27
6-20-78
25 sep to NTS

SAND 78-0663
Unlimited Release

MASTER

THE SANDIA SOLIDIFICATION PROCESS:
CONSOLIDATION AND CHARACTERIZATION
PART I. CONSOLIDATION STUDIES

J. K. Johnstone

Sandia Laboratories

SF 2900 Q(7-73)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Issued by Sandia Laboratories, operated for the United States
Department of Energy by Sandia Corporation.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DE 1984-DF(11-77)

Printed in the United States of America

Available from

National Technical Information Service

U. S. Department of Commerce

5285 Port Royal Road

Springfield, VA 22151

Price: Printed Copy \$5.50; Microfiche \$2.25

THE SANDIA SOLIDIFICATION PROCESS: CONSOLIDATION
AND CHARACTERIZATION

PART I. CONSOLIDATION STUDIES

J. K. Johnstone
Ceramics Development Division

ABSTRACT

NOTICE
This report was prepared as an account of work sponsored by the United States Government neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

The consolidation behavior of a complex polycrystalline ceramic nuclear waste form composed of titanates, zeolite, and metallic silicon was studied. Initial solidification takes place by an ion exchange process. The resulting powder exhibits a large surface area, $\sim 350 \text{ m}^2/\text{g}$, and several decomposition, crystallization and phase change reactions from room temperature to 1100°C . In spite of the large surface area, consolidation by cold pressing and atmospheric sintering to 1100°C was not satisfactory. Vacuum hot pressing was found to produce fully dense pellets ($<1\%$ residual porosity) under very mild conditions, 6.9 MPa (1000 psi) and 1100°C . The dominant densification mechanism was viscous flow. Under less than optimum hot pressing conditions, three stages of densification were observed. Initial densification took place by particle rearrangement which was described with a viscous flow model. Second stage densification occurred by a solution-precipitation process controlled by a phase boundary dissolution reaction. In several cases, a third, final densification stage was observed. Detailed studies describe the effects of heating rate, processing temperature, pressure, residence time, atmosphere, composition, heat treatment, and the addition of consolidation aids on the densification behavior. In addition, fully radioactive high level mixed fission product titanate/waste pellets (1.27 cm diameter) were hot pressed at Oak Ridge National Laboratory to demonstrate the feasibility of such a process in a remotely operated hot cell. High density uniform pellets were obtained.

TABLE OF CONTENTS

I. Introduction	3
II. Description of Materials	4
III. Experimental Procedure	7
A. The Waste Powder	7
B. Thermal Analysis	9
C. Cold Pressing and Sintering	9
D. Hot Pressing	11
IV. Results and Discussion	12
A. Waste Powder Characterization	12
1. Particle size of the dried powder	12
2. Thermogravimetric (TGA) and differential thermal analysis (DTA)	15
B. Cold Pressing and Sintering	18
C. Slump Tests	23
D. Hot Pressing	26
1. Reactive hot pressing	27
2. Hot pressing parameters	29
a. Heating rate	29
b. Maximum processing temperature	33
c. Pressure optimization	36
d. Residence time at T_{max}	39
e. Atmosphere	41
3. Compositional variations in the titanate waste	42
a. Batch behavior	42
b. Residual sodium content	42

c. Silicon and zeolite content	45
d. Consolidation aide - glass additions	45
e. Precalcined waste	47
f. Semicontinuous hot pressing	49
4. The mechanism(s) of densification	49
E. Hot Pressing High Level, Mixed Fission Product Titanate/Waste	60
V. Conclusions	67
VI. References	68

I. Introduction

The Sandia Solidification Process (SSP) offers an alternative means of solidifying aqueous radioactive wastes from nuclear power reactors. The process is based on an ion exchange reaction in which the radioactive cations are removed from the liquid waste stream by a newly developed hydrated inorganic titanate complex. The broad scope of the program in which this process was developed included study of the preparation of the ion exchange materials, study of the various chemical interactions between the ion-exchange material and cationic species in the waste stream, characterization of the solidified waste, evaluation of alternative consolidation methods and optimization of the most satisfactory method, characterization of the consolidated products, and finally, the generation of engineering data for possible future scale up and processing cost estimates.⁽¹⁾ This two part report describes the consolidation studies on the solidified waste and the characterization of the consolidated product for both simulated and fully radioactive wastes produced at the Oak Ridge National Laboratory (ORNL).

It appears that consolidation will be necessary regardless of the particular solidification scheme. In some solidification schemes such as the favored Battelle Pacific Northwest Labs (PNL) borosilicate glass process, consolidation is inherent in the nature of the process. However, upon completion of solidification of radwastes using one of the ceramic alternatives to glass, such as the titanate process, the product is at best a dry cake which is easily comminuted into a very fine fluffy powder. Consequently, consolidation is a separate step, the value of which must ultimately be judged on the relative merits of the final product. One reason, of course, to consolidate the titanate/waste is to limit both its mechanical and chemical dispersion potential. For example, should a shipping cask be breached during transport by some natural or manmade disaster, a light, fluffy,

highly radioactive powder could easily be carried off in a stream or by the wind and be virtually impossible to recover. In addition, the absolute leachability and volatility of the waste form is determined by its surface area. While the leach rate and vaporization rate of a particular radwaste expressed, for example, in $\text{g/cm}^2/\text{day}$ may be quite low, a sample with a specific surface area of $10^6 \text{cm}^2/\text{g}$ could release a considerable quantity of dangerous fission products if dumped in a river or caught in a fire.

Consolidation would also reduce the storage volume of the radwaste powder by at least one half and considerably more for the titanate/waste materials. Since the anticipated means by which storage costs will be assessed is volume, this is an important consideration. Finally, consolidation will drastically affect the centerline temperature and temperature gradient developed in the waste form by minimizing the residual porosity, thereby achieving maximum thermal conductivity.

II. Description of Materials

The vast majority of the materials generated in this program were prepared with a simulated high level liquid reactor waste (HLLW). The composition of the HLLW was that anticipated by Allied-General Nuclear Services for the Barnwell Plant which until recently was under construction in Barnwell, South Carolina and is given in Table I along with the actual composition of the simulant. Several of the elements present in the lowest concentrations were not included in the simulant.

Prior to the ion-exchange process, the waste simulant pH was adjusted to 0.5-1. This neutralization of the waste stream always resulted in precipitation of various solids which (for a column exchange process) were removed by centrifugation and saved to be added to the solidified waste later.

These reports only deal with the sodium form of the titanate exchange material. The empirical formula for the sodium titanate exchange material is given as

Table 1. Composition of AGNS Barnwell^a high level liquid waste from which simulant was derived.

