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WASTE SOLIDIFICATION DEMONSTRATION PROGRAM: CHARACTERIZATION OF NONRADIOACTIVE SAMPLES OF SOLIDIFIED HIGH-LEVEL WASTE

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WASTE SOLIDIFICATION DEMONSTRATION PROGRAM:
CHARACTERIZATION OF NONRADIOACTIVE SAMPLES OF SOLIDIFIED HIGH-LEVEL WASTE

by

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R. J. Thompson, J. E. Mendel, and J. H. Kleinpeter

ABSTRACT

The Waste Solidification Demonstration Program is a cooperative program involving the Pacific Northwest Laboratory, the Brookhaven National Laboratory, and. the Oak Ridge National Laboratory to provide the technological bases which will enable industry to convert to a safer solid form the high-level liquid waste from the reprocessing of nuclear fuel. The work has culminated in the operation of the Waste Solidification Engineering Prototypes by Battelle-Northwest, wherein engineering-scale radioactive demonstrations are being conducted with three alternative solidification systems: phosphate glass, spray solidification, and pot calcination.

A major activity associated with the demonstration studies is behavior determination of solidified waste products and evaluation of the safety and economic aspects of this behavior as related to the management of high level wastes. One of the means being used to evaluate the solidified waste is characterization of nonradioactive laboratory samples of phosphate glass and spray solids. The product characteristics that have been measured include leachability, thermal diffusivity, heat capacity, density, drip point, thermal shock, dispersibility, crystallinity, and linear coefficient of thermal expansion. These characteristics have been compared with the processing parameters of composition, melt-formation temperature, time at melt-formation temperature, rate-of-cooling to storage temperature, and storage temperature.

The study showed that the process temperature used to prepare the solid waste and the storage temperature of the samples have the greatest effect on the physical, chemical and thermodynamic properties of the phosphate glass and spray solids. The effect of process and storage temperature are most noteworthy in the degree of crystallinity of phosphate glass and in the physical and thermal properties of both products. High process temperature (1200 °C) tends to result in a more vitreous phosphate glass than does lower process temperature (1000 °C). Storage temperatures of 600 °C for 8 weeks promote crystal growth within phosphate glass samples, while 100 °C for 8 weeks has markedly less effect. The more crystalline phosphate glass is tougher, conducts heat better, and is less dispersible by mechanical impact than vitreous glass; it is, however, more water leachable.

High process temperature (1100 °C) and to a lesser extent long times at process temperature (25 hours) may result in a nonhomogeneous spray solid. Lower process temperature (800 to 1000 °C) produces a tough, durable, ceramic-like material that has a higher thermal conductivity on the average than phosphate glass. The leachability of spray melt is quite similar to crystalline phosphate glass, but is not as good as vitreous phosphate glass.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

WASTE SOLIDIFICATION DEMONSTRATION PROGRAM: CHARACTERIZATION OF NONRADIOACTIVE SAMPLES OF SOLIDIFIED HIGH-LEVEL WASTE

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1.0 INTRODUCTION

The purpose of the Waste Solidification Demonstration Program is to provide the technological bases which will lead industry to adopt at the earliest possible time the practice of solidifying the high-level liquid waste from nuclear fuel reprocessing. It is generally recognized that converting this intensely radioactive liquid waste to a solid, less mobile form produces a waste that is safer and therefore highly desirable. The establishment of soundly based techniques for converting liquid wastes to solids has required technical developments of processes and equipment, product and container evaluation, and techniques to assure the safe and economic handling of the secondary waste streams associated with the solidification process. Radioactive wastes must be stored for very long times under stable, controlled conditions. Five to ten centuries are required for the decay of radioactive fission products, and a storage period of hundreds of thousands of years is required for the small amount of plutonium present as a waste loss during reprocessing. Initial guidelines for such storage were recently proposed by a notice in the Federal Register(1) which stated that all high-level wastes should be solidified by the time the spent nuclear fuel (the source of the waste) has been at the reprocessing plant for 5 years. In addition, the solidified wastes must be shipped to and stored in as yet undesignated Federal repositories for final disposal within 10 years after receipt of the fuels at the reprocessing plant. Shipping high-level wastes as liquids will not be permitted.

A cooperative program involving Battelle-Northwest (BNW) at the Pacific Northwest Laboratory (PNL), the Brookhaven National Laboratory (BNL), and the Oak Ridge National Laboratory (ORNL) was established to provide the required technology. The program has reached its culmination with the demonstrations of the Waste Solidification Engineering Prototypes (WSEP) by Battelle-Northwest at the Pacific Northwest Laboratory. In this facility, pilot plant demonstrations are being conducted with three alternative solidification systems: phosphate glass solidification, spray solidification, and pot calcination. The demonstrations are performed with solutions which have chemical compositions and radioactivity levels comparable to those which will exist in high-level wastes from commercial plants which reprocess power reactor fuels.

The main incentive for converting high-level wastes to solid forms is the need for improved containment safety during the centuries required for the stored radioactive decay to nontoxic levels. The periods of greatest interest are the interim storage period before the waste is placed in a location for permanent storage where surveillance may be discontinued or greatly reduced, and the time during which the waste is transported through populous areas from its source to the location for permanent storage. The AEC position document requires that both interim storage and transport to permanent storage be completed within 10 years after solidification, when heat removal problems, product temperature, radioactivity, and rate of radiochemical changes are at their greatest.

BNW is responsible for:

- Characterizing the pertinent physical and chemical properties of the products from three solidification processes being demonstrated in the Waste Solidification Demonstration Program.
- Performing engineering and safety analyses of the product characteristics for direct application to the industrial reprocessors on Nuclear Fuels.

A product evaluation program was established to accomplish the above objectives. To provide the data needed to define the pertinent properties of the solidified waste products and enable engineering and safety analyses of the product characteristics, the three following types of measurement data are being obtained: nonradioactive laboratory, radioactive laboratory, and engineering scale.

The largest number of samples and measurements are being made in the nonradioactive laboratory to obtain maximum data (exclusive of radiation effects) at minimum cost. A large number of samples are being used to study various effects exclusive of radiation. For example, the effects upon product quality of the processing parameters (melter operating temperature, residence time in melter, cooling rate from melt to storage temperature) and storage temperature were studied using laboratory-prepared nonradioactive product specimens. The product characteristics measured were thermal conductivity, density, heat capacity, linear coefficient of thermal expansion, leachability, dispersibility, crystallinity, thermal shock, drip point, and porosity.

This report summarizes the studies from the nonradioactive laboratory sample product characterization portion of the Waste Solidification Demonstration Program.(2) The laboratory techniques and measurements on phosphate glass and spray solids are described in detail.* All pertinent product measurements are presented in the appendix.

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* Pot calcine was not evaluated because the form of the calcine involved cannot be readily duplicated in the laboratory, and some variations in processing parameters cannot logically be done for the batch process.

2.0 SUMMARY

The nonradioactive laboratory studies showed that the temperature used during preparation of the solids and the storage temperature of the samples have the greatest effect on the physical, chemical, and thermodynamic properties of the phosphate glass and spray solids. The effects of processing and storage temperatures are most evidenced in the degree of crystallinity of phosphate glass and in physical and thermal properties of both products. High temperature of melt preparation (1200 °C) tends to cause a more vitreous phosphate glass than does lower melt preparation temperature (1000 °C). Storage temperature of 600 °C for 8 weeks promotes crystal growth within phosphate glass samples, while 100 °C for 8 weeks has markedly less effect. The more crystalline phosphate glass is tougher, conducts heat better, and is less dispersible by mechanical impact than vitreous glass; however, it is more water leachable by a factor of approximately 10.

High solid-preparation temperature (1100 °C) and to a lesser extent long time at melt (25 hours) may result in a nonhomogeneous solid from spray solidification. Lower melt-preparation temperature (800 to 1000 °C) produces a tough, durable ceramic-like material that has a higher thermal conductivity on the average than phosphate glass. The leachability of spray melt is quite similar to crystalline phosphate glass, but is not as good as vitreous phosphate glass.

The average thermal conductivity for spray solids was somewhat higher than the average thermal conductivity of the phosphate glass: 1.05 $W/(m^2)(°C/m)$ as compared to 0.75 $W/(m^2)(°C/m)$. The density of most spray solids was 3.5 g/cm^3 except for product from PW-2 (sulfate-containing) waste which was 3.0 g/cm^3, whereas phosphate glass density was found to be approximately 2.9 g/cm^3 for all samples. The average heat

capacity for phosphate glass was between 0.18 and 0.23 cal/(g)(°C) while the average for spray solids was between 0.17 and 0.19 cal/(g)(°C).

Measurement of the linear coefficient of thermal expansion showed that phosphate glass and spray solids have coefficients of approximately 10×10^{6} in./in./°C which is compatable with mild and stainless steels. No differential thermal expansion problem is expected for long-term storage.

Slow leach tests, made at 25 °C with samples of known surface area, yield quantitative leach data in the units of grams leached/(cm^2)(day). However, these tests are much more time-consuming than the accelerated leach tests. The leach rate varies as a function of time, often decreasing in orders of magnitude during the first few weeks of leaching. Indications are that for many of the WSEP-type products, pseudo-equilibrium leach rates are obtained only after 8 to 9 months of leaching. Most of the slow leach tests have not been taken to pseudo-equilibrium at the time of this report. (The remaining leach data will be made available in a later report.) Nevertheless, sufficient slow leach data are available to make some conclusions. For instance, using the case and criteria of Watson, ~~et al~~.,(3) for WSEP-type products, the permissible leach rate for conditions of continual water contact is about 10^{-11} g/(m^2)(day). (Basis: 6 ft^2/ft^3 of solid and water flow are equal to 1 glass volume flow per day.) The most nonleachable WSEP product, nondevitrified phosphate glass, has a leach rate of approximately 10^{-6} g/(m^2)(day). Thus it is obvious that in most cases, even the best solidified waste products should be kept separate from man's environment. It is also important to note that the most nonleachable of the solidified wastes offer improved leach rate protection over liquid wastes of approximately 1×10^{5} to 1×10^{6}. In addition, the package waste made up of container and solidified waste is less mobile, has significantly smaller volume, and is much more physically rugged than the liquid waste counterpart. Devitrification of the phosphate glass products, which occurs above about 550 °C, results in products which are somewhat more leachable than the microcrystalline spray solidification products.

The results of the accelerated leach tests on pulverized samples in near boiling water corroborate the results of the slow leach tests. The total weight loss during accelerated leach tests was the least for noncrystalline phosphate glass PW-2 samples (nominally less than 5 weight%). Crystalline phosphate glass PW-2 and all other phosphate glass products showed accelerated leach test weight losses from 20 to nearly 60 weight%. Spray solid accelerated leach test for PW-4m product was less than 15 weight%, for PW-2 approximately 40 weight%, and for PW-1 approximately 5 weight%. The accelerated leach data show that there is overlap in the leachability of various spray solid and phosphate glass products. Phosphate glass PW-2 is the least leachable; spray solid is intermediate; and phosphate glass PW-4m is probably the most leachable.

The nonradioactive laboratory study of solidified high level waste is the least expensive and potentially the most comprehensive approach to the evaluation of solidified waste. Pot calcine, borosilicate and fluid bed solids need to be studied in more detail. Some external irradiation of nonradioactive laboratory samples could provide an important tie-in with large-scale solidification.

3.0 EXPERIMENTAL PROCEDURE

This section describes the experimental procedures and techniques used to prepare samples and make measurements for product characterization. The waste compositions used were chemically the same for the nonradioactive laboratory studies as for the large scale demonstrations using radioactive materials. Sample preparation consisted of preparing large (300 to 500 cubic centimeter) pretreated specimens and subdividing the large specimens into smaller samples for each individual measurement. Standard measurement techniques were used except where specialized tests were developed for particular situations.

3.1 WASTE COMPOSITIONS

Early in the Waste Solidification Demonstration Program it was recognized that the great diversity in possible compositions of high-level waste solutions would restrict study to a few typical compositions, which would encompass the characteristics of the most typical in detail.(4) The compositions chosen for detailed study in the nonradioactive laboratory portion of product characterization are shown in Table 3.1. These waste compositions represent different fuel exposures and different fuel reprocessing flowsheets. The PW-1, PW-2, and PW-4m types are from light water reactor fuel, and were chosen for detailed study. The LMFBR waste composition is shown for comparison purposes and except for "burnup" level is not greatly different from PW-4m.

The diverse compositions chosen incorporated processing modes, fuel exposure levels, and fuel types. Aqueous reprocessing of the power reactor fuels by a Purex flowsheet was assumed in all cases; the wastes were all nitrate solutions. PW-1 is a high salt content waste which would result from dissolving iron fuel containers along with the fuel cores. PW-2 is a high salt content waste that contains large amounts of sulfate from

TABLE 3.1. Chemical Compositions of High-Level Liquid Wastes for WSEP Demonstration and Nonradioactive Laboratory Studies

Constituent	Concentration, Molarity at 378 liters/tonne[a] PW-1	PW-2	PW-4m	LMFBR
General Chemical Composition of Inert Materials				
Na	low	high	low	low
Fe	high	med	low	low
SO_4	0	high	0	0
Actual Chemical Composition of Inert Materials				
H	3.70	3.90	0.50	0.50
Fe	0.93	0.44	0.050	0.16
Cr	0.012	0.024	0.012	0.046
Ni	0.005	0.010	0.008	0.023
Al	0.001	0.001	0.001	--
Na	0.14	0.93	0.10	0.10
U	0.010	0.010	0.010	0.010
Hg	<0.001	<0.001	<0.001	--
NO_3	7.5	5.4	2.4	4.7
SO_4	--	0.87	--	--
PO_4	0.003	0.006	0.003	0.060
SiO_3	0.010	0.010	0.010	--
F	<0.001	<0.001	<0.001	--
$\sum M^{+}_{chem}$[b]	3.03	2.48	0.37	0.83
kg oxide/ tonne	31.7	28.1[c]	4.6	9.7

Chemical Composition of Major Materials from Nuclear Fission

Constituent	Fuel Exposure in Thermal Reactors		Core Fuel Exposure in LMFBR
	20,000 MWd/tonne at 15 MW/tonne	45,000 MWd/tonne at 30 MW/tonne	100,000 MWd/tonne at 200 MW/tonne
Mo	0.065	0.130	0.24
Tc	0.014	0.031	0.060
Sr	0.015	0.036	0.040
Ba	0.019	0.041	0.068
Cs	0.035	0.078	0.21
Rb	0.007	0.014	0.019
Y+RE[d]	0.12	0.27	0.53
Zr	0.065	0.14	0.22
Ru	0.032	0.082	0.22
Rh	0.007	0.013	0.060
Pd	0.017	0.043	0.16
Ag	0.0008	0.0016	0.019
Cd	0.0008	0.0025	0.010
Te	0.006	0.014	0.034
Sn	0.0007	0.0016	0.010
Sb	0.0002	0.0004	0.003
$\sum M^{+}_{fp}$[b]	0.91	2.11	4.10
kg oxide/ tonne	22.0	49.0	101.1

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[a] *"Tonne" is a metric tonne, 1000 kg or 2205 lb.*

[b] *M^{+} is metal equivalents, or normality of metal ions (does not include acid).*

[c] *Does not include the sulfate. If sulfate is not volatilized, approximately 27 kg/tonne of additional oxides are formed.*

[d] *RE is rare earth elements.*

a reprocessing plant using ferrous sulfamate as a reducing agent. PW-4m is a "clean" waste with a low nonfission product salt content which would be produced by operation with a Purex flowsheet designed to add a minimum amount of nonvolatile chemicals during reprocessing. PW-1 and PW-2 are wastes from LWR fuels with moderate exposures, 20,000 MWd/tonne at 15 MW/tonne; PW-4m is waste from a higher exposure LWR fuel, 45,000 MWd/tonne at 30 MW/tonne. PW-1, PW-2, and PW-4m contain the fission product spectrum from uranium fission. The WSEP reference waste composition for Liquid Metal Fast Breeder Reactor (LMFBR) fuel is a relatively clean Purex waste stream based on the reprocessing of fuel from the core of a fast breeder reactor.

In both the laboratory studies and the engineering-scale demonstrations in WSEP, chemical substitutions are being used for several of the fission products, wherein use of the actual elements would be too expensive, or the elements would be difficult to obtain in the amounts required. Molybdenum is substituted for technetium, nickel for palladium, cobalt for rhodium, sulfur for tellurium, and copper for cadmium and silver. Although the process behavior of ruthenium is of extreme importance, it is impractical to use the full amounts present in the nominal waste compositions shown in Table 3.1. Approximately 10% of the nominal concentration is added as $Ru(NO_3)_3$. Although no other known chemical constituent behaves like ruthenium, iron was selected as a substitute for the remainder of the ruthenium.

3.2 SAMPLE PREPARATION

Two steps were required in the preparation of the phosphate glass and spray solid samples prior to measurement of specific properties. Relatively large samples (300 to 500 cubic centimeters) of the solids were prepared according to process, feed type, and processing conditions. First, the aqueous feed was calcined to dryness in platinum crucibles and further dried in an oven for a specified time and at a specified temperature. Ruthenium, the only chemical that was not included in the initial feed solution, was added to the dry calcine powder in the platinum crucible as aqueous ruthenium phosphate, and the mixture was placed in an oven. It was then melted and held at the required temperature for the planned time. Second, the final solid was then transferred to stainless steel beakers and cooled to the ultimate storage temperature at a controlled cool-down rate. The sample was held at the storage temperature for 8 weeks. At the conclusion of the storage interval, the solid sample was cooled and transferred to the measurements laboratory for subdivision of the large samples into pieces suitable for individual property measurements.

Most of the final cutting, polishing, and sizing of coupons for actual property determination was done in the optical laboratory. Samples that were ground and screened prior to accelerated leachability measurements and drip point measurements were prepared by technicians involved in the actual measurement.

Most of the solidified waste samples provided excellent coupons for characterization of the product. However, in some instances **it** was not possible to prepare adequate coupons. 'In these cases, the problem has been noted in the Appendix and where appropriate in Section 4.0, Results and Conclusions.

3.3 MEASUREMENTS

As the nonradioactive laboratory samples became available, the samples were cut, polished, and sized before proceeding to the specific sample measurements. A large number of measurements were obtained for each sample to characterize the sample properties. The measurements included thermal diffusivity (for calculation of thermal conductivity), density, heat capacity, linear coefficient of thermal expansion, leachability (both slow and accelerated), dispersibility, crystallinity, thermal shock, and porosity.

3.3.1 Thermal Diffusivity (a)

A flash method which makes use of locally built equipment was used to determine thermal diffusivity. The operating techniques, theory, and calculations for this instrument have been discussed by Baker(5) in detail and are summarized here. Briefly, a sample of 0.5-inch diameter and 0.027-inch thickness is placed in a controlled temperature chamber inside a quartz tube. The quartz tube has a flat window sealed on the end which faces the heat source, and a pair of thermocouple wires sealed into the other. The ends of the thermocouple wires are sharpened and placed approximately 1 millimeter apart in contact with the back side of the sample. Thus the sample completes the electrical circuit and the temperature of that surface is measured. In cases where the sample is a nonconductor a very thin layer of metal was deposited on the rear face of the sample. The samples are coated with approximately 0.01 millimeter of chromium and gold.

