Inconel electrodes enabled joule-heating to maintain the desired temperature and the startup heaters were removed. Startup proceeded smoothly without excessive foaming.

The first experiment, designated CFCM-6, involved ten consecutive days of calciner-melter system operation. The run was begun 4/17/79 at 23:00 and was completed on 4/27/79 at 22:00, for an elapsed time of 239 hours. Frit 411 was used as a glass former for the first 106 h of the experiment, and Frit 211 was used for the final 133 h. Feed to the calciner was shut off six times for a total downtime of 35 h (15%). Feed was shut off twice within the first 40 h for a total downtime of 17 h in order to dissipate foaming which was probably

caused from operating the melter at an insufficient glass temperature. The third shutdown (for 1 h) resulted when the calciner nozzle was disassembled for inspection. During the last 6 h of operation with the Frit 411 and at glass production rates of 65 to 70 kg/h, glass foam gradually began to accumulate in the melter tank. The feed to the calciner was shut off for 3 h to dissipate this foam before the experiment was continued with the 211 frit. The last two feed shutdowns, totaling 14 h, resulted when the frit-feeder airlock system failed, necessitating its removal and repair. During the final 96 h of the experiment there were no calciner feed interruptions.

Because of the limited current-carrying capacity of the electrode power cables (1040 amps), and the 1000-amp limit on the current-monitoring instrumentation, the power to the melter was limited to 970 amps during this experiment. At the 970-amp input, the maximum sustained melting rate with the glass former Frit 411 was only 55 kg glass/h, and the tank glass temperature was only 1170°C. However, with the higher-resistivity glass former Frit 211 the maximum sustained melting rate was 64 kg/h and the tank glass temperature was 1250°C.

Shortly after the experiment had been terminated and the cold cap had melted, a manual probe was devised to measure the extent of sludge accumulation on the melter tank floor. With this device it was estimated that a non-uniform layer of sludge ranging from 1/4 in. to 4 in. thick was present on the tank floor. The center of the tank up to the discharge throat appeared to have only a light, 1/4-in.-thick layer of sludge. The thickness increased to about 2 in. in front of the electrode foot, and to 2 in. on top of the electrode foot. Immediately adjacent to the melter wall on the side that includes the discharge throat, the sludge thickness appeared to be a uniform 2 in. on the electrode foot and 4 in. for about 6 to 8 in. in front of the foot, then tapered down to 1/4 in. at the throat.

Before starting the second experiment two additional cables were installed to increase the current-carrying capacity to the electrodes from 1040 to 1560 amps, and the 0-to-1000-amp current transducer was replaced with a 0-to-2000-amp unit to enable the current and power values to be monitored. The electrode power sensing leads were also shifted from the output buss bars on the power supply transformer to the electrode input lugs in order to eliminate the voltage drop and consequent power dissipation factor in the power cables.

The second experiment, CFCM-7, involved 26 consecutive days of calciner-melter operation. The run started at 21:30 on 6/4/79 and was completed on 6/30/79 at 11:30, for an elapsed time of 614 hours. Frit 211 was used as a glass former for the entire experiment. Feed to the calciner was shut off twenty-eight times for a total downtime of 109 h (18%). Most of these shutdowns (14, totaling 64 h) were required to dissipate the foam that accumulated as the melter was operated with low-input power levels and consequent low tank glass temperatures. Two shutdowns, for a total downtime of 21 h, were required to repair the airlock valve on the frit addition line to the calciner cone. Five shutdowns, totaling 11 h, involved problems with the canister-to-melter connecting section. The remaining shutdowns were of very short durations for miscellaneous maintenance purposes. During the final 122 h of the experiment there were no calciner feed interruptions.

A maximum glass melting rate of 85 kg glass/h was sustained for 9 h before the failure of the frit airlock valve necessitated a prolonged shutdown of the calciner system. During this maximum production period, the melter electrode current averaged 1200 amps, the tank glass temperature averaged 1280°C, and the melter tank resistance was steady at about 0.067 ohms. Direct air-cooling of the electrodes limited the maximum electrode temperature to about 1050°C.