Constituent	Total Abundance g/tonne of U	Concentration moles/liter	Simulant M
Fission Products			
Se	14.4	0.0003	0.0003
Br	13.7	0.0003	0.0003
Rb	347	0.0071	0.0071
Sr	828	0.0166	0.0163
Y	416	0.0082	0.0082
Zr	3710	0.072	0.0701
Mo	3560	0.065	0.0643
Tc	822	0.016	----
Ru	2330	0.041	0.0201 ^b
Rh	505	0.0086	0.0080
Pd	1520	0.025	0.0254
Ag	82	0.0013	0.0013
Cd	136	0.0021	0.0021
In	1.2	0.00002	----
Sn	25.7	0.00038	----
Sb	10.8	0.00016	----
Te	535	0.0074	0.0074
Cs	2600	0.034	0.034
Ba	1750	0.022	0.0224
La	1320	0.0167	0.0167
Ce	2540	0.032	0.032
Pr	1280	0.016	0.0160
Nd	4180	0.051	0.0507
Pm	35.6	0.0004	----
Sm	1010	0.0118	0.0119
Eu	174	0.002	0.002
Gd	122	0.0014	0.0014
Tb	1.8	0.00002	----
Actinides			
U	10,000	0.074	0.074
Np	482	0.0036	----
Pu	100	0.0007	----
Am	525	0.0038	----
Cm	24	0.0002	----
Impurities and Corrosion Products			
Na	100	0.0077	----
Fe	2000	0.063	0.05
Cr	200	0.0068	0.0067
Ni	80	0.0024	0.0025
Soluble Nuclear Poison			
Gd	9000	0.1007	0.1007
TBP Decomposition			
PO ₄ ⁻³	2000	0.037	----

a) Based on one tonne of 35,000 MWD/MTU fuel processed after 150 day cooling period.

b) Concentration of Ru in simulant was limited to 50% of that expected for economic reasons.

where sodium is the exchangeable cation. Similar exchange materials based on niobium and zirconium have been studied. Each has its own advantages and disadvantages; however, the sodium titanate exchange material was chosen as the base-line material on cost and efficiency of cation removal considerations.

The titanate exchange material also contained ~2 wt % minus 325 mesh metallic silicon. This was found by W. Ross (PNL)⁽²⁾ to prevent the formation of water soluble cesium molybdate in zinc borosilicate glass and at his suggestion solved a similar problem in the titanate materials.

The materials to be consolidated were produced by two methods; a column ion-exchange process and a batch ion exchange process. The column process entailed passing the simulant through a column containing the titanate exchange material. Since the titanate material is approximately 70% efficient, at best, at removing cesium from the waste stream, the effluent was subsequently passed through a column containing Zeolon 900 Na⁺, a cesium specific synthetic zeolite. Upon completion of the exchange process, the titanate material was washed, removed from the column and dried.

The batch process involved simply adding the proper weight of exchange material to a given volume of liquid simulant and mixing together in a beaker. After a specified reaction time the effluent was poured off (to be reacted with zeolite) and the exchanged material washed and dried.

In either process, the final product was composed of the exchanged titanate/waste material containing ~2 wt % metallic silicon, any precipitated solids which

[†]Norton Chemical Process Products Division, Akron, Ohio.

had been removed by centrifugation and 10 wt % zeolite. The mix was dried in air at 105°C for at least 8 hours prior to testing.

Materials from a large number of exchange experiments were used in the consolidation studies. Owing to the nature of the development program, the cost of the simulant, and the variety of studies throughout the program, no single exchange experiment provided enough material to meet the requirements of all the consolidation experiments. In some cases, a run provided enough material for only 5 or 6 pellets. Individual materials were assigned a code number, e.g. 33B+Z, where 33 is the preparation number, B means a batch process (C = column) and +Z means 10 wt % zeolon was added (+E means zeolon and silicon was added). Occasionally cross-checks were run and, except where noted, none of these revealed any significant differences in the consolidation behavior.

The fully radioactive liquid waste was obtained at ORNL by reprocessing portions of two fuel pins which had been irradiated an average of 30,500 MWd/tonne U. The initial enrichment was 4.32% ²³⁵U and they were discharged from the reactor in April, 1971. A detailed composition of the liquid waste was not determined. The materials to be consolidated were prepared by the column ion-exchange process.

III. Experimental Procedure

III. A. The Waste Powder

The solidified waste was obtained as a powder. The waste material, any solids previously removed from the waste stream and the zeolite bed were combined and blended by rolling in a plastic jar containing Lucite® rods. The resulting complete waste form was stored in tightly capped plastic bottles.

The fully radioactive titanate/wastes were mixed in an ordinary household blender for a total of twelve minutes. At one minute intervals the jar was opened to be sure that no packing or caking against the walls had occurred. The blended waste was also stored in a plastic bottle.

III. B. Thermal Analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out with a Dupont Model 990 analyzer system. Heating rates were 10 and 20°C/min up to a maximum temperature of 1100°C. Atmospheres included air, inert gas (Ar) and vacuum.

III. C. Cold Pressing and Sintering

Sample pellets were pressed in steel dies to 124 MPa (18000 psi). The pellets were measured and weighed to obtain a green density. Nominal dimensions were 0.95 cm dia x 0.95 cm long. The pellets were placed in a furnace at ambient temperature and pressure and were heated to a maximum sintering temperature of 1100°C. Soak times ranged up to 2 hours. Upon completion of the soak, the furnace was shut off and allowed to cool naturally after which the pellets were measured and weighed to obtain final density and weight loss.

III. D. Hot Pressing

The hot press used in these studies is shown in Figure 1. Right cylindrical pellets were hot pressed in graphite dies fabricated from TRA-1[†] or ATJ^{*} graphite. The dies were 7.62 cm long and 7.62 cm O. D. The pellet diameters ranged from 0.95 to 2.54 cm. Several large pellets, 5.1 cm in diameter, were also fabricated. For these pellets, the die was 15.2 cm long and 12.7 cm O. D.

The die assembly is shown schematically in Figure 2. A Grafoil[‡] disk was placed over each end of the powder charge to prevent reaction between the waste and the plungers. The Grafoil disks were backed by graphite spacers of the same composition as the die body, followed by the rams. The rams were either graphite or TZM

[†]Poco Graphite, Inc., Decatur, Texas.

^{*}Union Carbide Corp., Carbon Products Div., New York, New York.

[‡]Anax Specialty Metals Corp., Cleveland, Ohio.

Figure 1. Vacuum chamber and load frame of the inductively heated hot press.

Figure 2. Schematic drawing of the combination graphite hot pressing die and induction coupled susceptor.

alloy. Two thermocouple wells were positioned diametrically opposite one another and lined with closed end alumina sleeves. One thermocouple was attached to a programmer which controlled the heating rate (15-90°C/min), maximum temperature (900-1175°C) and soak time (0 to 4 hrs). The second thermocouple was used as a backup temperature monitor. The die body also served as the susceptor for the inductively heated system.

The waste powder was loaded into the die and brought up to the pressure to be used for the run. This served to set the powder in the die. The pressure was released and the die placed in the hot press, aligned and the pressure reapplied, thereby suspending the die in the center of the induction coil. The pressure was applied through the bottom plunger and maintained throughout the run. Pressures ranged from 1.0 to 165 MPa (150 to 24,000 psi). The plunger motion was monitored to the nearest 0.0025 cm with either a dial gage or a linear variable differential transformer (LVDT).

Nearly all of the hot press runs were performed in vacuum, 10^{-3} - 10^{-4} torr, which was maintained during the entire run. Several runs were carried out in argon at atmospheric pressure. In this case the chamber was evacuated and back filled twice with argon before the final fill. A slight flow of argon was continued through the chamber and exited through a bubbler.