The energy source is a xenon flash tube which emits a flash of very short (less than 1 millisecond) duration from which the sample absorbs enough heat to increase its temperature 1 to 36 °C. The change in sample temperature versus time is followed with an oscilliscope and is recorded photographically. Thermal diffusivity, a, is related to sample thickness and time by Equation (1):

$$\alpha = \frac{0.139\ L^2}{t_{1/2}} \qquad (1)$$

where L is the thickness of the coupon and $t_{1/2}$ is the time in seconds, required for one-half the temperature rise recorded.

Thermal conductivity may be calculated from density, heat capacity, and thermal diffusivity with the relationship expressed by Equation (2):

$$k = \alpha \rho C_p \qquad (2)$$

The sample density and heat capacity are determined experimentally.

3.3.2 Density (ρ)

The density was measured by a mercury displacement method using an Aminco-Winslow Porosimeter. With this instrument, a weighed sample of material is put into a tared container of known capacity. The volume of mercury displaced is calculated from the weight change. For nonporous samples, accuracies in the order of 0.1% are possible with this instrument.

3.3.3 Heat Capacity (C_p)

A Perkin-Elmer (Model DSC-1) Differential Scanning Calorimeter was used to determine the heat capacity. With this instrument, the temperature is programmed with both the sample and the reference maintained at the same level. When the sample absorbs (or evolves) energy, more (or less) electrical power is needed to keep the sample holder at the same temperature as the reference holder. The differential power, which is automatically and continuously varied, is recorded. The DSC records energy requirement as a function of temperature, which when the weight of the sample is known, can be converted to specific heat for the sample.

3.3.4 Linear Coefficient of Thermal Expansion (LCTE)

A locally built dilotometer was used to measure the thermal expansion of the laboratory samples. The linear expansion of the solidified waste samples were compared to the expansion of a quartz sample of known expansion characteristics. Both samples were maintained at the same temperature throughout the measurement cycle.

3.3.5 Leachability

Two types of experimental measurement have been used to determine the leachability of a sample. One method is termed the slow leach and the other the accelerated leach.

The slow leach testing device consists of a small glass vessel arranged with an airlift recirculator patterned after that used by Paige.(6) Samples of a known size and measurable surface area are placed in the leach vessel on the stainless steel screen support. Distilled water is added and circulated past the sample. The temperature of the vessel is held at room temperature. Periodically, leach water is drained from the vessel, collected in sample containers and analyzed for chemical composition.

The accelerated leach test(7) is most useful for rapidly obtaining comparative leachability. Product samples were crushed and sieved and the -45 mesh (350 micron) to +60 mesh (250 micron) fraction was used in the test. This fraction was freed of fines by washing with acetone and was weighed after drying into approximately 1 gram samples. These 1 gram samples were suspended in 200 mesh stainless steel cloth bags in 95 °C water for three 24-hour periods. The weight loss for each 24-hour period and the total weight loss was used as a measure of the sample leachability.

3.3.6 Dispersibility

A cylindrical sample of melt was cut to 3/4-inch diameter by 1/2-inch long and placed in a holder 13/16-inch inside diameter by 1/4-inch deep. The holder was placed on the concrete floor, and a 2.9 pound weight dropped from a height of 5 feet was allowed to strike the sample. The weight was armed with a hardened steel tip of 0.12-inch diameter and was guided in its descent by a well-vented transparent tube. The sample particles were collected and classified by particle size with sieves and divided into three sample groups: fines which were particles of less than 0.02-inch diameter, intermediate 0.02 to 0.1-inch diameter, and coarse greater than 0.1-inch diameter.

3.3.7 Thermal Shock

Test specimens were prepared from the large preconditioned laboratory samples of phosphate glass and spray solid. The specimen dimensions were 0.75 by 0.75 inches square by 0.5 inches thick. The specimens were heated to 600 °C in a vertically mounted tube furnace and dropped directly from the furnace into trichlorocthylene at 0 °C. The specimens were then removed from the quenching medium and photographed (where appropriate) to record the results. The distance from the bottom of the furnace to the surface of the quenching medium was less than 12 inches in all cases.

3.3.8 Crystallinity

The determination of the degree of crystallinity was accomplished with 80X and 40X photomicrographs and by visual inspection of the laboratory samples. The crystallinity determination is therefore considered qualitative rather than quantitative. Some electron microprobe work was done but was discontinued because of the high cost. The photomicrographs show the continuous glassy phase, crystal and crystal growth, and voids.

3.3.9 Porosity

The porosity of the samples was obtained at the same time the density measurements were made using the Aminco-Winslow Porosimeter. The amount of mercury forced into the pores of the sample was measured at specific pressure intervals.

Pressure and volumetric readings are plotted on semi-log paper where pore diameter and penetrations are obtained.

3.3.10 Drip Point

The drip point is an empirical measurement used as an indication of the temperature at which a waste can be processed. The details of the measurement have been described by Barton.(7) In basic outline, the procedure involves powdering a sample and placing 10 grams of the powder in a platinum funnel. The funnel is mounted vertically in a tube furnace and heated at a predetermined rate. The drip point is the temperature at which the first drop of molten sample falls from the funnel.

4.0 RESULTS AND CONCLUSIONS

The largest number of samples and measurements related to the Waste Solidification Demonstration Program have been made with simulated wastes in the nonradioactive laboratory. The main objectives of the nonradioactive laboratory studies are to study the effects of waste solidification processing parameters upon product characteristics and to characterize laboratory prepared samples. The processing parameters selected for study were process formation temperature (T_m), time at the process formation temperature (t_m), cool down rate (from process to storage temperature)(CR), and storage temperature (T_s). In addition to processing parameters, two products (phosphate glass and spray solid) were studied for each of three types of aqueous wastes (PW-1, PW-2, and PW-4m).

Some general observations regarding the experiments and the overall effects of the measurements and processing parameters are in order. Extrapolation of the information provided by this study to large-scale engineering work must be done with care because duplication of processing parameters between the two was not possible. Comparisons using core-drilled samples(8) from the engineering-scale studies will provide information on the effect of radiation on the solidified waste, and should provide additional data for establishing the relationship between hot cell and nonradioactive laboratory studies.

The phosphate glass samples from the three types of aqueous wastes were not greatly different. In general, the higher process temperatures (1200 °C compared to 1000 °C) and longer process times (25 hours compared to 1 hour) resulted in a more glassy sample than the samples made at lower process temperatures and with shorter process times. Visually, the glassy samples were brittle, shiny, and black. Photomicrographs showed little or no crystal structure in the glassy samples, whereas considerable crystal structure was observed in nonglassy samples. The high storage temperature (600 °C compared to 100 °C) tended to promote crystal growth within a sample. Crystal growth seems to cause the most significant changes in sample properties.

The samples of phosphate glass which were at least partially crystalline tended to be tougher (less dispersible by mechanical impact) and tended to have increased thermal conductivity. Phosphate glass samples with no crystal structure tended to be less leachable but were markedly more dispersible by mechanical impact. Different cool-down rates (100 °C/hr and 30 °C/hr) seemed to have the least effect on specimen properties.

At elevated temperatures beginning at about 350 °C, some of the phosphate glass samples also emitted or "sweated-out" a sticky material that was readily soluble in water. The approximate composition of the exuded material was the same as that of the overall sample composition. As in many of the other measurements, the phenomenon was apparently related to the degree of "glassiness." The more glassy the sample (hence, the better the solution on melting) the less likely the sample would "sweat." High quality "good glass" would appear to be a desirable goal for phosphate glass processing.

The spray solids from the three types of aqueous waste were not too different. The properties of the spray solids were not affected as much by the process parameters as were the properties of the phosphate glass. This difference is probably due to the ceramic crystalline nature of spray solid. High storage temperature (600 °C for 8 weeks compared to 100 °C for 8 weeks) seemed to increase thermal conductivity for spray solid. Nonhomogeneous samples (apparent phase separation) seemed to occur more often with the spray solids than with phosphate glass; however, phosphate glass samples did exhibit some phase separation. In several cases with the spray solids, the molten phase seemed to have drained away from the top, leaving a rather open network of cemented crystals with large voids in between. This phenomenon seemed to occur at the higher melt-forming temperatures (1100 °C) and long times at melt temperatures (25 hours). Phase separation requires increased care in interpreting the results of the studies. Most of the larger test coupons were cut from the more solid part of the melt and as a result may not be representative of the entire melt.

The spray solid tended to have a higher thermal conductivity, greater density, and be less dispersible from mechanical impact than phosphate glass. "Glassy" forms of phosphate glass tended to be less leachable than the spray solid. The degree of crystallinity of the phosphate glass, which is affected significantly by processing and storage temperatures, affects the relative positioning of the two products with respect to properties.

4.1 CRYSTALLINITY

A great deal can be learned of a qualitative nature about the phosphate glass and the spray solids through photomicrographs and photographs. Figure 4.1 shows photomicrographs of phosphate glass PW-2 specimens that were subjected to varying processing temperatures, times at processing temperature, cool-down rates and storage temperatures. The effect of process temperature on the crystallinity can be qualitatively evaluated by comparing sample pairs 4 and 12, 6 and 13, 5 and 14, and 11 and 17. For each pair, the 1200 °C processing temperature resulted in fewer crystals in the solid. Sample pairs 12 and 13, and 14 and 17 indicate that longer times at process temperature also results in fewer crystals in the solids. There is also some evidence to indicate that slow cool-down rate increases the crystallinity, but for the whole laboratory

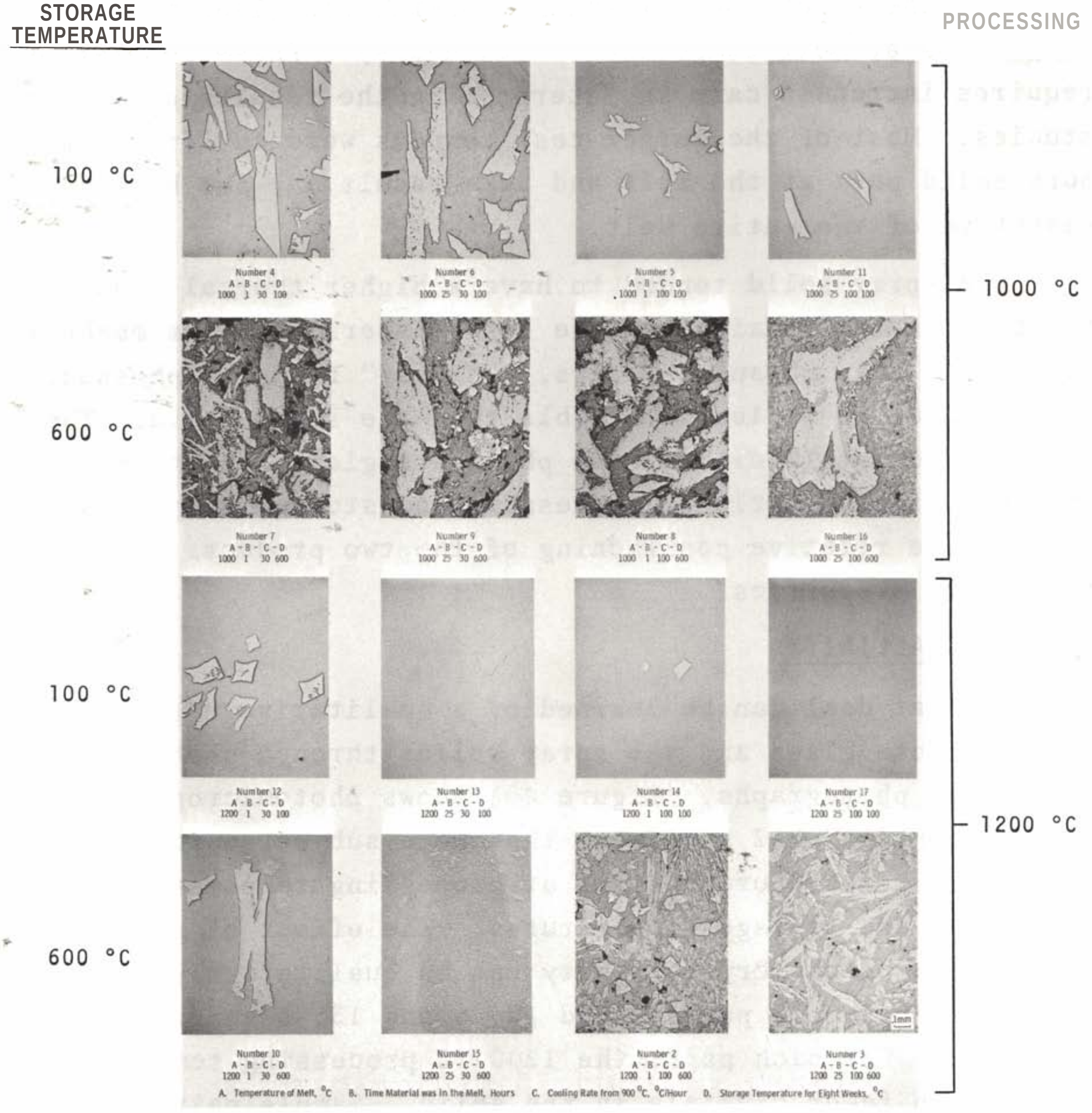

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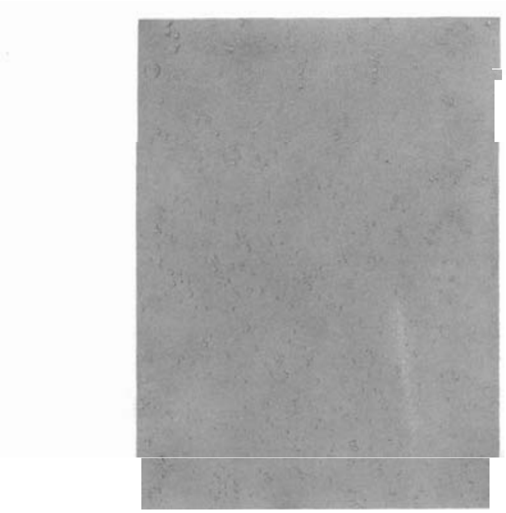
FIGURE 4.1. Phosphate Glass (PW-2) Photomicrographs. (Unetched 16X)

program the effect of cool-down rate was less pronounced than the effect of the first two processing parameters.

Figure 4.1, however, shows the overriding effect of storage temperature on the degree of crystallinity of phosphate glass. Compare samples 4, 6, 5, 11, 12, 13, 14, and 17, stored at 100 °C and samples 7, 9, 8, 16, 10, 15, 2, and 3, stored at 600 °C. The samples stored at 600 °C exhibit significantly greater crystallinity than the samples stored at 100 °C. Comparisons within samples stored at 600 °C are largely masked by the massive formation of crystals. Those samples stored at 100 °C were typically shiny, black, brittle glass samples. Those samples stored at 600 °C tended to be more granular, dull in luster, and black in appearance, with a marked tendency to exude sticky material.

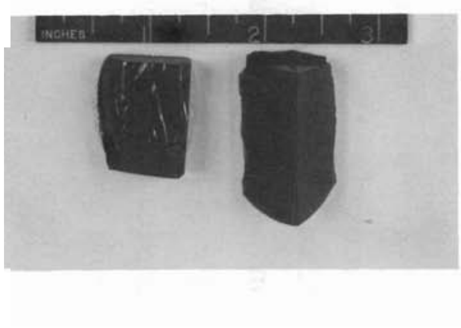
Figure 4.2a shows phosphate glass PW-1 samples 64 and 65 and photomicrographs of the samples. All processing parameters were the same (T_m: 1000 °C, t_s: 1 hour, CR: 100 °C/hr) except for the storage temperature. Sample 64 was quite similar to PW-2 phosphate glass specimens (samples) stored at 100 °C for the same processing parameters. Figure 4.2a shows the typical shiny black phosphate glass. Figure 4.2b shows a typical sample stored at 600 °C with large crystal formation and voids (black spaces in the photomicrograph). Discoloration and color variation with sample 65 indicates that some phase separation may have occurred.

The PW-4m spray solid (sample 53) shown in Figure 4.3 is, mostly, typical of spray solids. The samples are normally gray to black and rock-like in appearance with a few small pores. The photomicrograph in Figure 4.3 shows uniform large crystals with voids (black spaces) scattered throughout. Processing variables seem to have less effect on spray melts than on phosphate glass. However, a combination of high melt temperature (1100 °C) and 25 hours at melt temperature tends to result in a nonhomogeneous sample.



SAMPLE 64

PROCESS TEMPERATURE, T_m: 1000 °C
PROCESS TIME, t_p: 1 hour
COOL-DOWN RATE, CR: 100 °C/hr
STORAGE TEMPERATURE, T_s: 100 °C



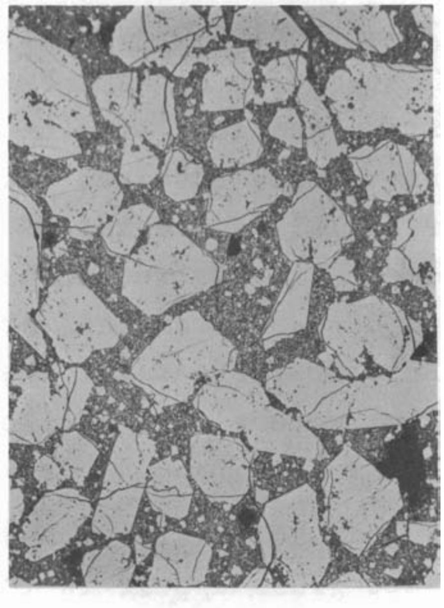
Neg 701028-11 (a)

SAMPLE 65

PROCESS TEMPERATURE, T_m: 1000 °C
PROCESS TIME, t_p: 1 hour
COOL-DOWN RATE, CR: 100 °C/hr
STORAGE TEMPERATURE, T_s: 600 °C

Neg 701028-8 (b)

FIGURE 4.2. Phosphate Glass (PW-1) Samples and Photomicrographs



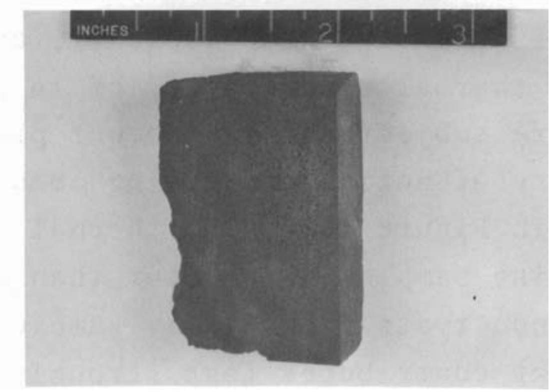
SAMPLE 53

PROCESS TEMPERATURE, T: 1000 °C

PROCESS TIME, t: 1 hour

COOL-DOWN RATE, CR: 30 °C/hr

STORAGE TEMPERATURE, T_S: 100 °C



Neg 701028-7

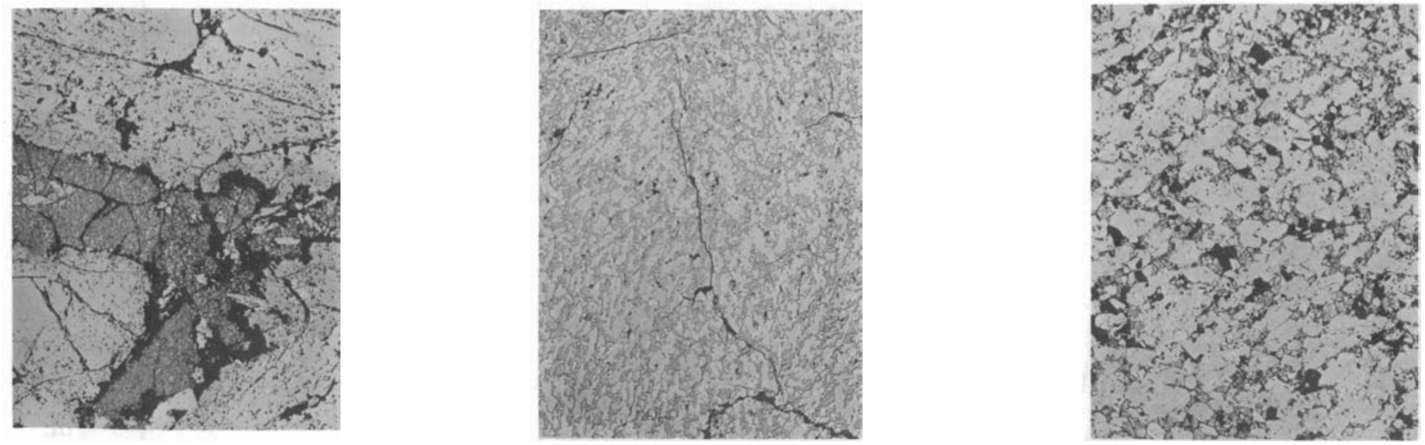
FIGURE 4.3. Spray Solid (PW-4m) Sample and Photomicrograph

Figure 4.4 shows the effect of high processing temperature for long periods. Sample 59 (Figure 4.4a) is reasonably typical of spray solid in general appearance and shows that high processing temperature alone does not apparently result in nonhomogeneous sample. Samples 60 and 61 (Figures 4.4b and 4.4c) show the nonhomogeneity created by the combination of high process temperature and long time at process temperature. Some melt appears to have "drained" away 'from the top surface leaving long crystal-like needles of solid. The photomicrographs (and subsequent samples for property characterization) for samples 60 and 61 came from the more homogeneous phase on the bottom. Both of these samples were gray to black in the bottom portion, but were a dirty yellow in the top portion.