After the calciner shutdown for the frit airlock repair, the capacity of the calciner melter system was limited to 70 kg glass/h because of an abnormally high differential pressure across the calciner off-gas filters. The cause of this sudden increase in filter pressure drop is not yet known. Thus, during the last ten days of the experiment the glass production rate was maintained at 70 kg/h and the input power was increased in the six steps, ranging from 66 to 81 kW, to establish the melter temperature parameters with the minimum power input that would sustain continuous operation. At 81 kW input power the melter current averaged 1150 amps, the tank glass temperature averaged 1275°C, the melter tank resistance was about 0.067 ohms, and the maximum electrode temperature was about 1040°C. Excellent operation was demonstrated at this power input for the last 122 h of the experiment.

At the lower power input levels the melter characteristically operated for 12 to 24 h before an increased foam accumulation in the melter required a feed shutdown. The onset of foaming was characterized first by a steady increase in the tank resistance value, then by a sharp decrease in the electrode temperatures. Apparently, if the power input is too low the bulk glass temperature slowly decreases, as indicated by the increase in the tank resistance. This increases the glass viscosity and inhibits the release of gases from the melt, producing a foam. As the foam level builds up, the frit and calcine feed pile that normally floats on the molten glass surface begins to sink into the foam. Eventually, the foam begins to roll, pulling the cold cap and the frit pile (both of which are relatively cold) into the foaming surface. This further cools the glass, further increases its viscosity, and generates more foam. Finally, there is no cold cap visible and the incoming feed is immediately engulfed in the foam, which now may extend down to the top of the discharge throat, as is evidenced by the appearance of foam in the discharge trough. By stopping the feed input to the melter and by either holding the input power constant or increasing it slightly, the foam can be dissipated and the melter temperatures returned to their normal values.

REMOTE CERAMIC MELTER - K. E. Eliason and D. H. Siemens

A joule-heated ceramic melter capable of being operated by completely remote means has been designed and installed in the High-Bay Engineering Laboratory of the 324 Building. This melter, shown in Figure 11, has several unique features. An airlift discharge system, in lieu of tilting, is used to drain the melter. A sump is located in the floor of the melter to provide required airlift submergence and to provide the ability for nearly complete draining of the melter. The floor of the melter is sloped towards the airlift sump. It is hoped that the combination of sloped-floor and sump-type discharge will eliminate the spinel buildup that has been experienced with other ceramic melters.

FIGURE 11. Remote Ceramic Melter

The melter is designed as an integral package--mounted on a track system and installed under a simulated spray calciner so that remote maintenance and replacement can be demonstrated. Other remote maintenance features will be added as requirements are identified. The ability for remote change-out of the glass receiver canister is also provided.

The melter has a nominal melting capacity of 30 kg/h of glass. The unit was successfully started up in June 1979 and is currently undergoing post-startup tests.

EXPERIMENTAL CERAMIC MELTER - R. A. Brouns

The experimental ceramic melter (ECM) is a joule-heated, ceramic-lined melter capable of operating at temperatures approaching 1500°C. This experimental melter was designed as a low-budget, expendable melter useful in developing and testing higher-temperature glasses and alternative waste forms. The ECM will also be used to study the processability of different glass formulations before testing in full-scale equipment. A wide variety of electrode material may be used, including Inconel-690 for standard operation and molybdenum for high-temperature operation. A drawing of the ECM is presented in Figure 12.

FIGURE 12. Experimental Ceramic Melter

As a lab-scale melter, the ECM offers the following advantages over existing full-scale equipment:

- broad flexibility in glass composition, processing temperatures, and waste forms
- easily removable, replaceable electrodes
- lower operating cost.

The ECM was started and brought to idling temperatures in March of 1979. Glass production was demonstrated for the first time when two powder-fed runs with simulated Savannah River waste were completed in May of 1979. The purpose of the runs was to test the operation of the melter and the processability of the feed before its use in the 5-d powder-fed run in the liquid-fed ceramic melter scheduled for July.