The hot press used to consolidate the fully radioactive waste at ORNL was built originally for fabricating ^{90}Sr titanate sources. The furnace was heated by a graphite resistance heater. An annular graphite sleeve 15.2 cm O. D. x 6.35 cm I. D. fit inside the heating element. A second annular graphite sleeve with a 1.27 cm I. D. was machined to fit inside the first for pressing the pellets. The same spacer arrangement was used between the sample and plungers as described above. The radioactive waste powder was dried at 105°C before hot pressing. The radioactive waste powder was poured into the die through a funnel. The powder was

prepressed to the maximum pressure that could be manually applied with a manipulator prior to loading into the hot press. Once the hot press was closed and sealed, a low grade vacuum was maintained in the chamber corresponding to about 66 cm of mercury. Pressure of 13.8 to 17.2 MPa (2000 - 2500 psi) was applied to the sample. The furnace conditions were inferred from the power input (amperage). Plunger motion was monitored with a machinists steel rule which had been mounted on the hot-press frame. The smallest reading was one sixty-fourth of an inch.

IV. Results and Discussion

The main criterion governing the waste consolidation effort was that the entire process be adaptable (eventually) to remote operation in a hot cell. With this in mind, the consolidation studies were approached from the simplest standpoint, both with respect to actual processes and anticipated maintenance of the equipment.

IV. A. Waste Powder Characterization

IV. A. 1. Particle size of the dried powder.

The particulate morphology has been described previously.⁽³⁾ Scanning electron micrographs of the waste powder are shown in Figure 3. The powders were suspended in epoxy and then polished so that agglomerate cross sections could be observed. The agglomerate sizes ranged from $\sim 0.5 \mu\text{m}$ to 2 mm and were found to be composed of loosely packed clusters of even smaller particles.

It was not possible to resolve the smallest particles with the SEM, consequently samples were examined with the higher resolution transmission electron microscope (TEM). The samples were prepared by the viscous shear particle dispersion technique. The resulting dispersions are shown in Figure 4. Even at these high magnifications, the individual particles are poorly resolved. The clusters

Figure 3. Scanning electron micrographs of the titanate/waste powder.

Figure 4. Transmission electron micrographs of waste powder.

appear composed of extremely small equiaxed (spherical) particles $\sim 100\text{\AA}$ in diameter. Electron diffraction patterns indicated the material was amorphous.

The dry bulk density was $\sim 0.5 \text{ gm/cm}^3$. Following drying, the powder was in the form of a friable cake. Upon blending with the zeolite and waste solids, the waste powder agglomerates became very finely divided ($\sim 5 \mu\text{m}$ diameter) such that it could be easily air floated by shaking the container. The zeolite particles did not disintegrate as easily and remained coarser.

The surface area of the titanate/waste was measured by the BET method and found to be approximately $350 \text{ m}^2/\text{g}$.

IV. A. 2. Thermogravimetric (TGA) and differential thermal analysis (DTA).

The powder mixture (titanate/waste, zeolite and waste solids) was thermally analyzed in an effort to identify the reactions which take place during consolidation. Typical TGA and DTA thermograms are shown in Figure 5. In general, the weight loss curves are rather featureless. Most of the loss occurs below 400°C followed by a continuing gradual weight loss up to 1000°C . The main weight loss is due to water followed by gases such as CO , CO_2 , NO_x due to the decomposition of residual carbonates, nitrates and possibly some hydrocarbons.

There are three features common to all of the DTA curves. Initially a large endotherm occurs between 100 and 200°C which is due to the dehydration of the powder. The endotherm also corresponds to the maximum rate of weight loss observed in the TGA studies. The loss of water within this temperature range is due to the release of water sorbed on the particle surfaces rather than structurally combined water. Even though the exchange material is a hydrated complex, $[\text{Ti}_2\text{O}_5\text{H}]_n^{-n}$, in which the hydroxyl groups are presumably coordinated in the structure, there was no sharp endotherm which can be associated with the collapse of such a structure as in the case of the dehydroxylation reactions observed in gibbsite $(\text{Al}_2(\text{OH})_3)$ and various clays.

Figure 5. Results of the thermal analysis of various constituents of the titanate wastes.

Several exotherms occur between 500 and 700°C. These are related to the development of a crystalline structure in the waste material. Heat treatments at temperatures less than 500°C yield featureless X-ray diffraction patterns which is consistent with the amorphous structure observed in the TEM studies. Samples heat-treated above 700°C yield a fairly well defined X-ray pattern.

Near 900°C, a small endotherm appears which is tentatively related to the appearance of an eutectic melt in the material. The existence of an eutectic liquid has not been confirmed by direct observation, but rather is inferred from other data such as heat capacity and sintering kinetics which will be discussed later. The liquid formation is most likely a result of the fluxing action of the alkali metal oxides.

The one feature in the differential thermograms which was not consistent from one batch of material to another was the large exotherm peaking between 300 and 400°C. The exotherm has been related to the evolution of CO₂ and CO resulting from the oxidation of small amounts of residual hydrocarbons in some samples.⁽⁴⁾ The source of the hydrocarbon has not been identified but its presence is not unexpected, as several organic solvents are used in the preparation of sodium titanate exchange material. The most baffling unanswered question is why the residual hydrocarbons are present in only some of the materials when all of the materials are prepared under virtually identical conditions.

The thermograms of the waste powders are unaffected by the zeolite or Si additions. A DTA thermogram of Zeolon 900 Na containing Cs is shown in Figure 5. In addition to exhibiting a rather nondescript thermogram, the zeolite content of the waste is only 10 wt %, consequently the affect of the zeolite on the complete waste thermogram is indiscernible. The same is true for the Si which is less than 2 wt % of the complete waste.

The TGA thermograms for the zeolite and the Si are also given in Figure 5. The zeolite exhibits a weight loss magnitude and profile very similar to the titanate waste. The Si shows a weight gain owing to oxidation starting about 900°C. However, less than 1.5 wt % of the Si was oxidized before a protecting layer of SiO_2 was formed around the particles thereby virtually eliminating any further oxidation. Similar to the DTA studies, no behavior which could be attributed to the zeolite or Si was observed in the thermogravimetric analysis of the titanate/wastes.

IV. B. Cold Pressing and Sintering

The characterization studies of the titanate/waste powder indicated that the powders should be highly active. The powder exhibits extremely small crystallite size and large surface areas. It undergoes a decomposition reaction, an ordering reaction and possibly the development of a liquid phase. All of these characteristics should enhance its sinterability.

The only identifiable crystalline phase in the waste powder using standard X-ray techniques was rutile. MacKenzie⁽⁵⁾ studied the affect of various additives and atmospheres on the sintering behavior of rutile. Two additives, Fe_2O_3 and NiO , were found to enhance sintering of rutile at 1250°C, while several others, MoO_3 , CdO and Na_2CO_3 , were found to retard densification. In view of the competing effects of these waste components as well as possibly others, no preconceived notions of the consolidation behavior of the waste were formed.