Sample photographs and photomicrographs of additional spray solids and phosphate glass appear in the Appendix. The main effects of the processing variables on the other laboratory prepared samples are applicable to all samples.

4.2 THERMAL CONDUCTIVITY (k)

The thermal conductivity of each of the phosphate glass and spray solid samples was calculated from the experimentally determined thermal diffusivity, heat capacity, and density. Figure 4.5 shows the thermal conductivity of 16 phosphate glass PW-2 samples that were subjected to different processing parameters. A summary of actual processing conditions is shown in the Appendix and in Figure 4.1. The thermal conductivity of the more crystalline samples is greater than the thermal conductivity of the noncrystalline glassy samples. The processing parameter that contributed most strongly to the formation of crystals was the storage temperature (100 °C versus 600 °C). Samples 2, 16, 7, 10, 3, 9, 8, and 15 were stored at 600 °C for 8 weeks before k values were determined. Samples 17, 12, 11, 13, 14, 4, 5, and 6 were stored at 100 °C for 8 weeks.



<u>SAMPLE 59</u>

PROCESS TEMPERATURE, T: 1100 °C
PROCESS TIME, t: 1 hour
COOL-DOWN RATE, CR: 30 °C/hr
STORAGE TEMPERATURE, T_s: 600 °C

<u>SAMPLE 60</u>

PROCESS TEMPERATURE, T: 1100 °C
PROCESS TIME, t: 25 hours
COOL-DOWN RATE, CR: 30 °C/hr
STORAGE TEMPERATURE, T_s: 100 °C

<u>SAMPLE 61</u>

PROCESS TEMPERATURE, T: 1100 °C
PROCESS TIME, t_m: 25 hours
COOL-DOWN RATE, CR: 30 °C/hr
STORAGE TEMPERATURE, T_s: 600 °C

Neg 701028-9 (a) **Neg 701028-3** (b) **Neg 701028-2** (c)

FIGURE 4.4. **Spray Solid (PW-4m) Samples and Photomicrographs**

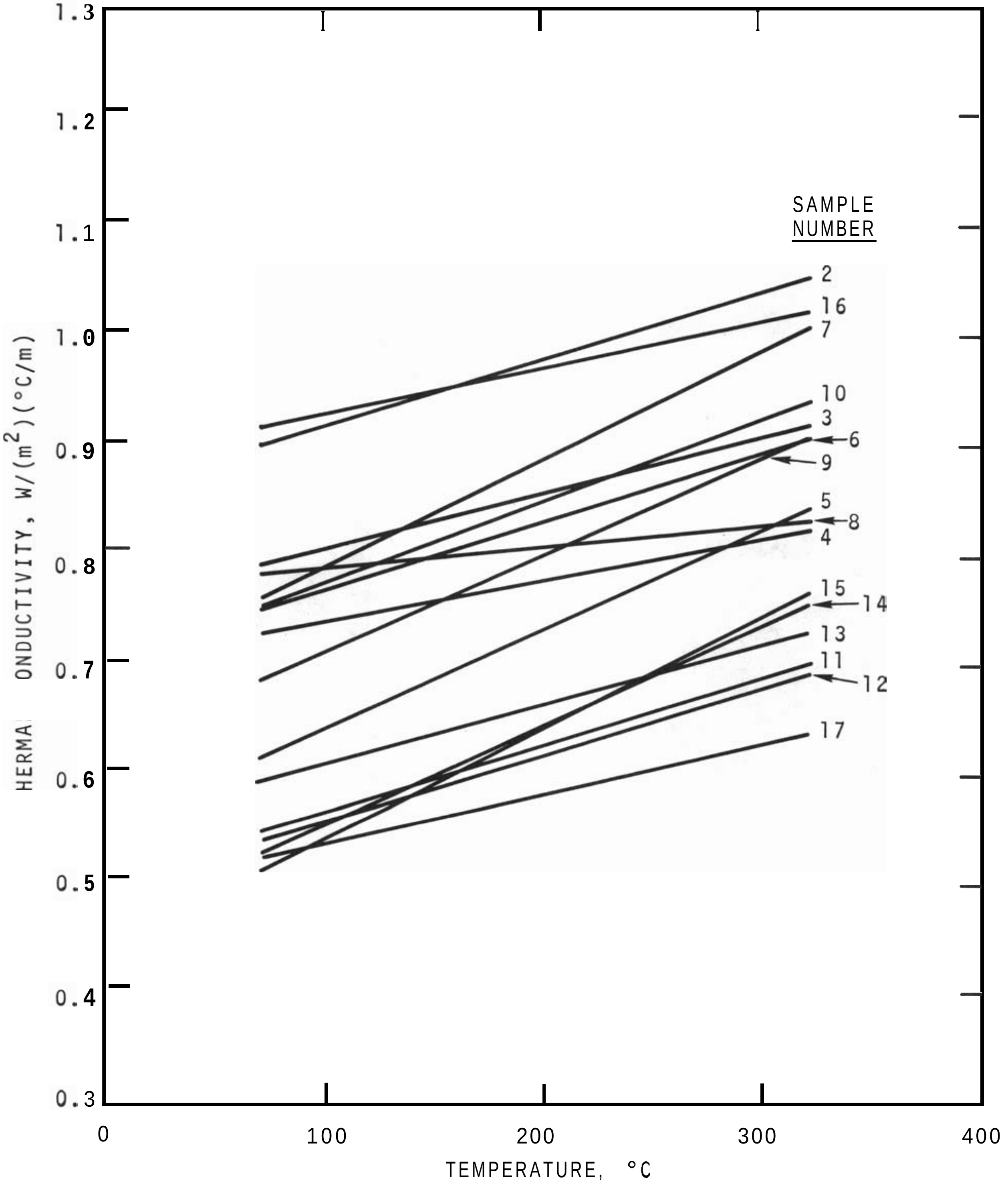


FIGURE 4.5. Thermal Conductivity of Phosphate Glass (PW-2) Samples

Some overlap of k values for the two different storage temperatures occurs in the mid-range of values which indicates other first order or second order effects of the processing parameters. Samples 9, 8, and 15 from the 600 °C stored samples and 4, 5, and 6 from the 100 °C stored samples form an overlapping interface.

Samples 4, 5, and 6 were formed at low process temperature (1000 °C), which tends to allow crystal formation. Sample 15 on the other hand is more glassy because of the high process temperature (1200 °C) and long time at processing temperature (25 hours). These two parameters tend to partially offset the high storage temperature and produce a glassy product. Sample 9 was prepared and handled the same as 8 except that 9 was held at processing temperature for 25 hours. Sample 9 should be more glassy than 8 (lower k), but this is not so. The fact that the thermal conductivity lines for samples 8 and 9 cross at about 215 °C is an indication of higher than first order interaction of the processing parameters. This contradiction is probably due to sample variability but could be interpreted as a demonstration of the lack of effect of long-time at processing temperature.

Unfortunately the variability of duplicate samples 62 and 63 of phosphate glass PW-2 was large, and a precise statistical study of the first and second order interactions was therefore not possible. More samples are needed to determine the variability of the data and to provide a complete statistical comparison. Generally speaking, the temperature at which the product is formed and the temperature at which the product is stored affect the thermal conductivity more than the cool-down rate and the time at processing temperature.

The effect of storage temperature on thermal conductivity of phosphate glass is depicted in Figure 4.6. Figure 4.6 shows the thermal conductivity of five identically prepared samples of phosphate glass PW-2 material that were stored at 100 °C,

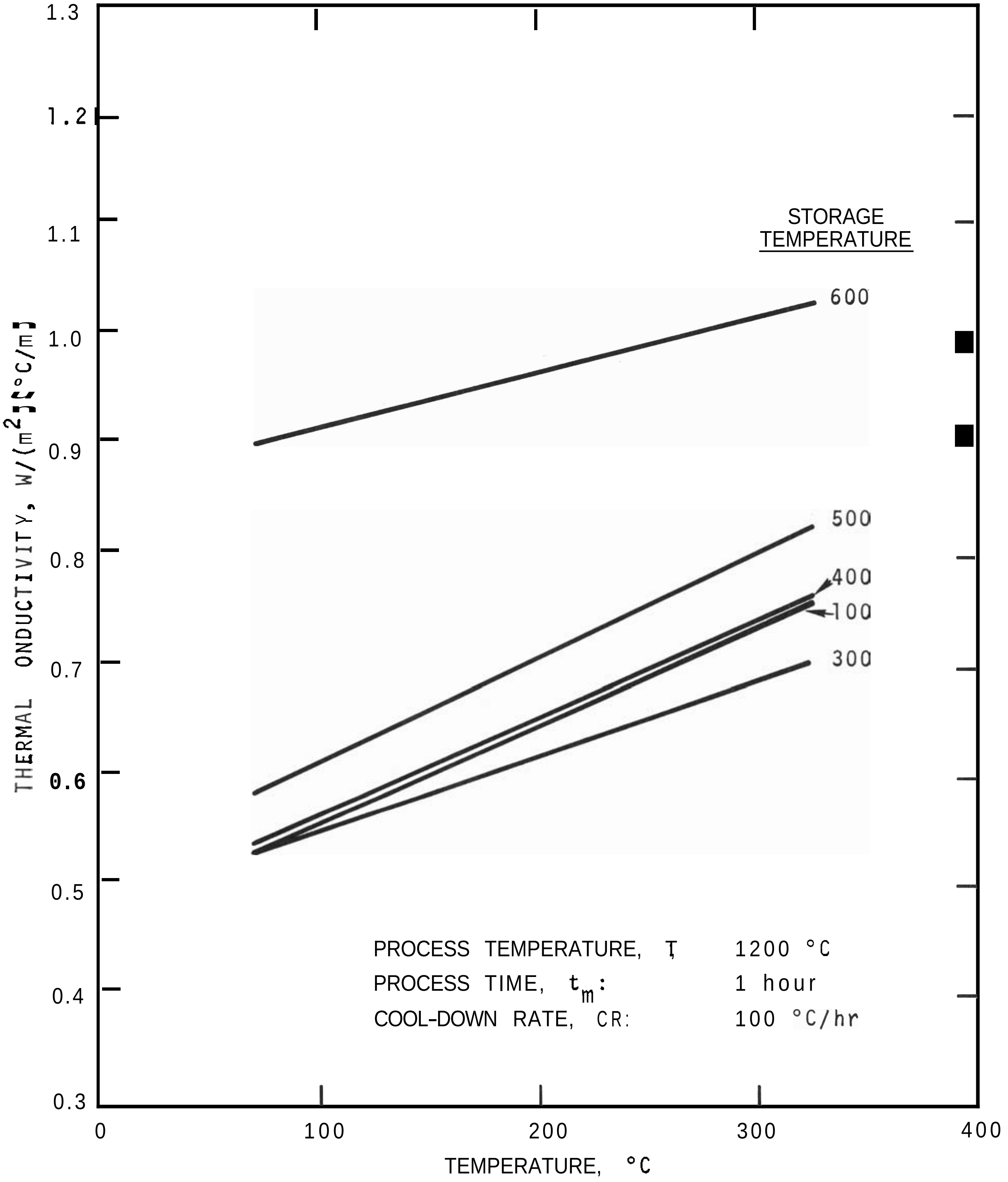


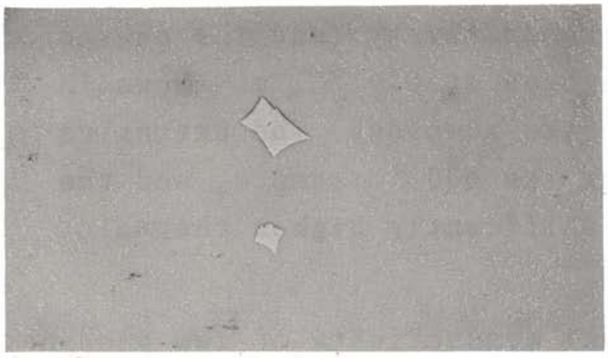
FIGURE 4.6. Thermal Conductivity of Phosphate Glass (PW-2) Samples as a Function of Storage Temperature

300 °C, 400 °C, 500 °C, and 600 °C for 8 weeks. There is a marked increase in the thermal conductivity (and the degree of crystallinity) for the sample stored at 600 °C, as shown in Figure 4.7, photomicrographs of the samples. The extensive crystal formation is evident for the 600 °C sample, and the 600 °C sample is marked by a significantly higher thermal conductivity.

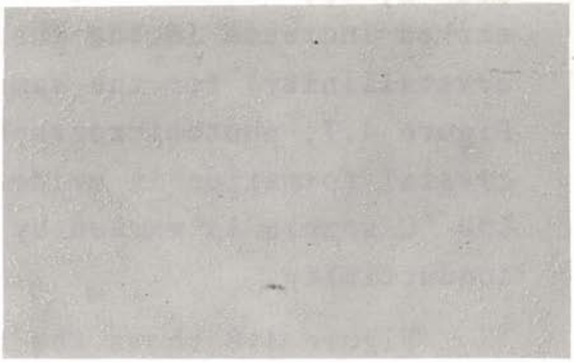
Figure 4.8 shows the thermal conductivity of two phosphate glass PW-1 solids that were processed identically but stored at two different temperatures. The process temperature was 1000 °C, the time at process temperature was 1 hour, and the cool-down rate was 100 °C/hr. Sample 65 was stored at 600 °C and sample 64 at 100 °C. Again, the crystal formation resulted in higher k for sample 65. The k of sample 64 is not too different from samples 11, 12, and 17 of the PW-2 phosphate glass (Figure 4.1). Sample 65 seems to be on the interface between PW-2 samples stored at 600 °C and those stored at 100 °C.

Figure 4.9 shows the thermal conductivity of PW-4m phosphate glass samples. The processing parameters for all three (except for storage temperature) was identical: process temperature was 1000 °C; time at process temperature was 1 hour; and cool-down rate was 100 °C/hr. Samples 49 and 50 were duplicates stored at 100 °C, and sample 51 was stored at 600 °C. Samples 49 and 51 seem to be in the proper perspective with respect to PW-1 and PW-2 samples. Sample 50 shows that wide variability can be expected within a measurement group. The variability in these data shows a need for additional sample measurement if the process parameter effects are to be determined in detail with statistical verification.

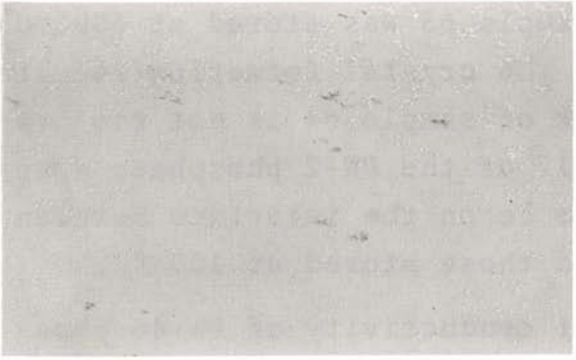
Figure 4.10 shows the calculated thermal conductivity for four PW-1 spray solids. Samples 25 and 28 were held at 1000 °C processing temperature for 1 hour and cooled at 100 °C/hr. Sample 25 was stored at 100 °C for 8 weeks while 28 was stored at 600 °C for 8 weeks. Samples 26 and 27 were held at 900 °C



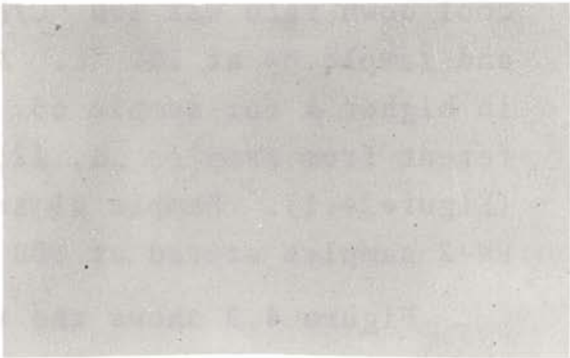
Neg 0690336 (a)



Neg 4C208A (b)



Neg 4C209A (c)



Neg 4C210A (d)

Neg 0690336-1 (e)

- Melt Temperature 1200 °C
- Time at Melt Temperature 1 hour
- Cool-Down Rate from Melt to Storage Temperature 100 °C/hr
- Storage Temperature
  - (a) 100 °C
  - (b) 300 °C
  - (c) 400 °C
  - (d) 500 °C
  - (e) 600 °C

FIGURE 4.7. Photomicrographs of Phosphate Glass (PW-2) Showing Effect of Storage Temperature