During the two runs a total of 74 kg of glass were produced at an average feed rate of 6.4 kg/h. Melting fluxes as high as 146 kg/h-m^2 were successfully demonstrated without the limitation of foaming.

Operation of the melter was very smooth. Batch feeding every fifteen minutes proved to be adequate by maintaining a well formed cold cap without excessive thermal cycling of the plenum refractory walls. The glass stream was continuous during most of the runs, with the exception of canister-change periods. Glass streaming and/or nesting problems were non-existent, even when the glass stream became thin before a feed batch addition. The successful operation of the overflow section is attributed to three factors: 1) the high melter-floor temperatures; 2) the short distance from the pouring tip to the glass level in the canister; and 3) the arrangement of the overflow heating, which concentrates over 50% of the heat generated on the front face and pouring tip.

PROCESS CHEMISTRY - J. M. Lukacs and C. C. Church

Behavior of Coal During Spray Calcination

Small concentrations of organics from ion exchange resins and coal filters are anticipated in Savannah River Plant waste streams. These organics have been assumed to decompose during the spray calcination process and to be absent during vitrification. Carbon can have a significant chemical reducing effect upon glasses, affecting several physical and chemical processes.

Two trials were run in the developmental spray calciner to determine if the defined level of anthracite coal anticipated in a simulated Savannah River Plant TDS waste solution would be decomposed during calcination. Trial 1 produced 3.58 kg of simulated TDS calcine (coal not added). Trial 2, in which the defined level of anthracite coal (0.59 wt% solids) was added to the liquid feed, produced 2.81 kg of simulated TDS calcine. Table 5 lists the waste compositions used for both trials. The anthracite coal used in Trial 2 was relatively coarse, with over 50 wt% larger than $300 \mu\text{m}$. With a constant heating rate, this anthracite lost 88 wt% between 400° and 600°C . A chemical analysis, however, showed the carbon content of the coal was only $37 \pm 3.9 \text{ wt\%}$, as shown in Table 6. The defined anthracite level of 0.59 wt% therefore adds only 0.22 wt% of carbon to the waste solution.

TABLE 5. Simulated Savannah River Plant TDS Waste Compositions

Component	Solids Content, wt%	
	Trial 1 (no anthracite)	Trial 2 (with anthracite)
Fe(OH) ₃	88.98	88.46
Al(OH) ₃	2.97	2.95
MnO ₂	2.46	2.45
Zeolite	1.61	1.61
Ni(OH) ₂	1.44	1.44
CaCO ₃	1.02	1.01
NaNO ₃	0.42	0.42
Na ₂ SO ₄	0.25	0.25
Anthracite	--	0.59
Total	99.15	99.18

TABLE 6. Chemical Analysis Results

Analysis	Total Carbon, wt%	Inorganic Carbon, wt%	Total Organic Carbon, wt%
Trial 1	0.22	0.11	0.11
Trial 2	0.69	0.06	0.63
Anthracite	37.0 ± 3.9	0.50	--

Representative samples of the calcine product from Trials 1 and 2 were examined to determine how much anthracite/carbon survived the calcination step. Significant quantities of anthracite coal were detected in Trial 2 calcine by x-ray diffraction and chemical analysis. While reproducibility of x-ray results were poor because of sample inhomogeneity, a clearly defined peak associated with the anthracite was always detected for the Trial 2 material. The chemical analysis technique used identified both the total amount of carbon present and the amount present in carbonate form. Table 6 presents this data. In Trial 1 the theoretical amount of carbon present as carbonate in the dry calcine is estimated at 0.16 wt%. This agrees well with measured carbon levels and indicates that this compound is not decomposed during calcination. If all the carbon added to the Trial 2 solution as anthracite was unaffected by calcination, the carbon content of the calcine would increase approximately 0.29 wt%. The actual increase in carbon content from Trial 1 to Trial 2 is slightly greater than anticipated. The variation in sample homogeneity could account for this discrepancy. Various particle size fractions of the Trial 2 calcine were examined by x-ray diffraction. Anthracite coal was positively identified in all fractions with particles larger than 75 μ m. It appears that the mixing and calcination process significantly reduced the particle size of the processed anthracite.