MacKenzie also showed that densification of rutile was promoted by flowing hydrogen/nitrogen and humid atmospheres and was found to be independent of oxygen partial pressure. In general, the overall enhancement of densification by these atmospheres relative to still air was minor. Furthermore, it was considered unnecessarily risky to introduce hydrogen into a hot cell environment. Consequently consolidation studies were limited to air, argon, or vacuum environments.

Initial studies were aimed at cold pressing the solidified waste into pellets followed by atmospheric sintering to form a dense compact. This approach was considered to be the simplest consistent with a low porosity product. 1100°C was considered the practical upper limit for sintering owing to excessive loss of Cs due to volatilization at higher temperatures. The results of this somewhat lengthy study are summarized in Table 2. The relative density was calculated with respect to the density of the same material which had been hot pressed. Samples were sintered in both air and inert (slowly flowing argon) atmospheres.

In general, the cold press/sintering approach was unsatisfactory. Nearly all the samples were laced with cracks and easily broken apart by hand. Pellets fired at 1000°C were slightly chalky which is undesirable. High residual porosities remained in all the sintered samples. Higher densities were obtained for samples sintered in argon than those sintered in air at the same temperature. The highest densities obtained were at 1100°C in argon. Even in this case there was still 20% residual porosity in the samples. The samples sintered in argon emerged grey (1000°) to black (1100°) in color while those sintered in air remained tan in color. The black (grey) color is due to the reduction of the rutile/complex titanate matrix and is uniform throughout the samples. Upon reheating at 1000°C in air, the reduced samples reoxidized and again assumed the tannish color.

MacKenzie⁽⁵⁾ found that argon retarded densification of TiO_2 when compared with air. No mention was made of matrix reduction effects. It appears that the presence of the simulated waste cations overrides atmosphere effects and in this case actually reverses their relative effect.

An attempt was made to improve the densification behavior by addition of minus 325 mesh (~44 μm maximum diameter) Corning #7052 borosilicate glass powder to the waste to serve as a sintering aid. The properties and composition of the 7052 glass are given in Table 3. This glass was chosen because of its low softening point

Table 2. Results of atmospheric sintering studies for titanate wastes[†]. Samples were held at temperature for 2 hours.

Temp °C	Atmosphere	Density gm/cm ³		Weight Loss %	Relative ρ^* %
		Green	Fired		
1000	air	1.59 ₄ **	1.97 ₅	14.3	47.8
1000	argon	1.52 ₁	2.25 ₀	14.3	54.4
1100	air	1.55 ₃	2.61 ₆	13.5	63.2
1100	argon	1.54 ₄	3.27 ₄	14.6	79.2

[†]Waste 33B+Z

* Relative to a density of 4.13₆ g/cm³ obtained by hot pressing the same material.

** Throughout this paper, the number in the third decimal place is included in subscript position for comparison, but it is of questionable significance.

(~700°C) and working temperature (1115°C). The glasses were added to the waste in two ways. In the first method, glass was added to the solidified waste subsequent to the exchange process. In this case, the materials were mixed with a mortar and pestle until uniform in appearance. In the second method, the glass was added to the sodium titanate exchange material during its preparation. This was accomplished by mixing the glass powder with the alkoxide-hydroxide solution prior to the hydrolysis step. Following hydrolysis, the glass appeared to be uniformly dispersed as if the glass particles acted as substrates upon which the exchange material precipitated. The advantages of this latter method of glass addition are twofold. The dispersion of the glass in the waste material is superior to that achieved by mechanical mixing and, in actual operation, the glass could be added to the exchange

material before it is introduced into the hot cell for waste processing. Consequently, the sintering aid is introduced effectively without complicating the hot cell processing scheme. 30 wt % glass was added to the samples. The wastes used in these studies did not include Si or zeolite.

Table 3. Composition and selected properties of Corning No. 7052 glass.

Composition	wt %
SiO ₂	65.0
B ₂ O ₃	18.0
Al ₂ O ₃	7.0
BaO	3.0
Li ₂ O	1.0
Na ₂ O	2.0
K ₂ O	3.0
Density (g/cm ³)	2.28
Softening Temp (°C)	710
Working Temp (°C)	1115

The waste/glass mixture was processed in the same manner as the plain wastes discussed above except that only air atmospheres were used. The results of these studies are summarized in Table 4. In general, the waste/glass samples displayed improved densification compared with their plain waste counterpart. All of the pellets formed hard, crack-free compacts during heat treatment. None of the chalking observed for the plain wastes was evident. It is also apparent from Table 4 that the pre-exchange glass additions yield materials with superior final densities compared to those resulting from the post-exchange glass additions. These results are consistent with the improved dispersion of the glass by the pre-exchange method.

Table 4. Effects of glass (Corning #7052) additions on the sintering behavior of titanate/waste forms.

	Density (gm/cm ³)		Weight Loss %	Relative %
	Green	Fired		
W ^(a)	1.28 ₄	1.64 ₄	10.1	35.4 ^(b)
W + 30 glass Post-Exchange	1.48 ₄	2.39 ₆	8.8	67.7 ^(c)
W + 30 glass Pre-Exchange	1.44 ₇	2.48 ₀	7.7	70.0

a) Material 23B, fired at 1000°C in air for 2 hrs.

b) Relative to the average density (4.64₉ gm/cm³) for the same material consolidated by hot pressing.

c) Samples containing glass additions are compared with the ideal density of 3.54₄ calculated using the hot pressed density of the plain material and the density of the glass, 2.28 gm/cm³.

While the overall improvement in densification was encouraging, it was surprising that it was not better considering that the samples were heat-treated at 1000°C which is 300°C above the softening point of the 7052 glass. Increasing the heat-treat temperature did not improve the consolidation because bloating occurred due to gases trapped in the closed pores. The net effect was a density decrease.

An explanation for the poorer-than-expected densification of the waste/glass materials may lie in the very large surface areas of the titanate waste powders. Upon heating, it appears that the glass softens before there is a significant reduction in the waste powder surface area. The softening glass is drawn into the highly porous waste particles thereby reducing the total surface energy in the system. Consequently, the potential for low porosity materials was not realized.

Even if the waste/glass materials had attained full density they would have still suffered a potentially important limitation - that of fission product concentration. An important criteria for any waste form is that it contain as high a concentration of fission products per unit volume as is consistent with yet to be established storage (disposal) parameters. The glass addition dilutes the final waste form and causes a lower maximum density ($\sim 3.54 \text{ gm/cm}^3$) compared with the plain wastes ($\sim 4.14 \text{ gm/cm}^3$). Thus, a fully dense waste with 30 wt % glass binder would contain ~ 0.6 gms of waste oxides per cm^3 compared to $\sim 0.9 \text{ gm/cm}^3$ for a fully dense complete waste. If disposal charges are to be based on volume as has been indicated, then there is considerable motivation for minimizing the amount of sintering aid in the final waste.

IV. C. Slump Tests

The high-temperature behavior of the solidified wastes was studied in slump tests which served as a semi-quantitative means of establishing refractoriness. These tests were for ranking materials and to study the effects of higher temperatures on consolidation behavior. They are not particularly useful for design purposes. The tests were performed on pellets which were fabricated by cold pressing (125 MPa) waste powder which had been calcined at 1000°C for 2 hrs. in air. The powder used for these studies did not contain Si or zeolite. The pellets were placed in a furnace and heated to the desired temperature as rapidly as possible (15 to 40 min.), held at that temperature for 15 min., then rapidly cooled (3 to 5 min.) to about 600°C , at which point they were removed from the furnace. They were then characterized by microstructural examination, density measurement, and weight loss.