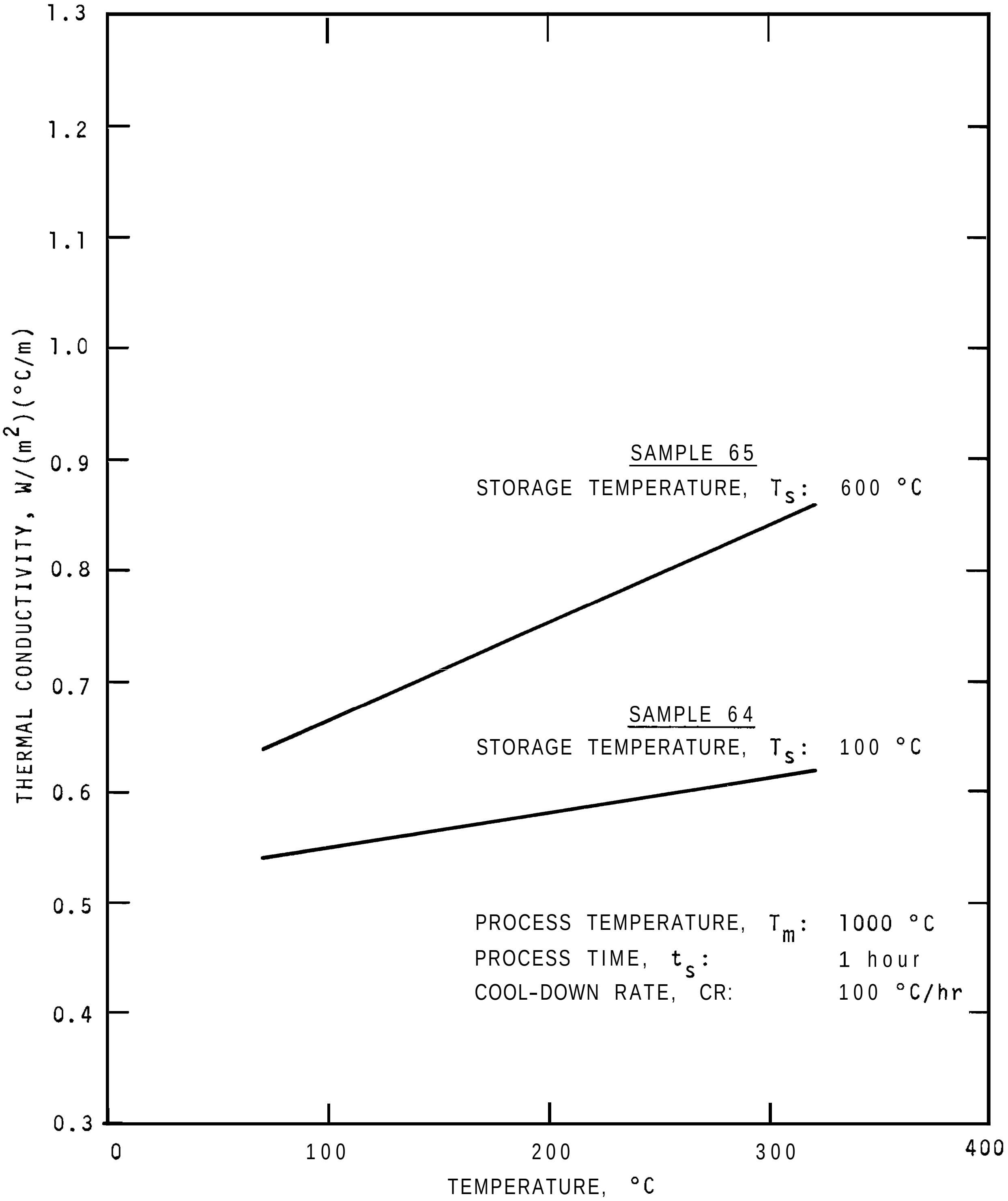


FIGURE 4.8. Thermal Conductivity of Phosphate Glass (PW-1) Samples

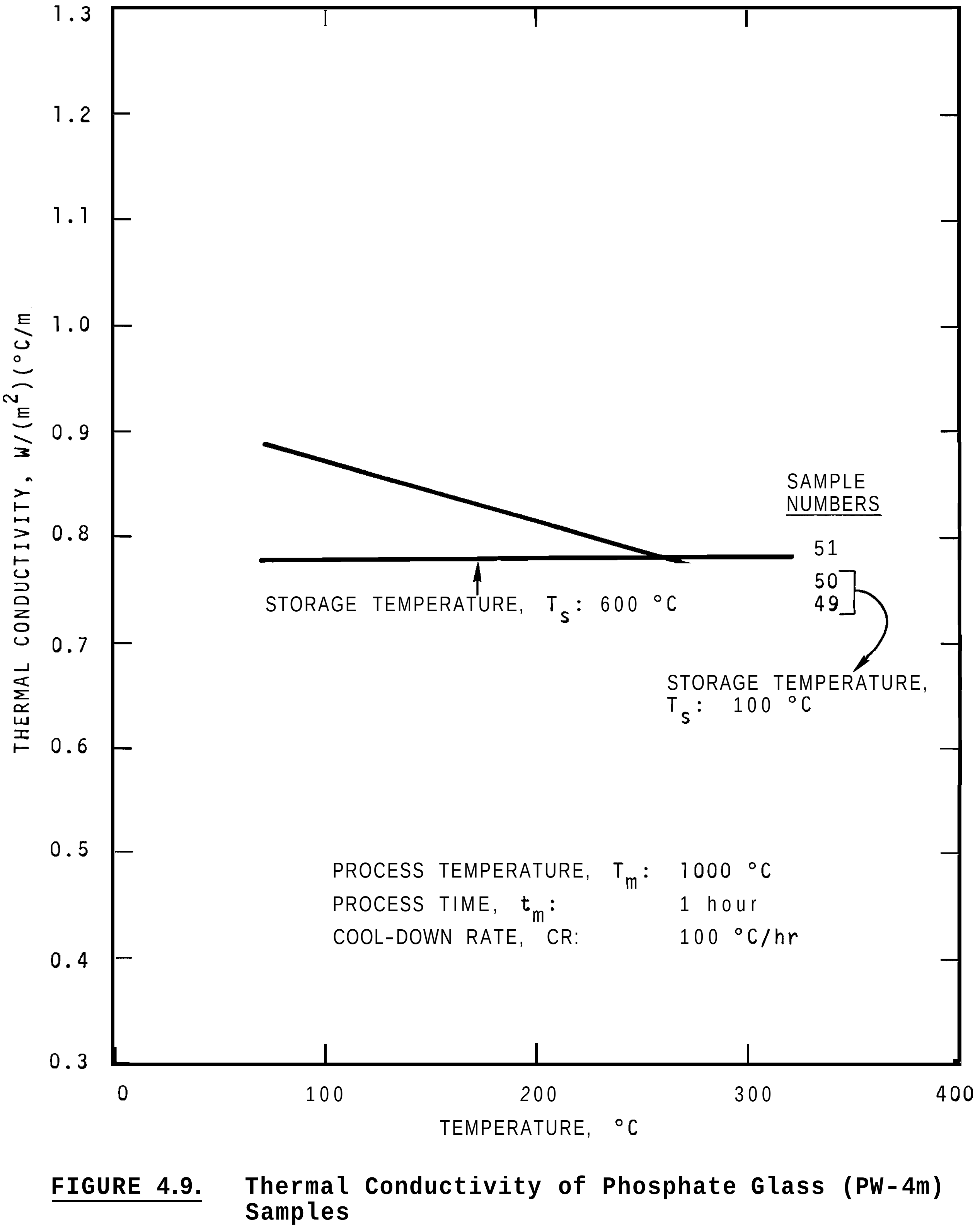
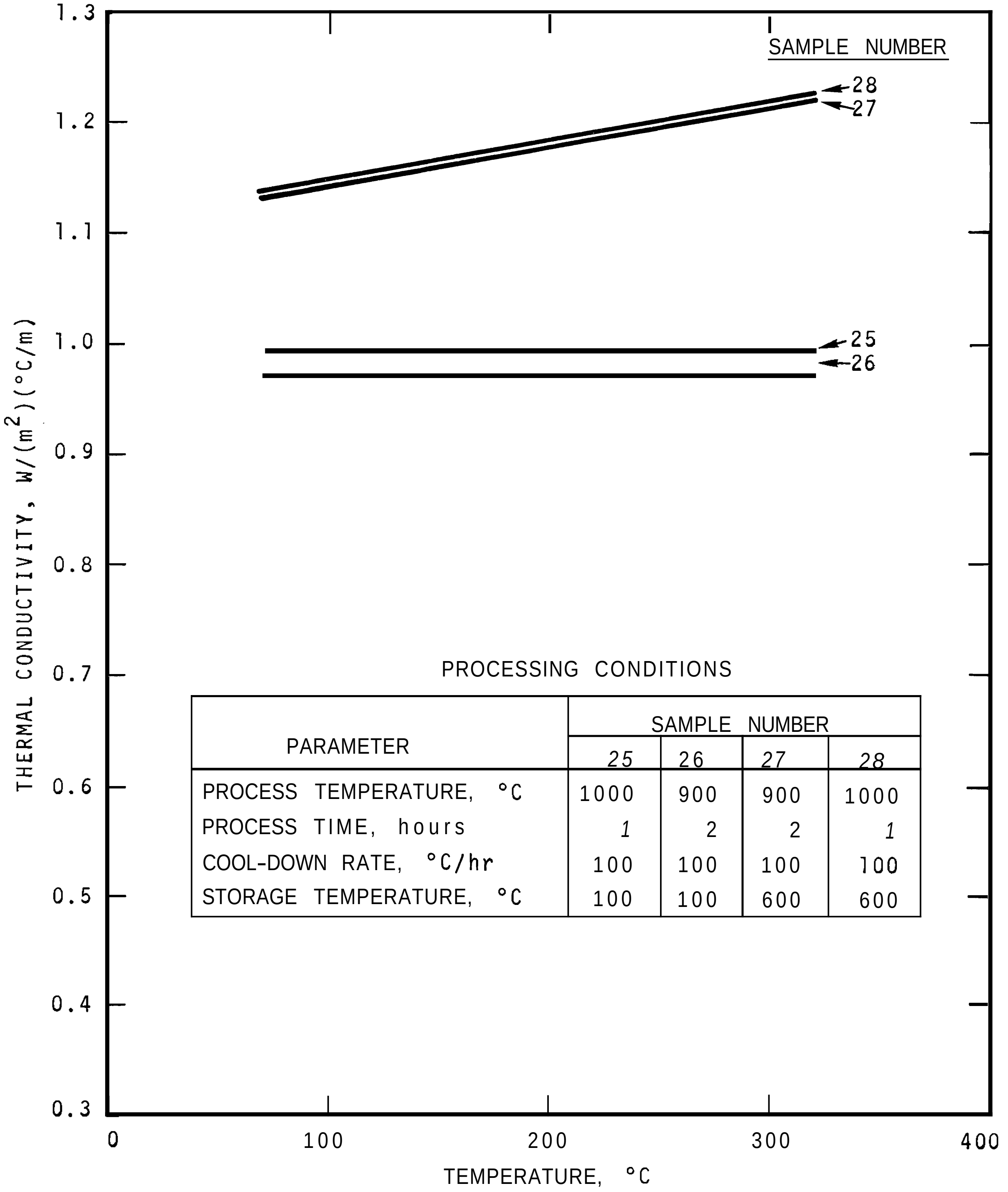


FIGURE 4.9. Thermal Conductivity of Phosphate Glass (PW-4m) Samples



PROCESSING CONDITIONS

PARAMETER	SAMPLE NUMBER			
	25	26	27	28
PROCESS TEMPERATURE, °C	1000	900	900	1000
PROCESS TIME, hours	1	2	2	1
COOL-DOWN RATE, °C/hr	100	100	100	100
STORAGE TEMPERATURE, °C	100	100	600	600

FIGURE 4.10. Thermal Conductivity of Spray Solid (PW-1) Samples

processing temperature for 2 hours and cooled at 100 °C/hr. The storage temperatures were 100 °C and 600 °C for samples 26 and 27, respectively. The thermal conductivity measurements for four samples fall into two groups that are apparently most strongly influenced by storage temperature. Similar to phosphate glass specimen, these spray solid samples show a higher k at 600 °C than at 100 °C storage temperature.

Figure 4.11 shows the calculated thermal conductivity for two spray solids from PW-2 aqueous waste. The two solids were prepared at 800 °C for 1 hour and cooled at 100 °C/hr. Number 31 was stored in 100 °C, whereas 32 was stored at 600 °C. The effect of storage temperature on the thermal conductivity is apparent. The thermal conductivity of PW-2 spray solid appears to be lower than PW-1.

The final series of thermal conductivity measurements on spray solid is from PW-4m waste. This series of samples presented the greatest amount of experimental difficulty of any of the laboratory samples. A summary of the individual processing parameters is given in the Appendix. The ranges of processing parameters for samples 52 through 61 were process temperatures of 1000 °C and 1100 °C; times at process temperature, of 1 hour and 25 hours; cool-down rate of 30 °C/hr; and storage temperatures of 100 °C and 600 °C. Three of the Samples (52, 53, and 54) were structurally weak, and adequate coupons could not be prepared for the thermal diffusivity measurement. Density and heat capacity determinations were comparable to the other spray solids. Two of the samples (57 and 58) broke during the diffusivity determination. With the loss of 5 coupons, conclusions regarding the effects of processing parameters on the thermal conductivity of PW-4m spray solids are difficult. In addition, it was previously pointed out (Section 4.0) that nonhomogeneous specimens made interpretation of the thermal conductivity of PW-4m spray solid data difficult.

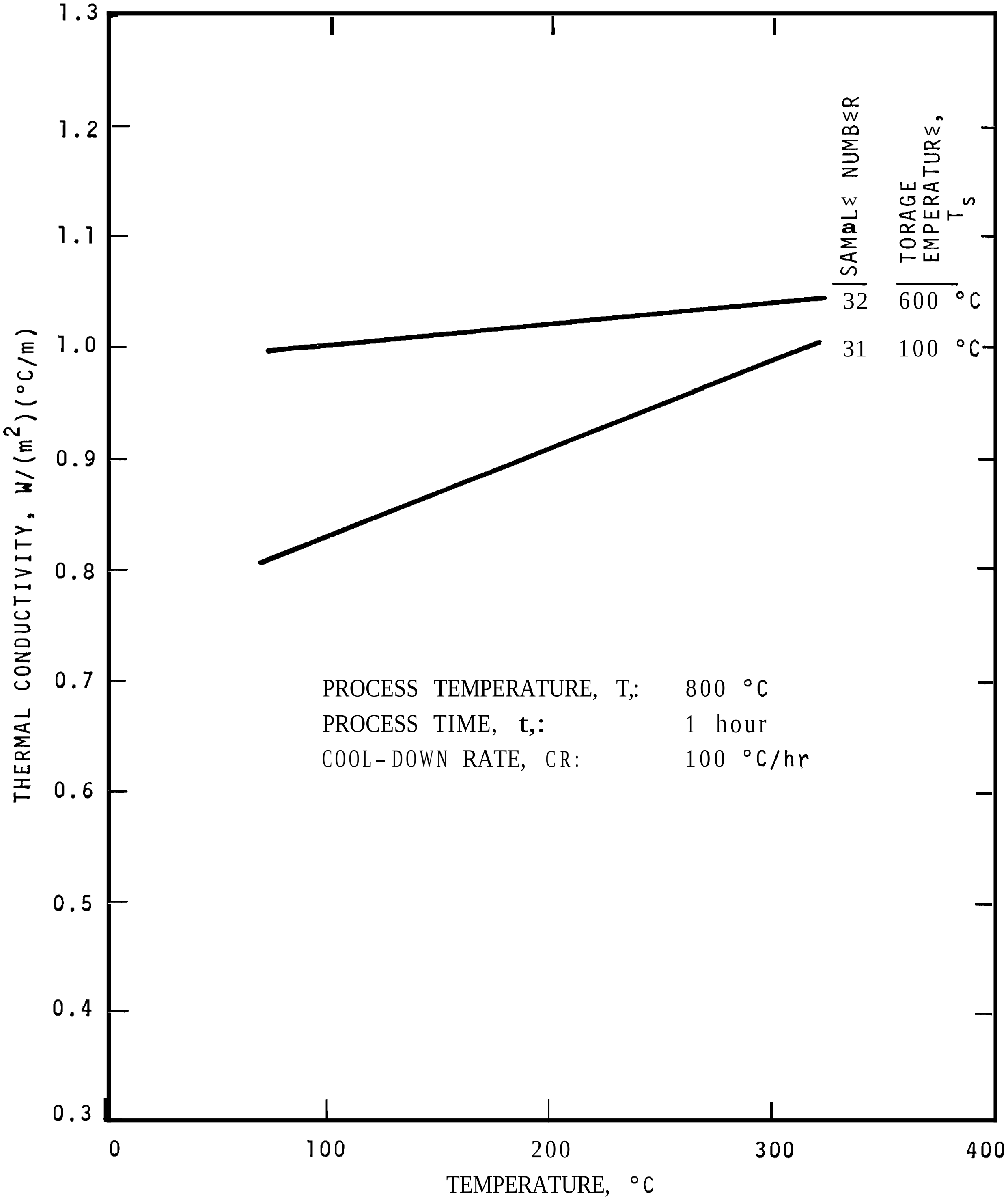


FIGURE 4.11. Thermal Conductivity of Spray Solid (PW-2) Samples

Figure 4.12 summarizes the results of the PW-4m spray solid thermal conductivity determinations. Results obtained were inconsistent. Possibly, the high 1100 °C melt temperature in conjunction with long melt times may have contributed materially to the nonhomogeneity. Reduced temperature processing conditions seem warranted for any future laboratory studies and probably for engineering scale studies as well.