It is a reasonable conclusion that the anthracite material used for Trial 2 was not significantly decomposed in the developmental spray calciner. The full-scale calciner may increase decomposition to some degree; however, this is expected to be a limited effect, since

spray-calcine samples from both units tend to be very similar. Subsequent trials with finer anthracite powder may shed some light on the decomposition kinetics, though an anthracite particle-size specification or defined level does not presently exist for the Savannah River Plant waste. It is fair to assume that some amount of organic carbon will enter any subsequent Savannah River Plant melting process. Characterization work with reduced Savannah River Plant glasses is necessary to establish whether this significantly impacts glass processing or storage properties.

Spray-Dried Waste Material

The production of simulated waste calcines in commercial spray-drying facilities can supplement the production from spray calciners for long-duration, continuous ceramic melting trials. Commercial spray drying, as opposed to waste-spray calcination, employs lower temperatures--making it possible to add all of the required frit constituents to the liquid waste before drying. The intimately mixed waste/frit batch, when dried, flows easily and melts readily at 1100°C.

Spray-dried material flows much more easily than does spray-calcined material. Table 7 presents powder density data for both types of simulated waste. The lower temperatures used in spray drying may not completely decompose hydroxide or nitrate feed compounds. Both $\text{Al}(\text{OH})_3$ and $\text{Ni}(\text{OH})_2$ were identified in the spray-dried TDS waste. Figure 13 presents the weight-loss behavior of this material as a function of temperature. More decomposition products are present in the spray-dried material. Increasing the waste solids loading content of the liquid feed or subsequently heating the calcine to 300°C could eliminate this additional weight before melting.

TABLE 7. Powder Densities of Simulated TDS Waste Calcines

<u>Material</u>	<u>Loose Bulk Density, g/cc</u>	<u>Tapped Bulk Density, g/cc</u>
Spray-dried TDS	1.12	1.24
Spray-dried TDS-411	0.87	1.04
Spray-calcined TDS (FSSC-25)	0.95	1.24

SPRAY-NOZZLE AIR CAP TESTING - L. A. Stout

Spray-nozzle air caps of four compositions were tested for durability against thermal shock and abrasive wear. These air caps are shown in Figure 14. Specifically, air caps of 96% alumina, silicon nitride, Cer-vit,[®] and a machineable glass-ceramic were tested for thermal shock resistance. These three compositions and 303 stainless steel were tested for wear resistance.

[®] Cer-vit is a registered trademark of Owens-Illinois, Inc.

FIGURE 13. Decomposition of Spray-Dried SRP TDS Waste

FIGURE 14. Location of Wear Measurements Taken

The thermal-shock testing determined the susceptibility of the air caps to stress from rapid cooling and heating. Rapid cooling was accomplished by heating the air cap to approximately 925°C, then suddenly introducing a flow of cold air. The air flow was varied to obtain different rates of cooling. For rapid heating, the air cap was moved from ambient conditions directly into the hot environment. If less rapid heating was desired, cooling air could be run through the air cap while it was heating. Initial rates of cooling ranged from 440°C/min to 1790°C/min, while the maximum initial rate of heating was 200°C/minute.

The abrasive wear test determined which of the air cap compositions is most resistant to wear from actual use. Because of its abrasive quality, SRP feed was chosen for use in the wear testing. Wear of the air caps was followed by measuring a mold of the air cap interior. Two measurements were made on each mold: length of the orifice tip, and diameter of the internal orifice at the original orifice tip length. These measurements are shown in

Figure 15, and they indicate that there was rapid initial wear as the internal orifice corners were rounded off--after which the wear rate decreased sharply.

The air cap compositions with the best thermal-shock resistance were Cer-vit and silicon nitride, while those with the best wear resistance were 96% alumina and silicon nitride--thus making air caps of silicon nitride the best, overall. Results of the thermal-shock testing are summarized in Table 8, and those for the wear testing are in Table 9.