Owing to the complex composition of the solidified wastes, a single well-defined melting point was not observed. Rather, the first appearance of melt was the result of complex phase interactions followed by a gradual increase in the

amount and a change in composition of liquid phase as the temperature was increased. Finally, enough melt was present so that the pellet could no longer support itself and slumping occurred. The slump condition was rather broadly interpreted to include any major deviation in sample shape. In one case, for example, the sample failed due to excessive bloating. Usually, however, the first indication that the self-support limit was being approached was the rounding of edges of the pellet.

The titanate/waste exhibited rather consistent behavior during these tests. The results are summarized in Figure 6 which includes data for a plain waste and a waste/30 wt % glass sample. Initially, a significant degree of densification took place which corresponded to a coalescence of the porosity into uniformly sized pores. As the test temperature increased, the bulk densities reached a maximum. As the temperature was increased further, the density decreased, the porosity increased and in particular, the development of isolated, large pores was observed. The reason for this behavior is that the maximum density condition in either sample corresponds to a residual porosity of ~10%, a value at which nearly all of the pores have been sealed into a closed configuration. The temperature at which this is achieved depends on the amount and viscosity of the liquid present, consequently the waste/glass sample reaches maximum density 150°C lower than the plain waste material. At higher temperatures, bloating was observed due to increased vapor pressure in the closed pores amplified by the loss of strength in the pellets as the liquid content increased.

These data show that materials with highly improved densities can be obtained by merely increasing the processing temperature, but not without penalty. The weight losses due to vaporization are significant, especially since the samples are at temperature for only 15 minutes. Keep in mind that the powders from which the pellets were prepared had previously been calcined at 1000°C. Thus the weight losses shown in Figure 6 are in addition to the 9-11% loss already incurred. It

Figure 6. Residual porosities and weight losses for titanate/waste (O) and titanate/waste + glass (□) samples heated at temperatures above the normal sintering temperature ($>1100^{\circ}\text{C}$)

appears that the upper temperature limits for these materials are controlled by their vaporization behavior rather than the slump behavior. This is particularly important for an encapsulated material where container rupture must be considered.

It was concluded that within the scope of these experiments and the temperature limitations imposed on the consolidation process, a satisfactory product could not be obtained by the cold press/sintering approach.

IV. D. Hot Pressing

Hot pressing as a means of consolidation was initiated following the rather poor results obtained by cold pressing and sintering (with or without sintering aids). The slump tests showed that a significant improvement in final density could be obtained at higher temperatures. Hot pressing could potentially circumvent the volatility problem by providing a semi-closed system, reducing the temperature required to attain a given density and by reducing the residence time at temperature. Other advantages usually associated with hot pressing^(6,7), include close dimension control and small uniform grain size. These considerations are important with regard to canning the consolidated waste for disposal and to limit the effects of possible fission product segregation on the total matrix respectively.

The titanate/wastes also fall within the broad realm of materials potentially subject to reactive hot pressing. Reactive hot pressing includes a number of modifications of ordinary hot pressing which Spriggs and Dutta⁽⁶⁾ categorize as thermochemical pressure sintering. In this process traditional diffusional and mechanical sintering mechanisms are enhanced by thermochemical processes. There are four such processes which include decomposition hot pressing, reactive hot pressing, reaction hot pressing and liquid phase hot pressing. The titanate/wastes would appear to benefit from all but the reaction hot pressing process. The breakdown of the hydrated titanate/waste with the concomitant generation of extremely fine

grained material and water vapor is typical of the decomposition process as described by Morgan.⁽⁸⁾ Reactive hot pressing⁽⁹⁻¹¹⁾ is characterized by the occurrence of a phase transformation during hot pressing. The titanate/wastes exhibit the crystallization reaction discussed earlier as well as the development of an equilibrium phase assemblage based on the numerous cations gathered during the ion exchange process. Finally the supposed appearance of a liquid phase inferred from the DTA results may be the most important single factor in determining the final density⁽¹²⁻¹⁴⁾.

McCarthy⁽¹⁵⁾ and McCarthy and Davidson⁽¹⁶⁾ have proposed hot pressing consolidation of nuclear wastes. However, their approach has been to encapsulate the waste calcine in a quartz matrix in which they found it necessary to add a low softening point borosilicate glass in order to achieve acceptable densification.

Our goal was to obtain acceptable densification of the titanate/ waste without the addition of consolidation aids. Toward this end a number of variables which were expected to affect the final product were evaluated and where appropriate, optimized. The variables were grouped into reactive hot pressing behavior, hot pressing parameters and composition variables.

IV. D. 1. Reactive hot pressing

A typical densification-temperature curve for the complete titanate/waste is shown in Figure 7. A similar curve⁽⁸⁾ for $\text{Mg}(\text{OH})_2 \rightarrow \text{MgO}$ is also included in the Figure. A marked increase in the density of the MgO is noted at the decomposition temperature $\sim 400^\circ\text{C}$ of the MgOH. In contrast, the titanate sample shows very little enhancement in densification during any of the lower temperature reactions previously discussed. Only in the region of the assumed melt formation does the densification rate increase significantly and the sample proceeds to maximum density with increasing temperature. Liquid phase hot pressing is generally recognized

Figure 7. Temperature dependence of relative density showing the typical densification behavior for the titanate/wastes (●). The error bars represent the scatter observed in five duplicate runs. Also included is the densification profile for $\text{Mg}(\text{OH})_2$ (Δ)⁽⁸⁾ which demonstrates reactive hot pressing by decomposition.

to produce high density materials at lower temperature and pressure than when there is no liquid phase present. These results show that the more commonly accepted forms of reactive hot pressing play a negligible roll in the densification of the titanate wastes.

The error bars on the titanate/waste curve in Figure 7 represent the total variation in densification behavior for five separate runs with the same material under identical conditions. In general the reproducibility is very good. As expected, the largest variations occur where densification proceeds most rapidly, e.g. $\sim 500^{\circ}\text{C}$ and above 800°C .

A typical microstructure of the hot pressed complete titanate/waste is shown in Figure 8 where (A) is the complex titanate matrix, the irregular regions (B) are the zeolite, (C) is a particle of metallic silicon, (D) is the SiO_2 layer formed during oxidation of the silicon particle and (E) is a pore. The complex titanate matrix is featureless at these magnifications and requires transmission electron microscopy for proper characterization.

IV. D. 2. Hot pressing parameters

These represent a group of variables which are inherent to the pressing process. Those expected to play major roles are heating rate, maximum temperature, pressure, residence time at maximum temperature and atmosphere. While sample sizes varied from 0.95 cm to 5.1 cm in diameter, the vast majority of the studies used 0.95 or 1.27 cm diameter samples.