4.3 HEAT CAPACITY (C_p) AND DENSITY (ρ)

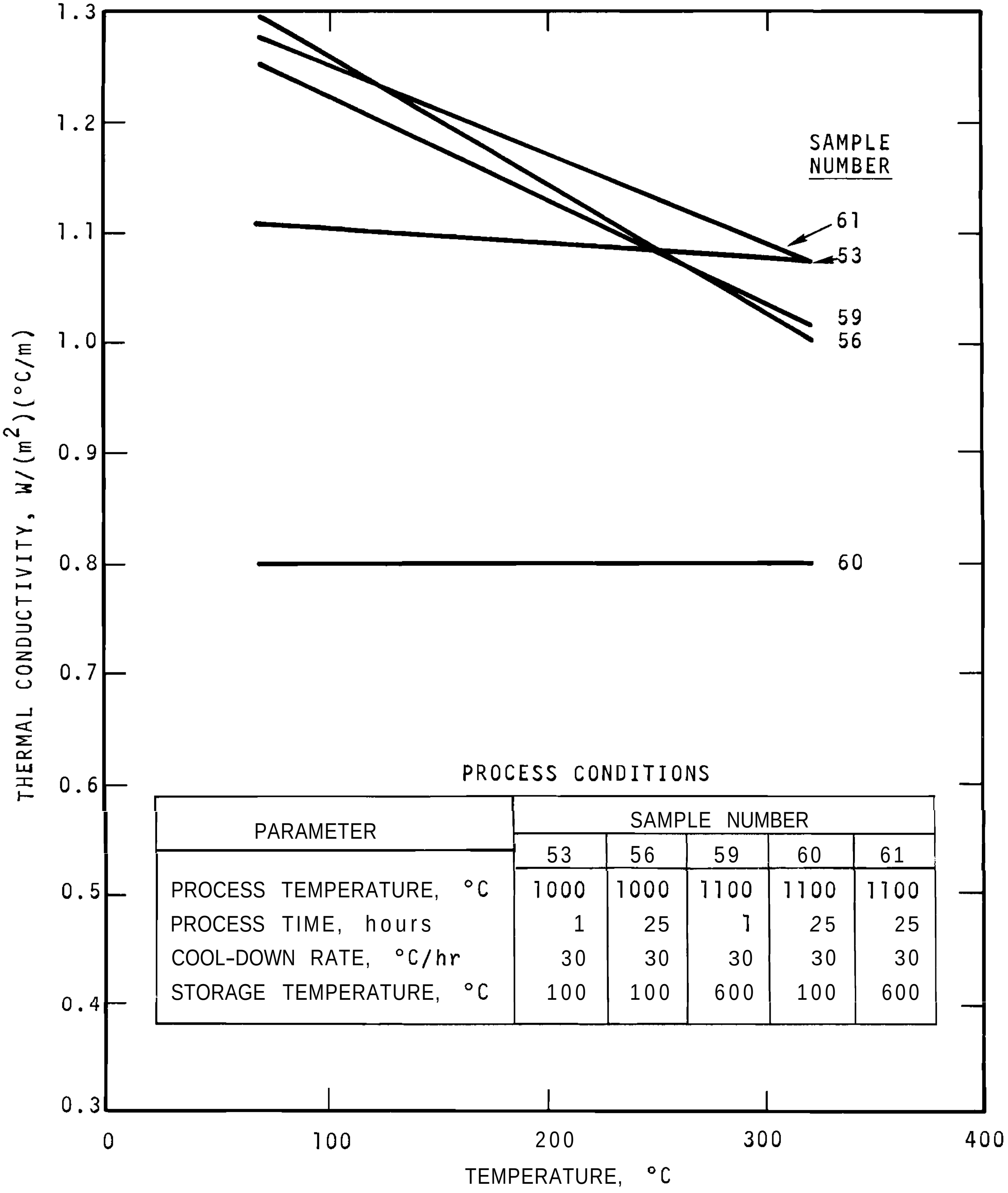
Detailed temperature-dependent summaries of the heat capacity and density measurements are given in the Appendix for the phosphate glass and spray solid. Some general observations concerning the data can be made:

As would be expected based on data from other ceramics and glasses,(9) the heat capacity of either phosphate glass or spray solid does not vary greatly with sample temperature. The average C_P for phosphate glass for all samples was between 0.18 and 0.23 cal/(g)(°C). The density of the phosphate glass material was consistently between 2.7 and 3.0 g/cm^3, with no apparent trend for a given product type.

The spray solid showed a consistent density of 3.4 to 3.5 g/cm^3 except for samples 31 and 32 which had densities of 2.9 g/cm^3. Most of the spray solids had an average C_P of between 0.17 to 0.19 cal/(g)(°C), but samples 31 and 32 showed average heat capacities of 0.22 cal/(g)(°C), which is more nearly equivalent to the C_P for the phosphate glass. Samples 31 and 32 were prepared at 800 °C, the lowest process temperature of all the spray solids, which may have contributed to the differences in product properties.

4.4 DISPERSIBILITY

The dispersibility test was established to provide an indication of the sample's tendency to be fragmented into



PROCESS CONDITIONS

PARAMETER	SAMPLE NUMBER				
	53	56	59	60	61
PROCESS TEMPERATURE, °C	1000	1000	1100	1100	1100
PROCESS TIME, hours	1	25	1	25	25
COOL-DOWN RATE, °C/hr	30	30	30	30	30
STORAGE TEMPERATURE, °C	100	100	600	100	600

FIGURE 4.12. Thermal Conductivity of Spray Solid (PW-4m) Samples

small, readily dispersible particles upon impact. It is felt that these data provide useful safety information on the mechanical ruggedness of the products.

The phosphate glass exhibits greater variation in the quantity of material that may be classified as fines or as large pieces than does spray solid. In general, crystalline structure is the governing factor in the breakup of samples subjected to the dispersibility test.

Table 4.1 shows that in nearly all cases where the phosphate glass was stored at 600 °C (crystal-structure formed) 90% or more of the particles produced were greater than 0.1-inch diameter. Less than 4% could be classified as fines of less than 0.02-inch diameter. Samples stored at 100 °C or the intermediate temperatures of 300, 400, and 500 °C (the glassy samples) showed 15 to 25% fines and correspondingly fewer large fragments. The higher dispersibility of the glassy samples may more than offset the low leachability (discussed in Section 4.7) when safety analyses are being performed on phosphate glass because of the greater surface area exposed.

Care must be taken in interpreting dispersibility data of the spray solid because of the nonhomogeneity of some samples. As previously noted, the coupons used in the dispersibility tests came by necessity from the more dense homogeneous parts of the sample.

In general, the dispersibility of the spray solid approaches that of crystalline phosphate glass rather than glassy phosphate glass (See Table 4.2). Dispersibility tests show that the fines (less than 0.02-inch diameter) account for approximately 5% of most spray samples. However, values as high as 13 and 25% were observed for samples 57 and 58, respectively. The spray solid tends also to have a larger fraction

TABLE 4.1. Dispersibility of Phosphate Glass

Laboratory Sample Number	Storage Temperature, °C	Weight% in Size Range		
		<0.02 inch	0.02 - 0.1 inch	>0.1 inch
4	100	14.5	10.0	75.5
5	100	16.9	36.2	46.8
7	600	1.1	1.5	97.4
8	600	0.9	1.4	97.7
6	100	23.1	23.6	53.3
11	100	15.0	40.7	44.3
9	600	1.7	1.4	96.9
16	600	1.9	5.3	92.8
12	100	26.0	38.7	35.3
14	100	18.3	30.7	51.0
10	600	18.6	36.6	44.8
2	600	1.5	3.5	95.0
13	100	16.3	37.5	46.2
17	100	17.9	29.7	52.4
15	600	(a)		
3	600	1.3	1.7	97.0
62	100	18.2	13.8	68.0
63	100	(a)		
49	100	12.6	28.6	58.8
50	100	(a)		
51	600	1.7	3.7	94.6
64	100	24.6	41.1	34.6
65	600	3.2	5.1	91.7
500	500	26.8	45.7	27.5
400	400	25.7	41.3	33.0
300	300	(a)		

---

a. *An adequate coupon could not be prepared.*

of intermediate-sized fragments (0.02 to 0.1-inch diameter) and a smaller fraction of large fragments (greater than 0.1-inch diameter) than the phosphate glass. Both the spray solid and the crystalline phosphate glass are relatively "tough" with respect to mechanical damage.

TABLE 4.2. Dispersibility **of Spray Solid**

Laboratory Sample Number	Storage Temperature, °C	Weight% in Size Range <0.02 inch	0.02 - 0.1 inch	>0.1 inch
25	100	5.7	7.9	86.4
26	100	(a)		
27	600	3.2	3.9	92.9
28	600	1.7	2.6	95.7
31	100	11.5	24.5	64.0
32	600	(a)		
52	100	(a)		
53	100	(a)		
54	100	(a)		
55	600	16.2	23.2	60.6
56	100	32.9	28.1	39.0
57	600	13.2	19.7	67.1
58	100	25.1	32.7	42.2
59	600	10.9	19.4	69.7
60	100	10.3	11.0	78.7
61	600	9.4	20.1	70.5

---

a. *An adequate coupon could not be prepared.*

4.5 LINEAR COEFFICIENT OF THERMAL EXPANSION (LCTE)

The main reason for characterizing the linear coefficient of expansion has been to determine the thermal expansion compatibility with mild and stainless steels in storage. The values of LCTE shown in Table 4.3 indicate that the solidified wastes are compatible with steel. Mild and stainless steel and the solidified waste have LCTE of approximately 10×10^{-6} in./(in.)(°C).

The temperature-dependent changes in volume for a crystalline or partially crystalline material are dependent on the structure and composition of the material.(9) In view of the mixture in both composition and structure of spray solid and phosphate glass, no attempt has been made to analyze the behavior of the melts except to determine compatibility with steels.

4.6 THERMAL SHOCK

Table 4.4 summarizes experimental observations from the thermal shock test. In general, the spray solids withstood the test and remained intact better than did the phosphate glass. Many of the phosphate glass coupons melted, softened, sweated, or shattered during the test. Least prevalent were samples that shattered due to thermal shock. A number of the samples melted in the 600 °C furnace and dripped into the cold bath at 0 °C without shattering. In some instances with either spray solid or phosphate glass, no adequate coupon of sufficient size could be prepared to run the test. Photographs made of the samples after the thermal shock test are in the Appendix.

Phosphate glass is known to have a low melting point (as opposed to the drip point). The melting point has previously been shown to be approximately 650 °C but may be closer to 600 °C as evidenced by the large number of samples that melted during the thermal shock test while the coupons were being heated in the furnace to 600 °C.

In two instances (samples 31 and 61), spray solids were observed to have exuded a liquid material. Sample 31 was

TABLE 4.3. Linear Coefficient of Thermal Expansion for Phosphate Glass and Spray Solid(a)

Process Type	Waste Type PW-	Laboratory Sample Number	LCTE × 10^6, in./(in.)(°C)			
			200 °C	300 °C	400 °C	500 °C
PG	2	4	9.8	10.6	12.8	
	2	7	5.8	12.6	9.4	2.3
	2	8	6.9	10.7	9.7	8.0
	2	6	9.1	10.8	11.6	
	2	9	7.1	8.5	7.6	
	2	16	10.1	13.8	14.2	11.6
	2	12	10.3	9.1	7.5	
	2	14	9.4	9.8	7.1	
	2	10	9.8	11.0	12.1	11.6
	2	2	10.8	11.8	14.4	11.7
	2	3	10.1	11.7	13.1	11.2
	2	62	6.5	8.0	9.1	11.2
	2	63	7.0	8.0	8.5	10.7
	4m	49	8.5	7.2	7.8	(b)
	4m	51	16.0	15.0	14.0	13.4
	1	64	7.5	8.5	9.5	9.0
	1	65	4.3	6.3	(b)	(b)
SS	1	25	6.02	6.59	6.19	7.01
	1	26	6.80	8.50	9.95	10.59
	1	27	6.31	6.92	4.98	5.53
	1	28	8.58	7.50	8.07	9.24
	2	31	11.60	14.80	16.70	16.87
	4m	55	4.0	6.2	7.5	11.1
	4m	56	2.3	3.8	4.6	5.0
	4m	57	4.5	5.5	6.8	7.2
	4m	59	3.2	4.0	4.6	5.1
	4m	60	3.8	4.8	5.3	5.6
	4m	61	4.0	5.7	7.1	--

---

a. *Adequate coupons could not be prepared from samples numbered 5, 11, 13, 15, 17, 50, 300, 400, 500, 32, 52, 53, 54, 58.*

b. *Sample melted.*

TABLE 4.4. **Thermal Shock Test Summary for Phosphate Glass and Spray Solid**

Sample Number	Process	Waste Type PW-	
2	PG	2	Did not break. Glassy.
3		2	Did not break. Glassy.
4		2	Did not break. Crystalline.
5		2	Melted. Glassy. Some fracture.
6		2	Did not break. Glassy. Sweated.
7		2	Did not break. Sweated.
8		2	Did not break. Glassy. Sweated and dripped.
9		2	Did not break. Glassy. Sweated.
10		2	Did not break. Glassy.
11		2	Glassy. One corner shattered.
12		2	No coupon.
13		2	Fractured off all edges. Glassy.
14		2	Did not break. Glassy.
15		2	No coupon.
16		2	Did not break. Glassy. Sweated.
17		2	Softened. Did not break.
62		2	Melted. Glassy.
63		2	Melted. Glassy.
49		4m	Melted.
50		4m	No coupon.
51		4m	Melted.
64		1	Melted.
65		1	Melted.
300		2	Softened. Did not break.
400		2	No coupon.
500		2	Shattered into numerous pieces.
25	SS	1	Did not break.
26		1	Did not break.
27		1	No coupon.
28		1	Did not break.
31		2	Did not break. Some sweating.
32		2	No coupon.
52		4m	No coupon.
53		4m	No coupon.
54		4m	No coupon.
55		4m	Did not break.
56		4m	Did not break.
57		4m	Did not break.
58		4m	Did not break.
59		4m	Did not break.
60		4m	Did not break. Some sweating.
61		4m	Softened. One piece chipped off.

prepared at the lowest processing temperature (800 °C) for just one hour. Complete mixing and solution of the mixture may not have occurred; hence, low melting material was exuded. Sample 61 was processed at 1100 °C for 25 hours which should produce (according to laboratory studies) a solid of nonhomogeneous structure and composition. The thermal shock test on sample 61 is probably not representative because of the nonhomogeneous sample originally prepared and discussed in Section 4.1.

The thermal shock test showed, that for the size of sample tested, little or no shattering of the products is expected. However, very large containers of product could undergo more shattering because of greater induced thermal stress. The phosphate glass and spray solid appear to be stable under rapid high temperature quench.

4.7 LEACHABILITY

Two types of leachability measurements have been made extensively in the evaluation of nonradioactive laboratory samples. The accelerated leachability tests are made at approximately 95 °C (and require about 1 week), while the slow leach tests are made at room temperature over periods of 8 to 40 weeks. The accelerated test consists of drying and weighing the sample after each of three consecutive 24 hour periods. Standard wet chemical analysis on the water leachout are used weekly on samples in the slow leach test.

4.7.1 Accelerated Leachability

All of the nonradioactive laboratory tests have been subjected to the accelerated leach test. Two duplicate measurements were made on samples 9, 14, and 17. Repetitive measurements for any one sample were in excellent agreement.

Storage temperature was a strongly influencing factor in the accelerated leachability test for phosphate glass. Samples that were stored at 600 °C and hence more crystalline tended to be more leachable than the glassy samples that resulted from storage at 100 °C.

Table 4.5 shows the accelerated leachability data for nonradioactive laboratory samples of phosphate glass. The samples can be divided into two groups within a waste type by storage temperature and by rate of weight loss during testing. With the exception of samples 3 and 10 in the PW-2 types, the samples stored at 100 °C resulted in a lower total weight loss at a constant rate than those stored at 600 °C. The samples stored at 600 °C predominantly underwent a high initial weight loss which resulted in high total weight loss for the 3 day test.

Some differences in the phosphate glass accelerated leachability measurements can be seen in Table 4.5 between waste types. The sample that showed the highest weight loss was number 65, a PW-4m sample that was stored at 600 °C. Sample 64, the other PW-4m sample and the PW-1 samples (49, 50, and 51), show weight losses approximately equivalent to PW-2 samples stored at 600 °C and less than the weight loss of sample 65. Within the PW-1 samples the storage temperature seems to affect the weight loss in the manner as for PW-2, but the differences between samples stored at 100 °C and 600 °C are less.

Table 4.6 shows the results of the accelerated leach test on spray solids. The results for PW-1 and PW-2 waste show that the total weight loss is constant within a feed type. However, there is a significant difference between the two waste types PW-1 and PW-2. The accelerated leachability of PW-4m spray solid is much more variable than either PW-1 or PW-2. This variability is probably due to sampling error in these relatively nonhomogeneous samples.

TABLE 4.5. Accelerated Leachability of Phosphate Glass

Sample Number	Waste Type PW-	Storage Temperature, °C	Accelerated Leach, % Weight Loss 1st 24 hours	2nd 24 hours	3rd 24 hours	Total
4	2	100	1.79	1.85	1.88	5.52
5	2	100	0.66	2.60	1.20	4.46
6	2	100	1.83	1.55	1.69	5.07
11	2	100	0.45	0.45	0.58	1.48
12	2	100	0.53	0.32	0.34	1.18
14	2	100	0.43	0.38	0.59	1.39
13	2	100	0.63	0.38	0.62	1.63
17	2	100	0.74	0.64	0.79	2.18
63	2	100	2.10	2.49	2.81	7.22
7	2	600	39.35	1.68	0.33	41.36
8	2	600	30.81	2.32	0.71	33.84
9	2	600	36.51	2.09	0.67	39.27
16	2	600	34.29	0.78	0.73	35.86
10	2	600	0.85	0.53	0.55	1.93
2	2	600	29.47	11.05	0.91	41.43
15	2	600	2.39	2.39	2.67	7.45
3	2	600	32.34	2.30	0.69	35.33
49	1	100	8.66	12.45	9.48	27.60
50	1	100	5.77	8.78	9.37	22.09
51	1	600	30.01	1.14	0.86	31.40
64	4m	100	6.53	8.48	7.85	21.17
65	4m	600	52.68	4.14	3.09	56.04

TABLE 4.6. Accelerated Leachability of Spray Solids

Sample Number	Waste Type PW-	Storage Temperature, °C	Accelerated Leach, % Weight Loss 1st 24 hours	2nd 24 hours	3rd 24 hours	Total
25	1	100	5.59	0.21	0.01	5.81
26	1	100	5.23	0.07	0.16	5.46
27	1	600	4.87	0.10	0.14	5.11
28	1	600	5.35	0.13	0.12	5.60
31	2	100	35.12	4.25	0.99	40.36
32	2	600	35.31	1.28	0.64	37.23
52	4m	100	5.60	5.63	2.85	14.08
53	4m	100	4.98	3.75	2.15	10.88
54	4m	100	1.41	2.09	2.34	5.84
56	4m	100	1.82	3.37	4.51	9.70
58	4m	100	0.57	0.44	0.56	1.57
60	4m	100	0.38	0.30	0.31	0.99
55	4m	600	10.24	0.42	0.26	10.92
57	4m	600	8.86	4.13	1.36	14.35
59	4m	600	12.77	1.62	0.48	$4.87
61	4m	600	12.62	1.38	0.44	14.44

The leachability of PW-1 spray solid approaches that of the glassy phosphate glass PW-2 material according to the accelerated leach test. The PW-2 spray solid leachability, however, is in the same range as that of the crystalline PW-2 phosphate glass. As a general observation, the leachability of the PW-4m spray solid is lower than that of the PW-4m phosphate glass.

4.7.2 Standard (slow) Leach Tests

Standard (slow) leach rates were measured on selected nonradioactive solidified waste samples. The data are plotted in Figures 4.13 through 4.17. The standard leach rates proved. to be very dependent upon melt composition and thermal history, with measured rates varying over five orders of magnitude.

It is interesting that in many cases the leach rate for the first week was very low. On the second week the leach rate increased greatly and was aligned in a regular manner with subsequent leach rates obtained at later times. This "induction" period for the inception of leaching occurred with a sufficient number of samples so that it is real, but no explanation for the mechanism can be given at this time. After the "induction" period, the leach rates decreased with time, and in most cases had not reached equilibrium in twelve weeks. Other tests have indicated that at least 40 weeks leaching is required to reach a pseudo-equilibrium rate. Some of these tests will be continued for at least 40 weeks and the results reported in a subsequent report.

Leach rates obtained on two sets of triplicate laboratory solidified waste preparations are presented in Figure 4.13 to indicate the experimental precision that was obtained in this work.

When the products are stored at 100 °C, the glassy phosphate glasses products are significantly less leachable than the microcrystalline spray solidifier products (Figure 4.14). Processing at higher temperatures tends to decrease leach rates; slow cooling tends to increase leach rate. Storing the products at 600 °C, rather than 100 °C, did not affect the leachability of the spray products (Figure 4.15), but seriously increased the leachability of the phosphate glass products (Figure 4.16). The increased leachability occurred when the phosphate glass product devitrified, as discussed above. Devitrification occurs between 500 and 600 °C (Figure 4.17).