SPRAY CALCINER/CERAMIC MELTER OFF-GAS ANALYSIS - T. A. Nelson

The following components have been identified in the off-gas system and their concentrations estimated: CO_2 , H_2O , NO , NO_x , H_2 , O_2 , N_2 and CO . A Monitor Laboratories Oxides of Nitrogen analyser was used to identify NO and NO_x , and the other components were identified with a Hewlett Packard 5840-A Gas Chromatograph.

Table 10 shows the mean volume-percent of the off gas from the full-scale spray calciner running PW-7a (acid) feed and from the 5-d run using SRP feed. The PW-7a feed was at one-half the concentration of regular PW-7a. Both sets of data were taken from the venturi scrubber inlet (the beginning of the off-gas cleanup system).

Table 11 shows the mean concentration and volume-percent for the 10-d run of the full-scale spray calciner using SRP feed. The mean values for the 20-d-run ceramic melter off-gas concentrations and the volume percentages for the first week of the run are also included. Samples from the 10-d run were taken from the venturi scrubber inlet.

FIGURE 15. Spray Nozzle Assembly

TABLE 8. Results of the Thermal-Shock Testing

Air Cap	Test Performed		Results
	Rapid Cooling	Rapid Heating	
96% Al ₂ O ₃	x		Failed at initial cooling rate of 440°C/min
96% Al ₂ O ₃	x		Failed at initial cooling rate of 1790°C/min
96% Al ₂ O ₃	x	x	Did not fail
Cer-vit	x		Did not fail
Cer-vit		x	Failed at initial heating rate of 200°C/min
Cer-vit	x	x	Did not fail
Si ₃ N ₄	x	x	Did not fail
Si ₃ N ₄	x	x	Did not fail
Si ₃ N ₄	x		Did not fail

TABLE 9. Results of the Abrasive Wear Testing

Air Cap	Hours Used	Average Internal Orifice Diameter Increase, in.	Length of Orifice Tip, in.
Cer-vit	0	--	0.066
	15	0.026	0.045
	30	0.037	0.038
303 SS	0	--	0.062
	15	0.004	0.050
	30	0.018	0.040
96% Al ₂ O ₃	0	--	0.068
	15	0.052	0.062
	30	0.057	0.0615
	45	0.054	0.061
	60	0.057	0.060
Si ₃ N ₄	0	--	0.069
	15	0.011	0.064
	30	0.018	0.063
	45	0.022	0.062
	60	0.024	0.062

TABLE 10. Compositions of the Off Gas From the Full-Scale Spray Calciner Running PW-7a (acid) Feed and SRP Feed.

Component	PW-7a Feed, mean vol%	SRP Feed, mean vol%
CO ₂	0.649	0.05
H ₂ O, NO _x	1.50	1.75
O ₂	22.1	19.3
N ₂	75.2	78.8
CO	0.005	trace

TABLE 11. Mean Concentration and Volume-Percent for the 10-d Run and 20-d Run of the Full-Scale Spray Calciner Using SRP Feed.

Component	10-d-run mean off-gas concen- trations, g/l(a)	10-d run, mean vol%	20-d-run mean ceramic-melter gas, g/l(a)	20-d run, mean vol%
H ₂	7.4×10^{-5}	0.121	8.03×10^{-5}	0.125
CO ₂	3.37×10^{-3}	0.235	4.4×10^{-3}	0.418
H ₂ O, NO _x	1.56×10^{-2}	2.87	2.11×10^{-2}	3.79
O ₂	0.149	15.4	0.176	17.8
N ₂	0.689	81.4	0.673	77.9
CO	1.76×10^{-6}	0.0002	trace	--
NO _x ^(b)	--	--	1175 ppm	0.118
NO	--	--	750 ppm	0.075
TOTAL	0.857	100.0	0.875	100.0

(a) measured at 5 in. H₂O vacuum and 100°C

(b) from the NO_x monitor

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