IV. D. 2. a. Heating rate

The heating rate is important for production reasons since it will control to a large extent the quantity of material which can be processed in a given time. It is also a parameter which will be quite sensitive to the sample size, since, ideally, one would prefer to maintain a uniform temperature throughout the sample during processing. Figure 9 illustrates the difference in compaction behavior

Figure 8. Light optical micrograph of the microstructure of the hot pressed complete titanate/waste where (A) is the complex titanate matrix, (B) is a zeolite region, (C) is a particle of metallic silicon, (D) is the SiO_2 layer formed during oxidation of the silicon particle, and (E) is a pore.

for heating rates of 15, 35, and 90°C/minute. (The relative density has been inferred from ram motion.) The samples were 0.95 cm diameter. Below 800°C the compaction behavior is identical for the three samples. Above 800°C the curves begin to separate, the degree of compaction for the 90°C/min. heating rate lagging behind the other two. Such behavior would be expected if temperature gradients were established. However, the relative compaction behavior between the curves for the two slower heating rates are reversed from what is expected although both achieve full density at the same temperature, ~1050°C. In this case the fastest and slowest heating rate runs were carried out in the same die. For the 35°C/minute run a new die was used. Apparently, when other conditions can be considered equal, the quality of the die can affect relative compaction behavior.

The final densities of the three samples were 4.22₂, 4.22₇ and 4.16₆ g/cm³ respectively. The densities of the two samples compacted at the slower heating rates are virtually identical. The sample compacted at 90°C/minute reached maximum density that was 1.5% lower at a temperature 50°C higher (~1100°C) than the other two. In spite of the fact that all the samples were held at 1100°C for 10 minutes before cool down, the sample compacted at the highest heating rate never made up the deficit. From these data, the standard heating rate for the rest of the studies was chosen to be 35°C/minute.

The combined influence of heating rate and sample diameter on the details of the compaction behavior is also shown in Figure 9. The lower curve represents the compaction behavior for a 5.1 cm diameter sample heated at ~35°C/minute. The pressure is considerably lower (4.1 MPa) than for the other samples (75.8 MPa) in the figure, however studies have shown that this does not significantly alter the compaction behavior. This sample does not exhibit the low temperature features in the density vs time curve that are characteristic of other samples.

Figure 9. Densification profiles for heating rates of 15(▲), 35(+) and 90(●) °C/minute (0.95 cm dia samples). Included for comparison is a 5.1 cm dia sample hot pressed at a heating rate of 35°C/minute (■).

The reason is the gradient established in the sample; high temperature at the perimeter and lower temperature at the centerline of the sample. When 1100°C was reached the sample was only ~64% dense. However >99% relative density was attained within five minutes at 1100°C. No additional densification was observed after a residence time of ten minutes which suggests that isothermal conditions existed.

IV. D. 2. b. Maximum processing temperature

The processing temperature required to obtain maximum density pellets was rather easily and unambiguously determined through the use of compaction curves of the type shown in Figure 9. Once heating rate effects were eliminated, it was found that compaction of the titanate/wastes occurred as fast as the temperature was raised. Typically, maximum density was obtained between 1030 and 1070°C. As shown in Figure 9 compaction proceeds rapidly above ~800°C, then ceases rather abruptly and no reasonable increase in temperature, pressure or residence time causes any further increase in densification. This behavior was consistent among all of the various materials tested in this program. Some materials reached full density nearer 1030°C while others were closer to 1070°C, a difference which is probably not significant. This variation is apparently due to small variations in composition and also to the quality of the die, alignment in the press, etc. At very low pressures maximum density was not obtained. This is discussed in the next section.

It was observed that the maximum densification rate occurred at about 1000°C. A series of studies were initiated to determine if satisfactory densification could be obtained at maximum temperatures less than 1100°C. A pressure of 13.8 MPa (2000 psi) and temperatures of 1000, 950, and 900°C were chosen for these runs. Each sample was held at temperature for 240 minutes. The results are shown in Figure 10. The final density after each run is listed in Table 5. The densities of samples hot pressed at 1100°C for 10 minutes are included for comparison.

Table 5. Comparison of final densities of isothermally hot pressed titanate/wastes.

Material	Sample Number	Temperature °C	Final Density g/cm ³
33B+Z	218	1000	4.11 ₈
	219	1000	4.15 ₃
	225	950	4.01 ₂
	224	900	3.64 ₅
	215	1100	4.13 ₄
31C+Z	217	1000	4.17 ₂
	187*	1100	4.17 ₈

* hot pressed at 31 MPa (4500 psi).

The samples of 33B+Z hot pressed at 1000°C achieved full density within 4 to 7 minutes. No additional densification occurred over the remainder of the 240 minute residence time. In contrast, the sample of 31C+Z hot pressed at the same temperature did not achieve full density for 180 minutes, although it was >99% dense within 90 minutes. The reason for the large discrepancy is not known, but it may simply represent ordinary variations between materials.

The samples hot pressed at the lower temperatures never achieved maximum density within the allotted time. The trend is toward continued densification for longer residence times; however 240 minutes is much longer than a practical limit for an actual process.

These data suggest that acceptable consolidation can be achieved at 1000°C should the lower temperature be desirable. Nevertheless, 1100°C was chosen as the baseline processing temperature which insured that effects of individual sample variations were eliminated and that consistently uniform materials were

Figure 10. Densification behavior for isothermal conditions at temperatures below the optimum hot pressing temperature ($<1100^{\circ}\text{C}$).

turned out. 1100°C also seems to be well within acceptable limits with respect to constituent volatilization.

IV. D. 2. c. Pressure optimization

The pressure effect studies were the most important since pressure represents the processing addition which was expected to greatly improve the density of the final product over that obtained by cold pressing and atmospheric sintering. Examples of the affects of pressure, varying from 4.34 to 168 MPa (630 to 24,400 psi), on the compaction behavior of the titanate/wastes are shown in Figure 11. In general, increased pressure serves merely to adjust the compaction curves upward. No significant variation in the densification behavior is observed. More importantly, above 4.1 MPa there is no significant difference in the temperature at which maximum density is achieved nor is there any increase, as shown in Table 6, in the value of the maximum density with increasing pressure. In fact, the data indicate a slight decrease in the final density as the processing pressure is increased.

One deleterious effect caused by the high pressures was rapid degradation of the hot pressing dies. High pressure enhanced interaction between the titanate waste and the die walls. Subsequent removal of the pellet from the die caused severe scoring and abrasion of the die wall. At the highest pressures, the dies fractured during sample extraction. In general, the lower the processing pressure, the longer a die remained in service.

The processing pressure also affected the compaction ratio. The compaction ratio is a measure of the total punch travel during processing of a sample and is defined as the ratio of the height of the compacted powder charge at the onset of heating to the height of the final pellet. At the highest pressures this ratio was approximately 3 and at the lower pressure it was about 4. That is, the final

Figure 11. Effect of pressure on the titanate/waste densification profile;
 (●) 4.34 MPa; (■) 15.2 MPa; (▲) 86.9 MPa; (◆) 168 MPa.

pellet was about one fourth the thickness of the prepressed initial powder charge. The differences are not large, but may need to be considered should the process be scaled up.

Table 6. Comparison of final density with applied pressure during hot pressing. Heating rate = 35°C/min.