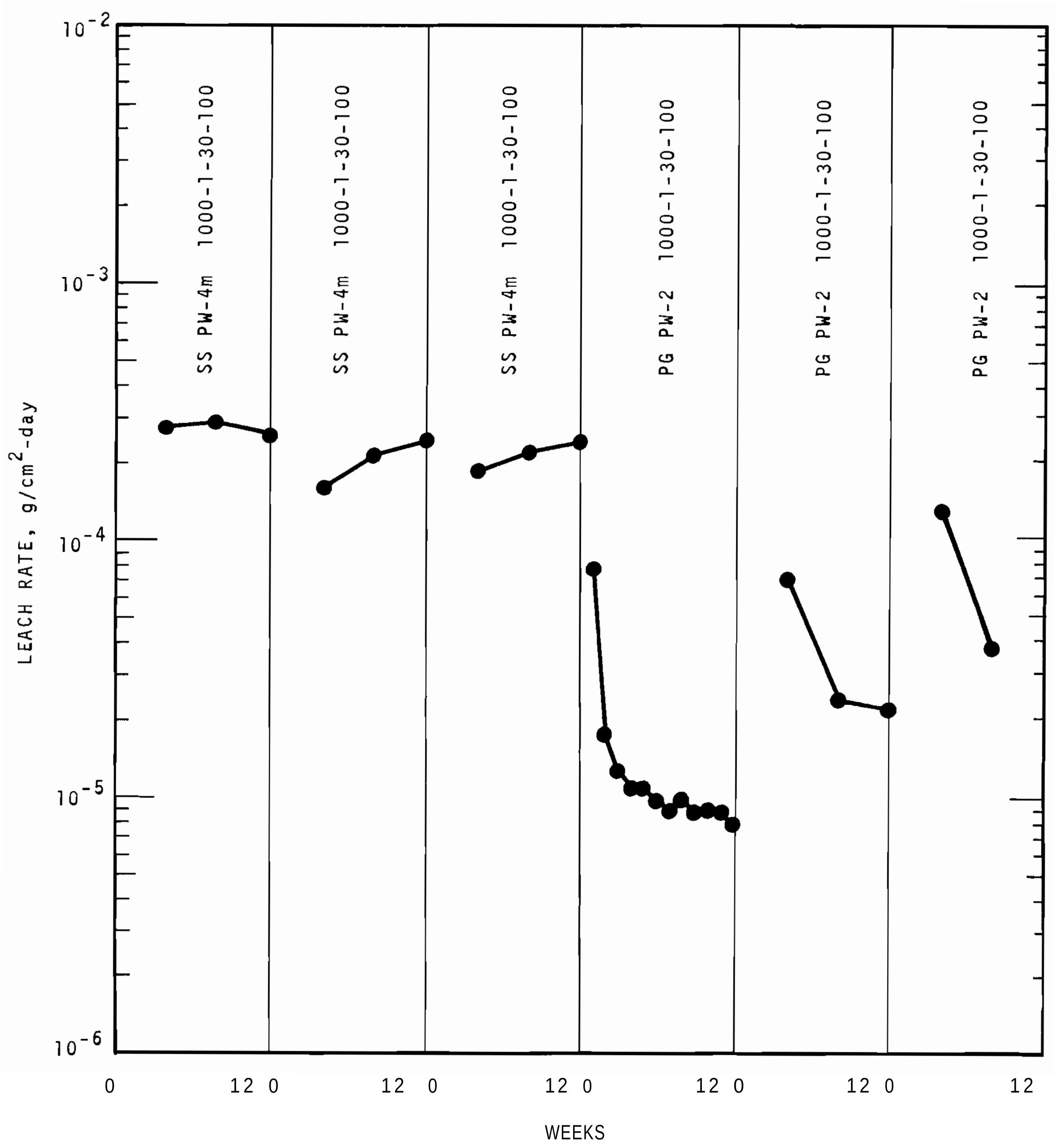


FIGURE 4.13. Precision of Standard Leach Rate Measurements

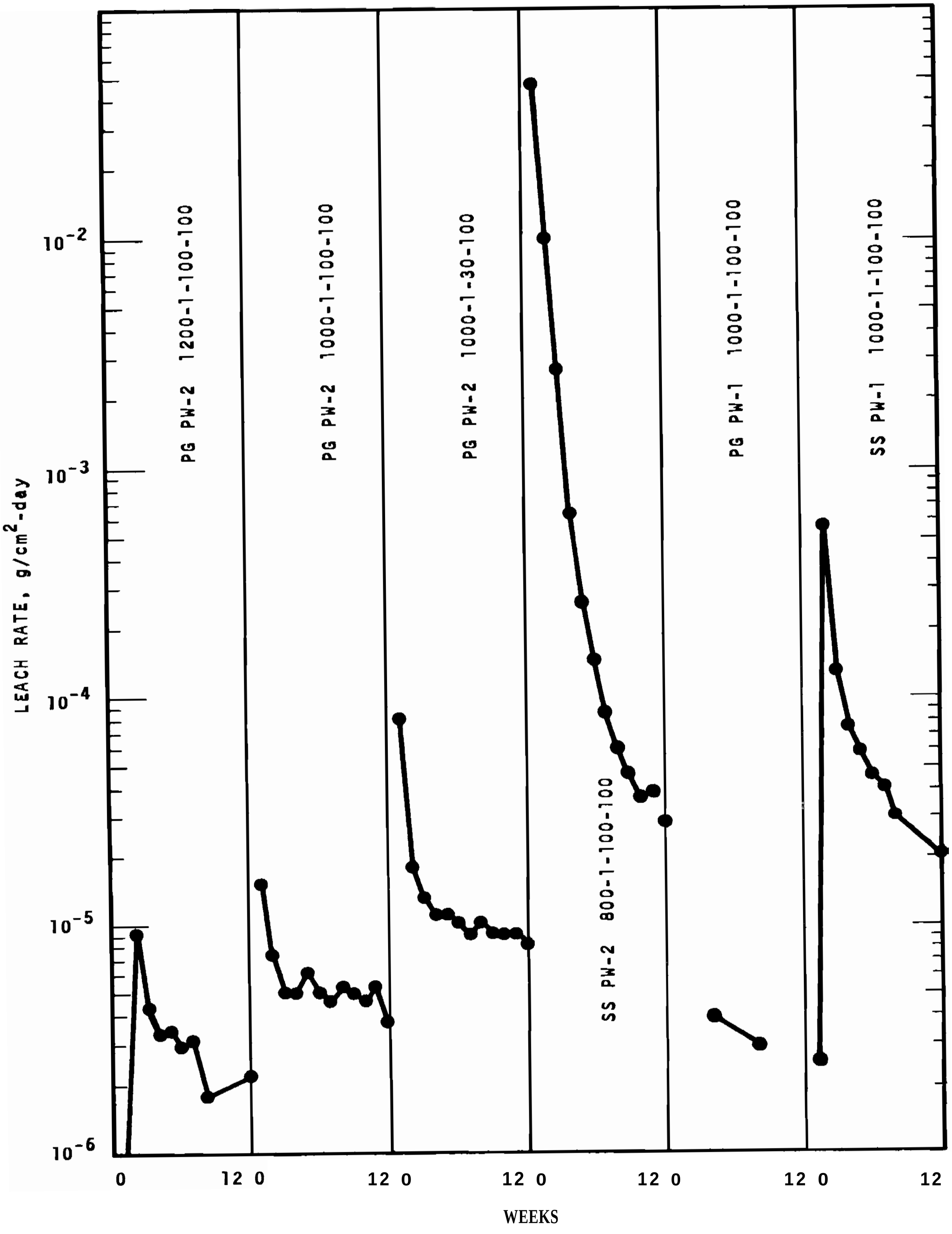


FIGURE 4.14. Comparison of Phosphate Glass and Spray Solids

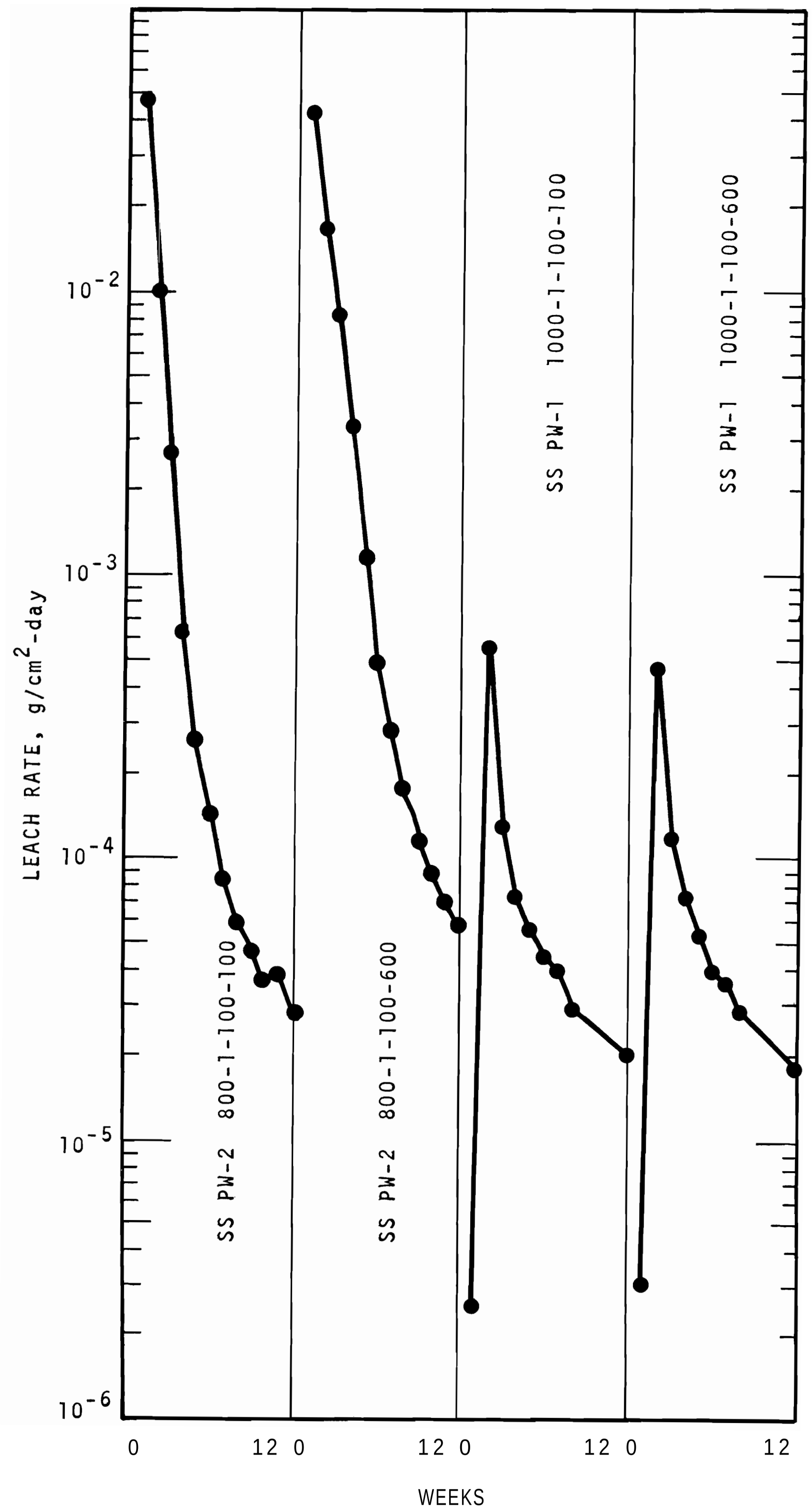


FIGURE **4.15.** **Effect of Storage Temperature on Spray Solids**

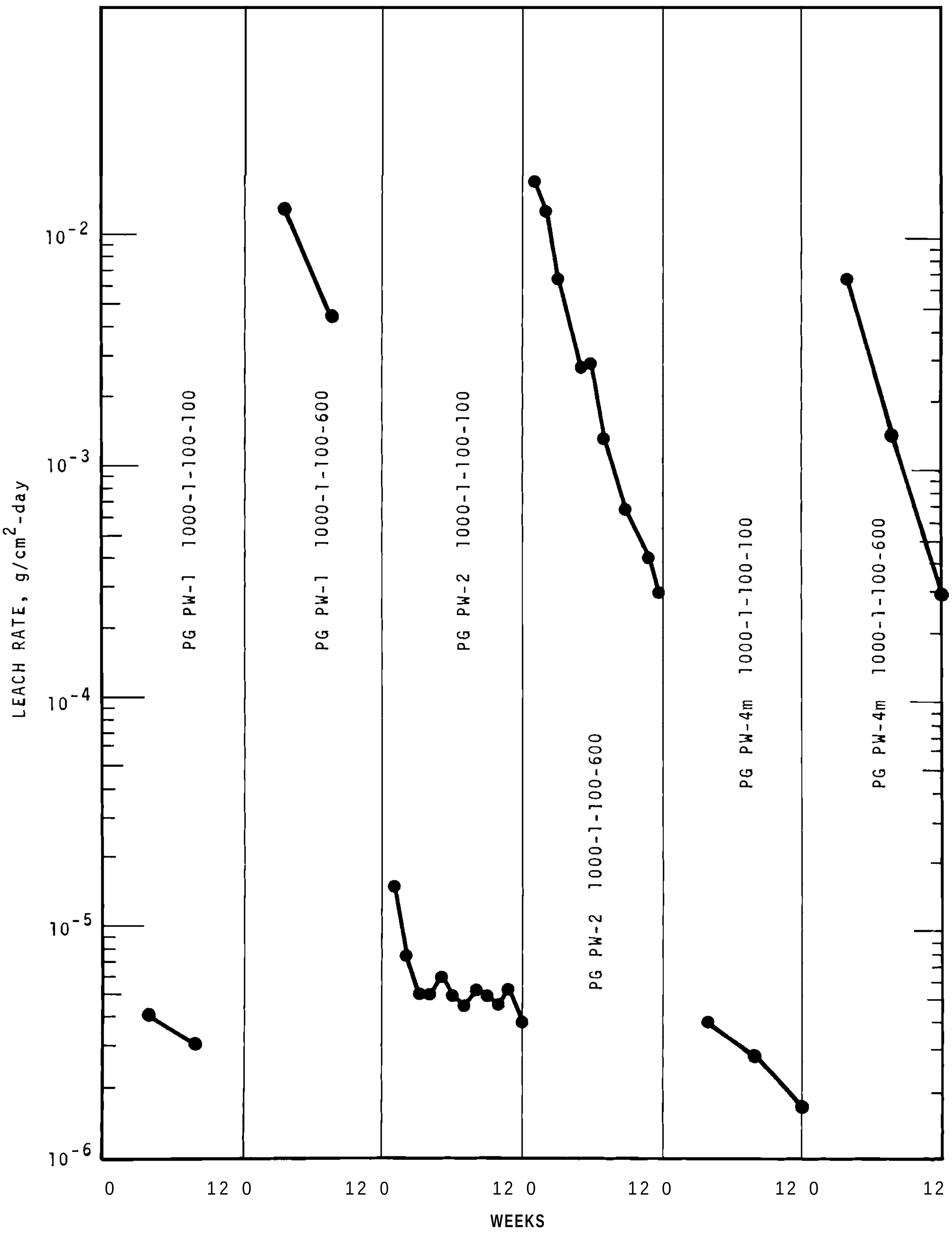


FIGURE 4.16. Effect of Storage Temperature on Phosphate Glass

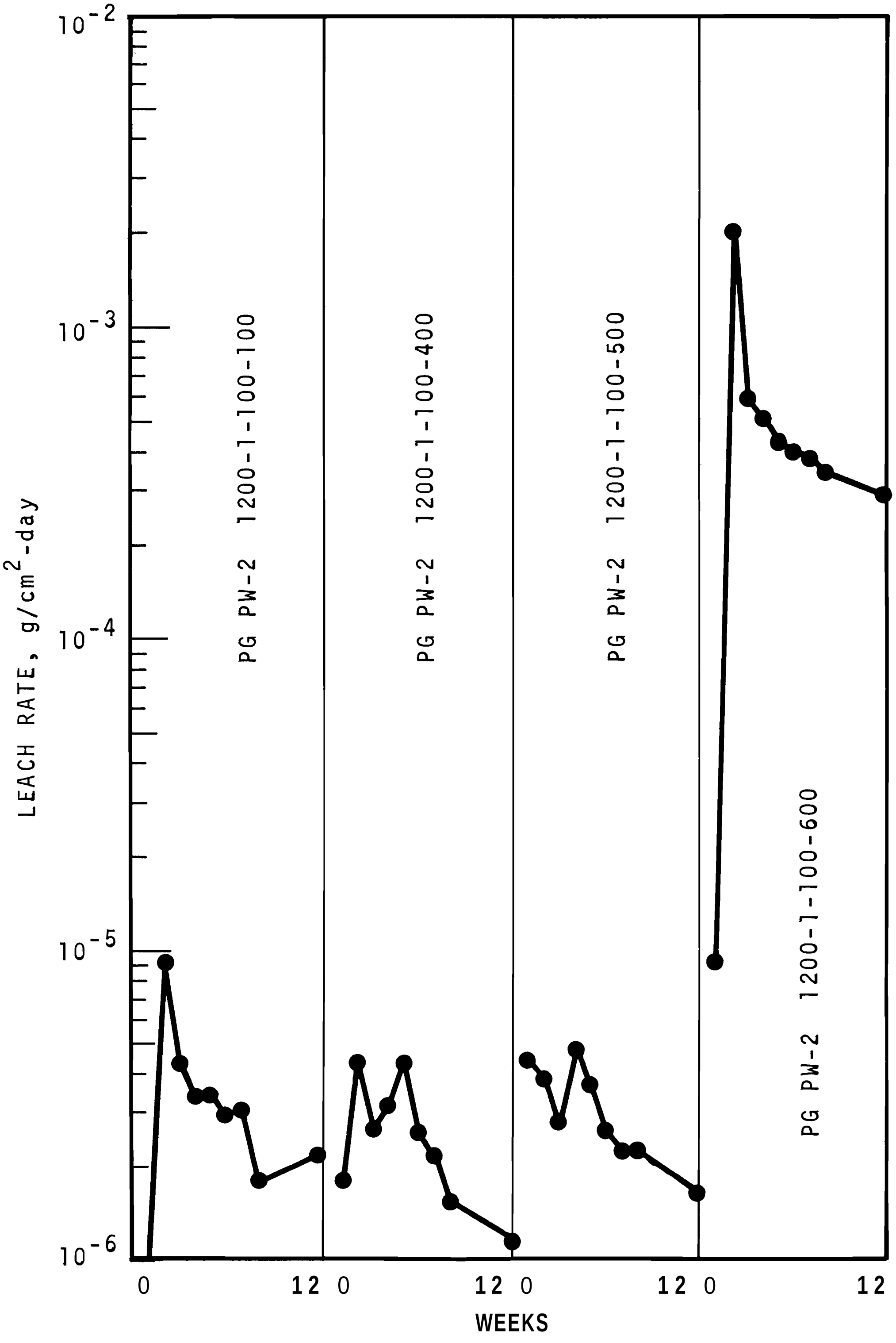


FIGURE 4.17. Effect of Storage Temperature on Phosphate Glass (PW-2)

5.0 RECOMMENDATIONS

The characterization of the properties of high level radioactive solidified waste by means of nonradioactive techniques is a valuable tool for industry. Obviously not all the types of possible processes and waste types have been considered in this study. Evaluation and characterization of other melt-formed systems such as the borosilicate glasses and fluidized bed solids would be valuable. Solidified waste that contains soluble poisons (large amounts of boron or cadmium and smaller amounts of gadolinium) are potential wastes of the future and should be studied. A common set of evaluation techniques and standards should be established such as leachability (accelerated and/or slow), thermal conductivity, etc., so that common characteristics can be evaluated and compared between systems.

The nonradioactive sample approach could be used to improve the quality of solidified waste products through variation of processing parameters and product additives. This is particularly true in the case of phosphate glass where processing parameters affect the end product greatly. The nonhomogeneous samples of spray solid could be studied further to determine the effects of process temperature and process time in more detail.

A limited program of sample irradiation by an external source such as ^{60}Co could be undertaken to establish the effects of radiation on small scale laboratory samples. Correlation of the basically nonradioactive laboratory work with large scale demonstration work would be more meaningful if the effects of radiation on nonradioactive samples were better understood.

Studies of alternative solidified waste products could take full advantage of this evaluation technique. The nonradioactive laboratory samples approach is the least expensive and potentially the most comprehensive of the available avenues.

6.0 APPENDIX

This appendix provides a tabulation of data collected during the nonradioactive portion of the product evaluation program. Tables 6.1 and 6.2 present phosphate glass and spray solid data on density, porosity, drip point, thermal conductivity, heat capacity, accelerated leachability, dispersibility, and linear coefficient of thermal expansion.

Figures 6 1, 6 2, and 6 3 are photographs and photomicrographs of phosphate glass PW 1 and PW-4m samples and of spray solid PW-2 and PW-4m samples Figures 6 4, 6 5, and 6 6 are photographic records of phosphate glass and spray melt samples taken after the thermal shock test

TABLE 6.1. **Phosphate Glass Data**

Laboratory Sample Number	Remarks	Process	Waste Type PW-	Process Temp., °C	Time at Process Temp., hr	Cool-Down Rate, °C/hr	Storage Temp.,(a) °C	Density, g/cm^3	Porosity	Drip Point, °C	Thermal Conductivity, W/m °C						
											72 °C	122 °C	172 °C	222 °C	272 °C	322 °C	$\overline{K}$
4	Sticky (Black)	PG	2	1000	1	30	100	2.944	2.93	845	0.732	0.749	0.761	0.778	0.790	0.824	0.806
5	Glassy (Black)	PG	2	1000	1	100	100	2.890	1.0	855	0.619	0.661	0.707	0.753	0.990	0.845	0.762
7	Sticky (Black)	PG	2	1000	1	30	600	2.988	2.25	800	0.765	0.828	0.883	0.945	1.008	1.071	0.917
8	Sticky (Black)	PG	2	1000	1	100	600	2.981	3.24	800	0.786	0.791	0.795	0.807	0.820	0.837	0.806
6	Glassy (Black)	PG	2	1000	25	30	100	2.814	2.81	825	0.753	0.782	0.807	0.841	0.870	0.908	0.827
11	Glassy (Black)	PG	2	1000	25	100	100	2.897	0	915	0.552	0.586	0.615	0.644	0.673	0.703	0.629
9	Sticky (Black)	PG	2	1000	25	30	600	2.977	2.40	795	0.690	0.732	0.778	0.820	0.866	0.908	0.799
16	Sticky (Black)	PG	2	1000	25	100	600	2.926	2.31	845	0.920	0.933	0.954	0.975	0.996	1.025	0.813
12	Glassy (Black)	PG	2	1200	1	30	100	2.906	0	875	0.544	0.573	0.602	0.636	0.661	0.694	0.618
14	Glassy (Black)	PG	2	1200	1	100	100	2.916	0	870	0.531	0.581	0.627	0.669	0.715	0.757	0.647
10	Slightly Sticky (Black)	PG	2	1200	1	30	600	2.882	0	872	0.757	0.820	0.845	0.878	0.908	0.941	0.858
2	Sticky (Black)	PG	2	1200	1	100	600	2.920	0	855	0.904	0.929	0.957	0.987	1.021	1.058	0.976
13	Glassy (Black)	PG	2	1200	25	30	100	2.897	0	875	0.598	0.577	0.602	0.632	0.657	0.732	0.633
17	Glassy (Black)	PG	2	1200	25	100	100	2.909	0	870	0.527	0.540	0.561	0.581	0.598	0.640	0.574
15	Glassy (Black)	PG	2	1200	25	30	600	2.918	0	895	0.615	0.640	0.673	0.699	0.732	0.770	0.688
3	Sticky (Black)	PG	2	1200	25	100	600	2.874	2.06	865	0.795	0.812	0.832	0.862	0.891	0.920	0.852
62	Duplicate (Black)	PG	2	1000	1	30	100	2.944	0.80	(d)	0.778	0.711	0.715	0.724	0.732	0.736	0.733
63	Duplicate (Black)	PG	2	1000	1	30	100	2.940	0.033	810	0.824	0.849	0.862	0.878	0.887	0.891	0.865
9	Repetition	PG	2	1000	25	30	600			-	-	-	-	-	-		
9	Repetition	PG	2	1000	25	30	600			-	-	-	-	-	-		
14	Repetition	PG	2	1200	1	100	100			-							
14	Repetition	PG	2	1200	1	100	100			-	-	-	-	-	-		
17	Repetition	PG	2	1200	25	100	100			-	-	-	-	-	-		
17	Repetition	PG	2	1200	25	100	100			-	-	-	-	-	-	-	-
49	Duplicate, Glassy (Green)	PG	4m	1000	1	100	100	2.967	0.218	895	0.569	0.602	0.632	0.665	0.699	0.736	0.650
50	Glassy (Green)	PG	4m	1000	1	100	100	2.992	0	885	0.887	0.841	0.803	0.778	0.757	0.745	0.802
51	Glassy (Green)	PG	4m	1000	1	100	600	3.004	1.59	855	0.778	0.774	0.778	0.782	0.791	0.782	0.781
64	Glassy (Black)	PG	1	1000	1	100	100	2.735	0.258	815	0.540	0.556	0.573	0.590	0.602	0.623	0.581
65	Discolored, Not Homogeneous	PG	1	1000	1	100	600	2.807	2.75	735	0.640	0.707	0.753	0.799	0.837	0.862	0.766
500	Glassy (Black)	PG	2	1200	1	100	500	2.832	0	895	0.586	0.640	0.686	0.736	0.782	0.824	0.709
400	Glassy (Black)	PG	2	1200	1	100	400	2.881	0	890	0.541	0.561	0.627	0.673	0.719	0.765	0.647
300	Glassy (Black)	PG	2	1200	1	100	300	2.843	0	895	0.531	0.569	0.607	0.644	0.673	0.707	0.622

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a. Samples at storage temperature for 8 weeks.
b. Sample melted.
c. No adequate coupon could be cut from sample.
d. Not measured.

TABLE 6.1. (contd)

Heat Capacity, cal/g °C × 10^3							Accelerated Leach. % weight loss				Dispersibility, %			LCTE × in./in. °C			
72 °C	122 °C	172 °C	222 °C	272 °C	322 °C	$\bar{C}_p$	1st 24 hr	2nd 24 hr	3rd 24 hr	Total	10.02 in.	0.02 - 0.1 in.	>0.1 in.	200 °C	300 °C	400 °C	500 °C
170	182	193	204	215	226	198	1.79	1.85	1.88	5.52	14.5	10.0	75.5	9.8	10.6	12.8	
173	188	204	219	234	249	211	0.66	2.60	1.20	4.46	16.9	36.2	46.8	(c)			
174	196	217	239	261	283	228	39.35	1.68	0.33	41.36	1.1	1.5	97.4	5.8	12.6	9.4	2.3
163	178	193	208	223	238	200	30.81	2.32	0.71	33.84	0.9	1.4	97.7	6.9	10.7	9.7	8.0
162	175	188	201	214	227	194	1.83	1.55	1.69	5.07	23.1	23.6	53.3	9.1	10.8	11.6	
156	166	176	187	197	207	181	0.45	0.45	0.58	1.48	15.0	40.7	44.3	(c)			
144	167	191	214	238	262	203	36.51	2.09	0.67	39.27	1.7	1.4	96.9	7.1	8.5	7.6	
168	185	203	220	237	255	211	34.29	0.78	0.73	35.86	1.9	5.3	92.8	10.1	13.8	14.2	11.6
159	170	181	192	203	214	186	0.53	0.32	0.34	1.18	26.0	38.7	35.3	10.3	9.1	7.5	
168	178	187	195	204	213	191	0.43	0.38	0.59	1.39	18.3	30.7	51.0	9.4	9.8	7.1	
159	173	188	203	217	231	195	0.85	0.53	0.55	1.93	18.6	36.6	44.8	9.8	11.0	12.1	11.6
163	179	195	211	227	243	203	29.47	11.05	0.91	41.43	1.5	3.5	95.0	10.8	11.8	14.4	11.7
157	173	189	205	222	238	197	0.63	0.38	0.62	1.63	16.3	37.5	46.2	(c)			
156	166	176	186	196	206	181	0.74	0.64	0.79	2.18	17.9	29.7	52.4	(c)			
169	180	192	203	214	226	197	2.39	2.39	2.67	7.45	(c)			(c)			
151	167	184	200	217	233	192	32.34	2.30	0.69	35.33	1.3	1.7	97.0	10.1	11.7	13.1	11.2
163	168	173	178	184	189	176	(d)				18.2	13.8	68.0	6.5	8.0	9.1	11.2
170	182	193	205	217	229	199	2.10	2.49	2.81	7.22	(c)			7.0	8.0	8.5	10.7
-	-	-	-	-	-	-	33.9	3.56	1.94	39.40	-	-	-	-	-	-	-
-	-	-	-	-	-	-	31.3	3.81	2.40	37.51	-	-	-	-	-	-	-
-	-	-	-	-	-	-	0.48	0.47	0.66	1.61	-	-	-	-	-	-	-
-	-	-	-	-	-	-	0.50	0.24	1.03	1.77	-	-	-	-	-	-	-
-	-	-	-	-	-	-	0.55	0.68	0.68	1.91	-	-	-	-	-	-	-
-	-	-	-	-	-	-	0.42	0.22	1.04	1.68	-	-	-	-	-	-	-
145	160	175	189	204	220	182	8.66	12.45	9.48	27.60	12.6	28.6	58.8	8.5	7.2	7.8	(b)
179	183	186	190	194	198	188	5.77	8.78	9.37	22.09	(c)			(c)			
149	163	178	192	207	221	185	30.01	1.14	0.86	31.40	1.7	3.7	94.6	10.0	15.0	14.0	13.4
181	187	192	198	203	209	195	6.53	8.48	7.85	21.17	24.6	41.1	34.6	7.5	8.5	9.5	9.0
155	178	200	222	245	267	211	52.68	4.14	3.09	56.04	3.2	5.1	91.7	4.3	6.3	(b)	(b)
151	167	182	197	213	228	190	1.09	0.95	1.74	3.74	26.8	45.7	27.5	(c)			
155	169	184	198	213	228	191	0.66	0.59	1.10	2.33	25.7	41.3	33.0	(c)			
159	172	185	198	211	224	192	0.67	0.70	1.21	2.56	(c)			(c)			

TABLE 6.2. Spray Solid Data

Laboratory Sample Number	Remarks	Process	Waste Type PW-	Process Temp., °C	Time at Process Temp., hr	Cool-Down Rate, °C/hr	Storage Temp., °C[(a)]	Density, g/cm^3	Porosity	Drip Point, °C	Thermal Conductivity, W/m °C: 72 °C	122 °C	172 °C	222 °C	272 °C	322 °C	$\overline{K}$
25		SS	1	1000	1	100	100	3.468	5.0	—	0.983	1.042	0.991	0.983	0.983	0.983	0.994
26		SS	1	900	2	100	100	3.507	3.5	915	1.029	0.941	0.945	0.954	0.979	0.979	0.971
27		SS	1	900	2	100	600	3.527	6.5	895	0.945	1.150	1.167	1.201	1.234	1.221	1.153
28		SS	1	1000	1	100	600	3.544	4.0	905	1.134	1.159	1.171	1.188	1.205	1.226	1.180
31	Homogeneous (Black)	SS	2	800	1	100	100	2.994	—	685	0.807	0.845	0.883	0.920	0.962	1.004	0.962
32	2 Phases (Gray)	SS	2	800	1	100	600	2.980	0.94	665	0.991	1.008	1.016	1.029	1.029	1.025	0.986
52	Homogeneous (Black)	SS	4m	1000	1	30	100	3.458	6.4	905	(d)						
53	Homogeneous (Black)	SS	4m	1000	1	30	100	3.463	3.13	—	1.108	1.096	1.075	1.071	1.075	1.092	1.086
54	Homogeneous (Black)	SS	4m	1000	1	30	100	3.457	6.18	950	(d)						
55	Large Pores (Discolored)	SS	4m	1000	1	30	600	3.503	2.29	—	(d)						
56	Homogeneous (Black)	SS	4m	1000	25	30	100	3.470	2.95	950	1.297	1.238	1.180	1.125	1.062	0.996	1.150
57	Homogeneous (Black)	SS	4m	1000	25	30	600	3.480	4.32	925	(d)						
58	Homogeneous (Black)	SS	4m	1100	1	30	100	3.460	3.18	925	(d)						
59	Homogeneous (Black)	SS	4m	1100	1	30	600	3.408	6.64	920	1.226	1.192	1.163	1.121	1.071	1.016	1.131
60	Not Homogeneous	SS	4m	1100	25	30	100	3.478	2.17	910	0.799	0.791	0.791	0.795	0.803	0.816	0.799
61	Not Homogeneous	SS	4m	1100	25	30	600	3.475	1.55	—	1.267	1.234	1.201	1.163	1.113	1.075	1.175

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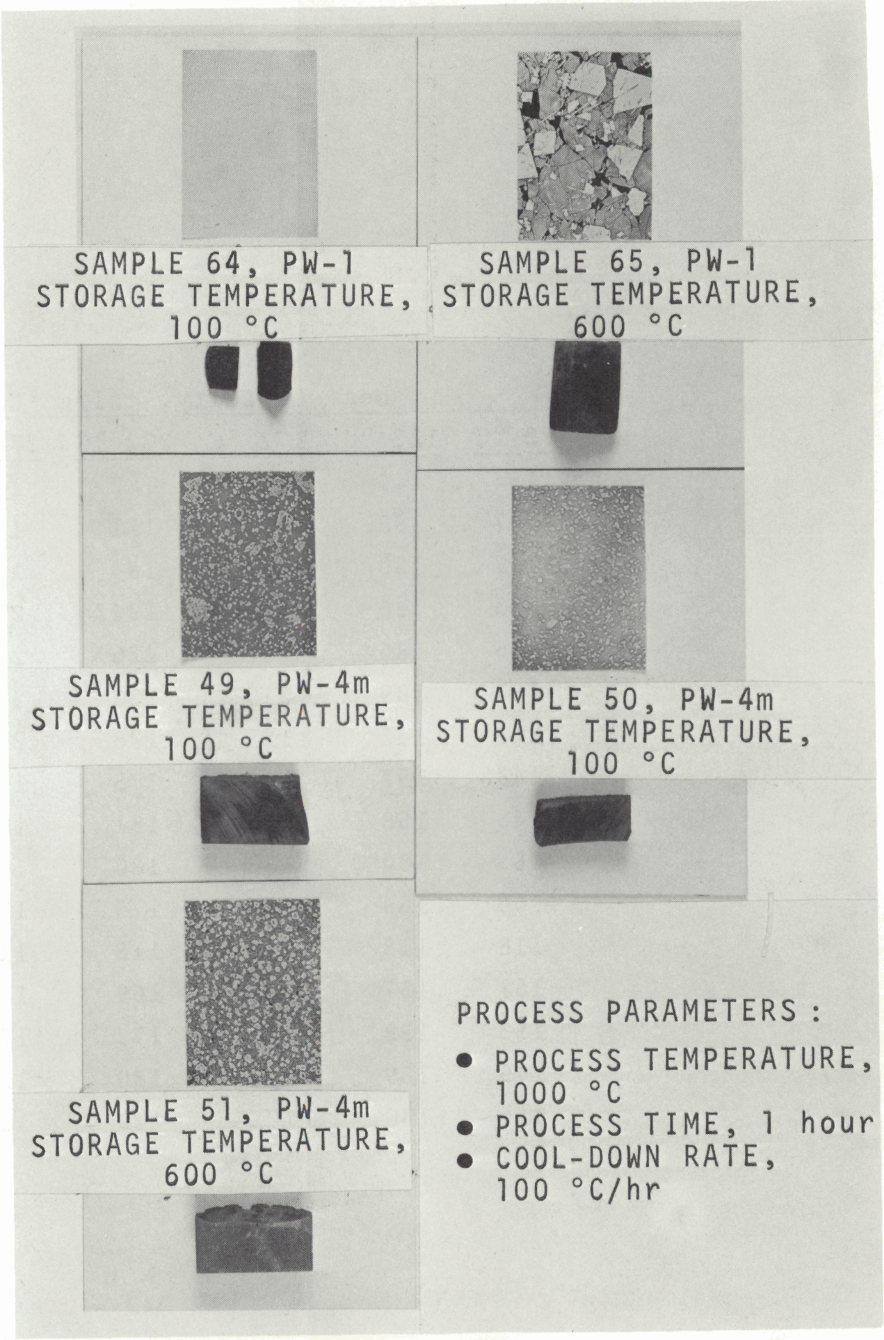
a. Samples at storage temperature for 8 weeks.
b. Sample melted.
c. No adequate coupon could be cut from sample.
d. Not measured. Sample broke under test.