Material	Sample No.	Pressure MPa (psi)	Final density g/cm ³	T °C
31C+Z	187	33.1 (4,800)	4.17 ₈	1060
	185	79.31 (11,500)	4.22 ₇	1050
	184	168 (24,400)	4.15 ₂	1050
33B+Z	222	4.34 (630)	4.14 ₇	1100 + 1 minute
	215	15.2 (2,200)	4.13 ₄	1060
	214	86.9 (12,600)	4.12 ₈	1050

It was noted in Table 6 that at 4.34 MPa, full density was not obtained until after one minute at 1100°C. The 1100°C isothermal densification behavior at lower pressures is shown in Figure 12. The compaction during heating proceeded in a manner similar to that shown in previous figures. However when 1100°C was reached, the samples had not reached maximum density. Each sample was held at 1100°C for ten minutes or until no further densification was observed for a period of five minutes. The final density of each sample is listed in Table 7. The final densities of the samples hot pressed at pressures ≥ 2.76 MPa (≥ 400 psi) were all within 1% of the highest density obtained for this material. This is well within the estimated experimental error of these studies. Furthermore the maximum density was achieved within a short time, approximately ten minutes, which is within any practical time frame which would be considered for a full scale process. At hot pressing pressures less than 2.76 MPa, the end point densities were unacceptably low.

Table 7. End point densities of samples hot pressed at low pressures. Heating rate, 35°C/minute; $T_{\text{isothermal}} = 1100^{\circ}\text{C}$; Material, 34B+Z

Sample No.	Pressure MPa (psi)	Final Density g/cm^3	Residence time @ 1100°C minutes
226	13.8 (2000)	4.16 ₃	10
227	3.79 (550)	4.15 ₁	10
231	3.52 (510)	4.12 ₁	15
230	2.76 (400)	4.12 ₆	15
229	2.07 (300)	4.01 ₆	25
228	1.03 (150)	3.85 ₃	30

IV. D. 2. d. Residence time at T_{max} .

The residence time at the maximum processing temperature must be considered with respect to ultimate production rate, sample size, heating rate, component volatilization and processing pressure. A minimum residence time insures maximum production rate and minimum constituent loss due to volatilization. However, as has been discussed before, the residence time must be sufficiently long to insure isothermal conditions and sample uniformity for the combination of heating rate, sample size and processing pressure. The final compromise between these parameters must be established along with the ultimate process configuration. The current studies have described the range of behavior that can be expected by varying the various hot pressing parameters and should make the final optimization studies relatively simple to design.

Figure 12. Densification behavior for 1100°C isothermal conditions at pressures less than 4.34 MPa (630 psi).

IV. D. 2. e. Atmosphere

Most of the hot pressing runs were performed in vacuum. This was primarily because of the ease of operating in this mode and also to facilitate removal of the rather large quantities of gas evolved from the samples during heating. Two runs were carried out to evaluate the effect of hot pressing in an inert atmosphere (argon). The samples were composed of the same titanate/waste, but 10 wt % zeolite was added to one. The results of these runs compared with those on the same materials vacuum hot pressed are given in Table 8. The final densities for a given starting material are virtually the same for either argon or vacuum. Consequently, vacuum was chosen as the baseline operating condition since it was the easiest to maintain.

Table 8. Comparison of the final densities of pellets hot pressed in vacuum and argon. $T_{\max}$, 1100°C; Pressure, 69.0 MPa (10,000 psi).

Material	Sample No.	Atmosphere	Final Density g/cm ³
28C(CB)	137	argon	4.49 ₆
	126	vacuum	4.50 ₃
	129	vacuum	4.50 ₅
	134	vacuum	4.48 ₄
28C+Z	142	argon	4.14 ₇
	127	vacuum	4.22 ₇
	131	vacuum	4.21 ₀
	136	vacuum	4.13 ₀

IV. D. 3. Compositional variations in the titanate/waste

The complete waste form, as described earlier, is a complex mixture of decidedly dissimilar materials including the cation loaded titanate exchange material, partially cesium loaded aluminosilicate and metallic silicon. A series of studies were undertaken to determine the affect of various compositional variations on the consolidation behavior.

IV. D. 3. a. Batch behavior

A large number of different batches were prepared during the program to study a host of different variables. Several pellets were hot pressed from every batch which allowed comparison of the densification behavior for a wide range in preparatory conditions. While small differences in the magnitudes of the characteristic features of the densification plots were noted from time to time, no significant variations in the densification behavior were observed.

There were distinct differences in the final densities of the hot pressed materials which could be related to various compositional variables discussed below.

IV. D. 3. b. Residual sodium content

Usually the ion exchange experiments were designed such that the sodium titanate exchange material was loaded to nearly 100% of its capacity. In reality, complete exchange was seldom achieved which resulted in the retention of small amounts of sodium in the exchanged material. It was found that increasing sodium contents resulted in decreasing density of hot pressed pellets as shown in Figure 13. Note that these results are for pure titanate/wastes with no silicon or zeolite added. These data represent results of hot pressing a variety of titanate wastes including materials prepared by both batch equilibration and the column exchange method. The error bars on various data points represent the extremes

in density when more than one pellet was fabricated. In general, the column materials tend toward lower densities for a given sodium content than the batch materials. This is probably because the column process causes fractionation of the waste during the exchange, presumably limiting the residual sodium to the bottom portion of the column. The waste must be blended prior to consolidation in order to achieve a homogeneous material, but, apparently, the blended material is not as uniform as that obtained by the batch process; consequently, the fluxing action obtained from the alkalis and other complex eutectic reactions is not as efficient at promoting consolidation. The overall density decrease is due to the lower concentration of the heavier polyvalent waste cations.

In an actual process it is not practical to attempt to load the sodium titanate material in a column configuration to its theoretical limit because of the increased risk of fission product breakthrough. One reason breakthrough is likely near theoretical loadings is because it is difficult to determine the actual cation concentration in the waste stream and relatively large variations are expected. Consequently, it is expected that a column would only be loaded to 90% of capacity corresponding to a 10% excess of the sodium titanate exchange material or, expressed another way, an additional 1.2% of sodium.

The affects of the increased sodium content on the consolidation behavior were studied by comparing the compaction curves of an exchanged material with one to which 10% excess unreacted exchanger had been added. The waste materials contained silicon and zeolite. The compaction curves were virtually identical. The only differences in the behavior of the materials was in the final densities, 4.20_6 g/cm^3 for the standard waste vs 4.03_8 g/cm^3 for the standard waste with 10% excess unreacted exchange material. It is apparent from these data that reasonable variations in the ion-exchange efficiency do not affect the consolidation

IV. D. 3. c. Silicon and zeolite content

Neither the silicon nor zeolite contents were found to affect the densification behavior. Limited to a maximum concentration of 2 wt %, the silicon would not be expected to cause much change in a material as complex as the titanate wastes. The zeolite, on the other hand, was 10 wt % of the final composition. While no change in the densification behavior was observed, a significant decrease in the final density occurred for zeolite containing waste compared with plain waste, 4.19 vs 4.44 g/cm³ respectively, owing to the lower density of the zeolite. In either case, the respective samples were >99% maximum density. Consequently the only drawback of the zeolite (and silicon) additions is the increase in volume associated with the incorporation of a less dense material into the waste form.