TABLE 6.2. (contd)

Heat Capacity, cal/g °C × 10^3							Accelerated Leach, % weight loss				Dispersibility, %			LCTE × 10^6, in./in. °C			
72 °C	122 °C	172 °C	222 °C	272 °C	322 °C	$\bar{C}_p$	1st 24 hr	2nd 24 hr	3rd 24 hr	Total	<0.02 in.	0.02 - 0.1 in.	>0.1 in.	200 °C	300 °C	400 °C	500 °C
154	163	173	182	192	201	178	5.59	0.21	0.01	5.80	5.7	7.9	86.4	6.02	6.59	6.19	7.01
147	155	163	171	179	187	167	5.23	0.07	0.16	5.45	(c)			6.80	8.50	9.95	10.59
147	159	171	184	196	209	178	4.87	0.10	0.14	5.11	3.2	3.9	92.9	6.31	6.92	4.98	5.53
153	166	179	192	205	218	186	5.35	0.13	0.12	5.60	1.7	2.6	95.7	8.58	7.50	8.07	9.24
166	186	206	226	246	266	216	35.12	4.25	0.99	40.36	11.5	24.5	64.0	11.60	14.80	16.70	16.87
187	199	210	222	233	245	216	35.31	1.28	0.64	37.23	(c)			(c)			
148	162	175	188	202	217	182	5.60	5.63	2.85	14.08	(c)			(c)			
145	157	165	175	186	197	171	4.98	3.75	2.15	10.88	(c)			(c)			
148	158	170	181	192	202	175	1.41	2.09	2.34	5.84	(c)			(c)			
185	184	182	180	179	177	181	10.24	0.42	0.26	10.92	16.2	23.2	60.6	4.0	6.2	7.5	11.1
166	168	171	173	175	177	172	1.82	3.37	4.51	9.70	32.9	28.1	39.0	2.3	3.8	4.6	5.0
118	118	118	118	118	118	118	8.86	4.13	1.36	14.35	13.2	19.7	67.1	4.5	5.5	6.8	7.2
151	157	163	169	176	182	166	0.57	0.44	0.56	1.57	25.1	32.7	42.2	(c)			
153	159	166	172	179	185	169	12.77	1.62	0.48	14.87	10.9	19.4	69.7	3.2	4.0	4.6	5.1
149	159	170	180	191	201	175	0.38	0.30	0.31	0.99	10.3	11.0	78.7	3.8	4.8	5.3	5.6
166	170	175	179	183	188	177	12.62	1.38	0.44	14.44	9.4	20.1	70.5	4.0	5.7	7.1	(b)



Neg 701217-2

FIGURE 6.1. Phosphate Glass (PW-4m and PW-1) Samples and Photomicrographs

SAMPLE 31
STORAGE TEMPERATURE
100 °C

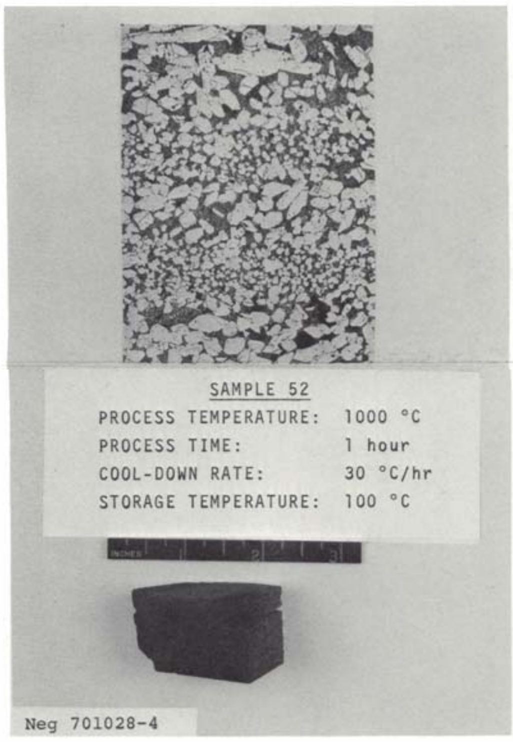
SAMPLE 32
STORAGE TEMPERATURE
600 °C

PROCESS PARAMETERS:

- PROCESS TEMPERATURE, 800 °C
- PROCESS TIME, 1 hour
- COOL-DOWN RATE, 100 °C/hr

Neg 701217-1

FIGURE 6.2. Spray Solid (PW-2) Samples and Photomicrographs

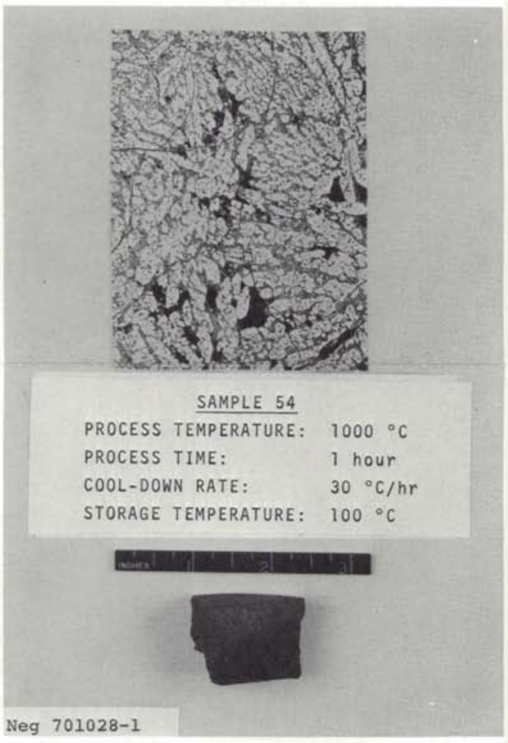


SAMPLE 52
PROCESS TEMPERATURE: 1000 °C
PROCESS TIME: 1 hour
COOL-DOWN RATE: 30 °C/hr
STORAGE TEMPERATURE: 100 °C

Neg 701028-4

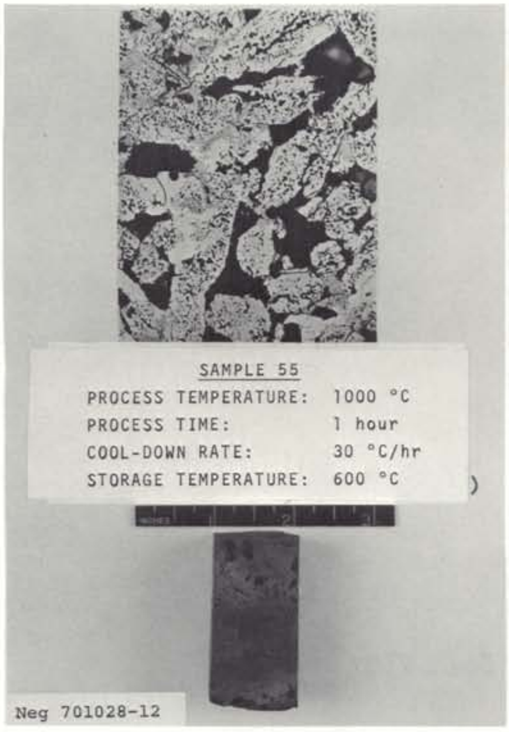
SAMPLE 53

SEE FIGURE 4.3



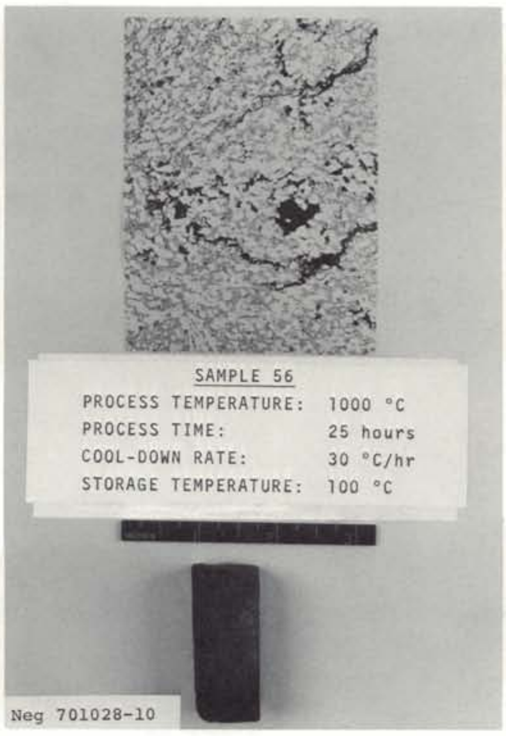
SAMPLE 54
PROCESS TEMPERATURE: 1000 °C
PROCESS TIME: 1 hour
COOL-DOWN RATE: 30 °C/hr
STORAGE TEMPERATURE: 100 °C

Neg 701028-1



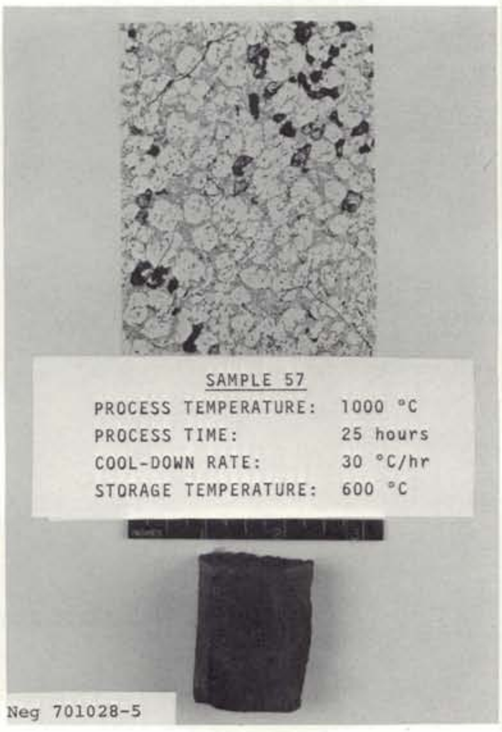
SAMPLE 55
PROCESS TEMPERATURE: 1000 °C
PROCESS TIME: 1 hour
COOL-DOWN RATE: 30 °C/hr
STORAGE TEMPERATURE: 600 °C

Neg 701028-12



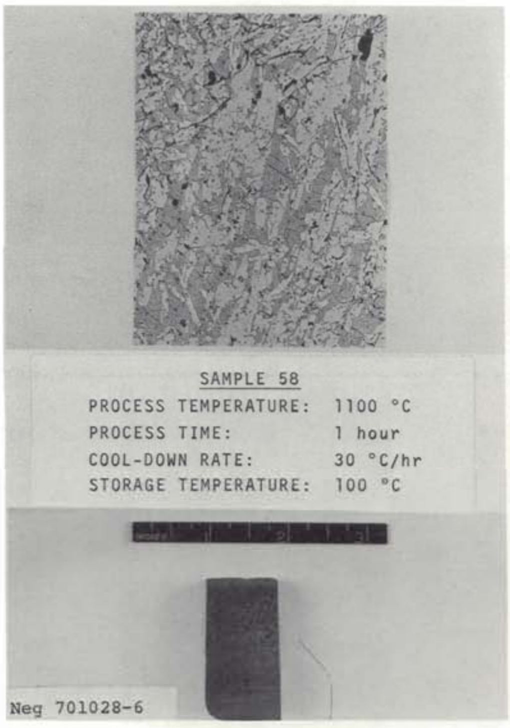
SAMPLE 56
PROCESS TEMPERATURE: 1000 °C
PROCESS TIME: 25 hours
COOL-DOWN RATE: 30 °C/hr
STORAGE TEMPERATURE: 100 °C

Neg 701028-10



SAMPLE 57
PROCESS TEMPERATURE: 1000 °C
PROCESS TIME: 25 hours
COOL-DOWN RATE: 30 °C/hr
STORAGE TEMPERATURE: 600 °C

Neg 701028-5



SAMPLE 58
PROCESS TEMPERATURE: 1100 °C
PROCESS TIME: 1 hour
COOL-DOWN RATE: 30 °C/hr
STORAGE TEMPERATURE: 100 °C

Neg 701028-6

SAMPLE 59

SEE FIGURE 4.4a

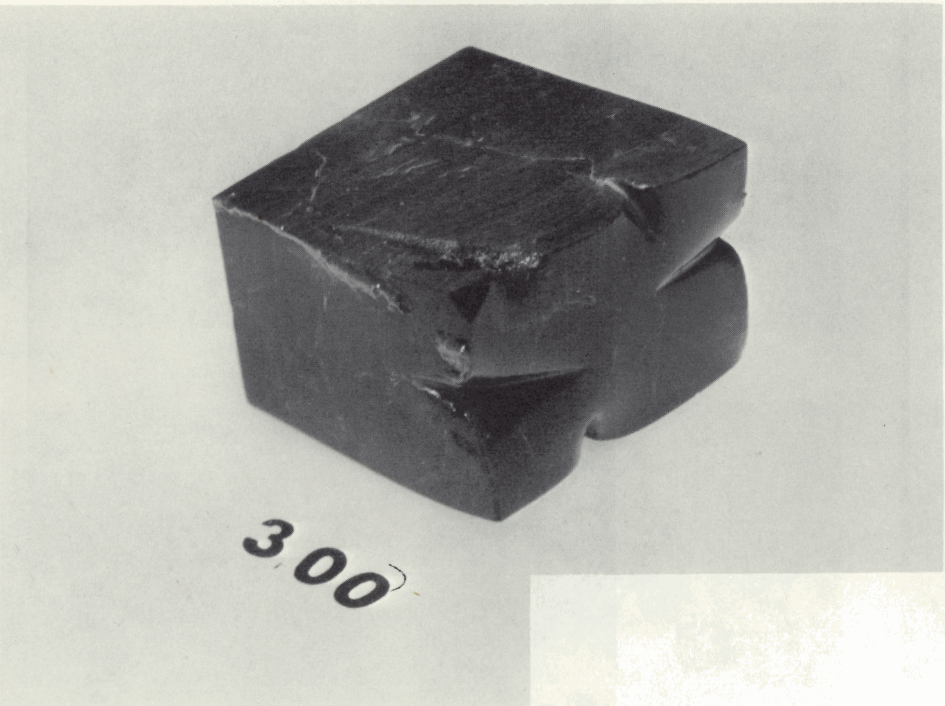
SAMPLE 60

SEE FIGURE 4.4b

SAMPLE 61

SEE FIGURE 4.4c

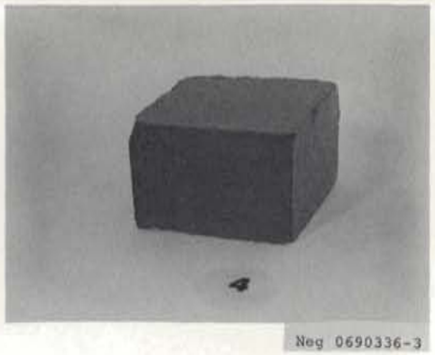
FIGURE 6.3. Spray Solid Photomicrographs and Samples from PW-4m Waste



Neg 0641967-4

Neg 0641968-3

FIGURE 6.4. Thermal Shock Test Coupons for Phosphate Glass (PW-2) at Intermediate Storage Temperatures (300 °C and 500 °C)



Neg 0690336-3

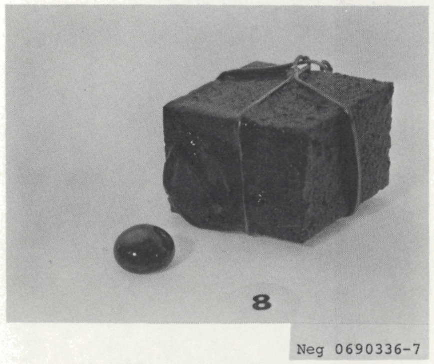
Neg 0690336-5

Neg 0690336-4

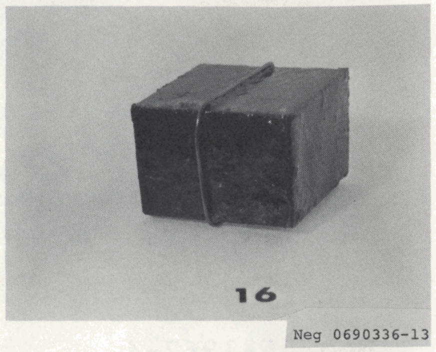
Neg 0690336-10

Neg 0690336-6

Neg 0690336-8

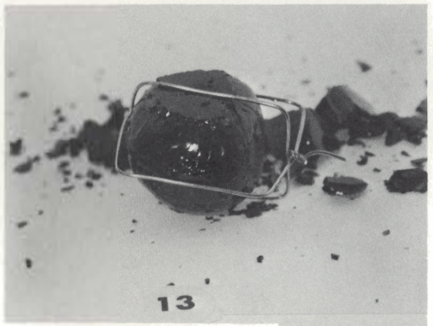


Neg 0690336-7

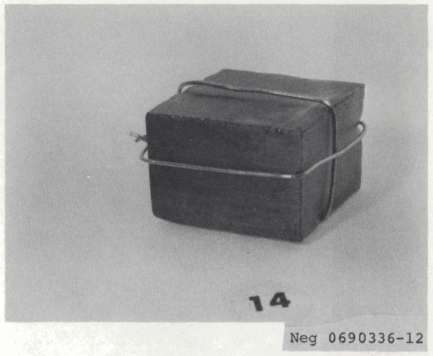


Neg 0690336-13

SAMPLE 12
NO COUPON

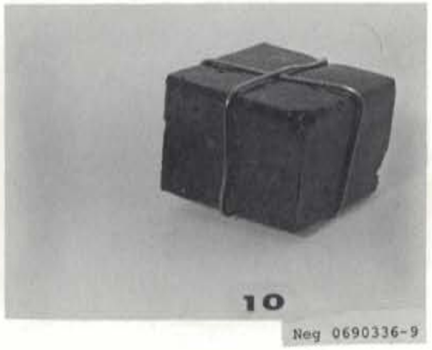


Neg 0690336-11



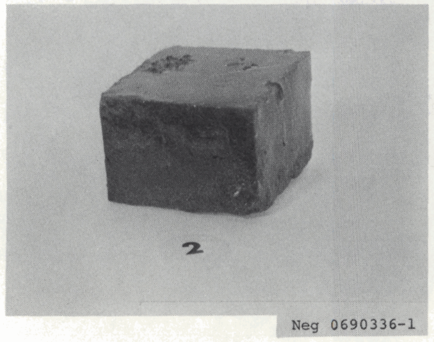
Neg 0690336-12

Neg 0690336-14

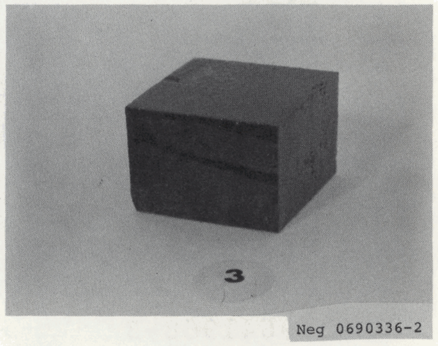


Neg 0690336-9

SAMPLE 15
NO COUPON

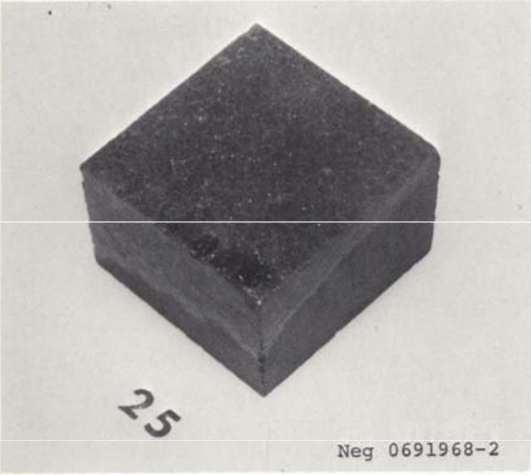


Neg 0690336-1



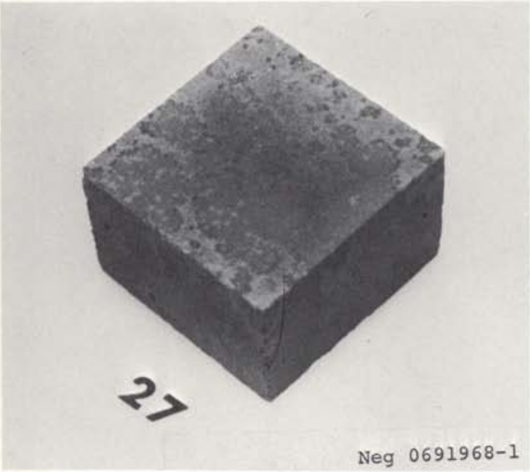
Neg 0690336-2

FIGURE 6.5. Thermal Shock Test Coupons for Phosphate Glass (PW-2). Wire sample holder is shown in some photographs.



SAMPLE 26

NO COUPON



SAMPLE 32

NO COUPON

FIGURE 6.6. Thermal Shock Test Coupons for Spray Solid (PW-1 and PW-2)

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