IV. D. 3. d. Consolidation aids - glass additions

In view of the improved densification obtained in the cold press/sintering studies when glass was added to the waste form, a similar series of studies were conducted for the hot pressing technique. Note that the glass was not intended as a host, but merely as a consolidation aid. The same glass was used in these studies as was used before (Table 3). For these studies it was added subsequent to the exchange process and mixed with a mortar and pestle; however, the pre-exchange addition discussed previously is equally applicable. The results for various glass additions are shown in Figure 14. The general densification behavior is the same for all the glass additions. The final processing temperature decreased from 1000, 950 to 900°C as the glass content increased from 5, 15 to 30 wt % respectively. While significant reductions in processing temperatures were obtained the same penalty is realized here as before, namely a volume dilution of the waste cations leading to higher total waste volumes and consequent higher custodial costs.

Figure 14. Densification profiles for titanate/wastes containing 5(▲), 15(●) and 30(■) wt % additions of Corning No. 7052 glass.

IV. D. 3. e. Precalcined waste

The main thrust of the program was to consolidate the titanate/waste after drying without any intermediate processing. As noted earlier, the dried (105°C) waste loses 10-13 wt % during heat treatment to 1100°C and >90% of that loss occurs before 400°C. These losses are not minor in terms of the volume of gas generated. During hot pressing of the 5.1 cm diameter pellets (initial charge ~100 gm) the rate of volatile evolution from the sample exceeded the pumping capacity of the vacuum system. Consequently, in an actual process, the heating rate over the critical temperature range would have to be reduced or the material would require precalcining to remove the majority of the volatiles prior to hot pressing.

To determine the affects of such a heat treatment on the consolidation behavior, a sample of titanate/waste was calcined at 500°C in air for one hour and hot pressed in the usual manner. The densification behavior is shown in Figure 15. Curves for the non-heat-treated waste and for waste containing 5 wt % glass are included for comparison. The same waste form and hot pressing conditions were used in each case.

The precalcined titanate/waste exhibits no increase in density at temperatures below the calcining temperature. Above the calcining temperature densification proceeds in the characteristic manner. By 850°C, the densification curves for the standard and precalcined wastes are essentially identical as are the final densities, 4.18 vs 4.21 g/cm³. The final product is apparently unaffected by precalcination and as long as the calcination temperature is chosen judiciously there is little chance that there will be any loss of waste cations by volatilization. An advantage is that by removing all of the volatiles below the calcination temperature, the hot pressing dies would not have to cool to room temperature prior to loading, thereby reducing the total processing time.

Figure 15. Comparison of the densification profile for precalcined (500°C in air for 1 hour) titanate/waste (●) with normally dried titanate/waste (□) and titanate/waste + 5 wt % glass (Δ).

IV. D. 3. f. Semicontinuous hot pressing

From a practical standpoint, the pellet length is limited by the condition that the aspect ratio, l/d , is ≤ 1 where l and d are the pellet length and diameter. Consequently the maximum pellet volume and, hence, the production rate is established by the diameter of the pellets. A means by which the production rate could be increased is with semicontinuous hot pressing.⁽¹⁷⁻¹⁸⁾

In this method, the hot pressed pellet is not ejected from the die at the end of a cycle, but rather is displaced a specified distance and then serves as the base upon which the next pellet is pressed. The procedure is repeated resulting in the formation of a rod of material.

The applicability of this technique was evaluated for the titanate/wastes using the standard hot pressing conditions. Three successive pressings were carried out, one upon another. The final product is shown in Figure 16. The resulting pellet was mechanically sound with the individual pellets bonded tightly together. The interpellet boundary was defined by a line of pores as shown in the micrograph in Figure 17. Otherwise, the microstructures were identical from one pressing to another. Semicontinuous hot pressing appears to be entirely feasible for the titanate/waste materials. No technical factor limits the number of successive loadings. In addition to increasing production rate, the resulting cylinders would simplify handling and loading the consolidated waste into the canisters.

IV. D. 4. The mechanism(s) of densification.

It was shown that reactive hot-pressing was not a significant factor in the densification behavior of the titanate/wastes. The chemical and physical complexity of the titanate/wastes preclude casual identification of a densification mechanism(s). However, the presumed appearance of an eutectic melt suggests that liquid phase sintering processes may describe the densification behavior.

1 cm

Figure 16. Pellet formed by three successive simicontinuous hot pressings compared with a pellet formed by the usual single hot pressing.

Figure 17. Light optical micrographs showing the interpellet boundary for a semicontinuous hot pressed sample.

Lenal, et. al.^(19,20) and Gurland and Norton⁽²¹⁾ described the three stages of liquid phase sintering. They are in chronological order, the particle rearrangement stage, the solution-precipitation stage and the final stage. The stages are shown graphically in Figure 18. Kingery⁽²²⁾ derived expressions of the form

$$\frac{\Delta L}{L_0} \propto t^m \quad (1)$$

where $\Delta L/L_0$ is the linear shrinkage and m has a value less than one, to describe the sintering kinetics during the solution-precipitation stage. The value of m depends on the rate limiting step and the powder morphology in the following manner; $m = 1/5$ corresponds to a process controlled by diffusion-through the liquid phase and angular particles in edge contact only; $m = 1/3$ corresponds to the diffusion controlled process for spherical or equiaxed particles or, to a phase boundary dissolution controlled reaction and angular particles; $m = 1/2$ corresponds to the phase boundary dissolution controlled process for spherical or equiaxed particles. Kingery, Woulbroun and Charvat⁽¹²⁾ expanded the expressions to include the pressure applied during hot pressing. Application of pressure resulted in no change in the time dependence of the various processes.

Prill, Hayden and Brophy⁽²³⁾ showed that errors in the interpretation of the rate controlling process determined by using Kingery's⁽²²⁾ method occurred when the contributions of the preceeding rearrangement stage were not accounted for. They described a means by which the rearrangement contributions could be removed from the data so that the solution-precipitation processes could be unambiguously analyzed.

Prior to Kingery's work, densification of powders by hot-pressing had been described by a viscous flow process. The rate equation for densification by

Figure 18. Schematic diagram of the three stages of liquid-phase sintering.

plastic flow during hot pressing was derived by Murray, Livey and Williams⁽²⁴⁾ as

$$\frac{d\rho}{dt} = \frac{3P}{4\eta} (1 - \rho) \quad (2)$$

where P is the applied pressure, t is time, η is the equivalent composite viscosity and ρ is the relative density of the compact. Upon integration, the equation becomes

$$\ln (1 - \rho) = -\frac{3P}{4\eta} t + c \quad (3)$$

The densification behavior of samples hot-pressed at four different pressures is plotted as the logarithm of linear shrinkage ($\Delta l/l_0$) vs logarithm of time in Figure 19. The heating rate was the same for each sample and the isothermal temperature was 1100°C. Usually l_0 is the initial length of the unsintered compact. In this case, pressure was applied at room temperature and maintained during the entire heat treat cycle, consequently, the l_0 refers to the length of the pellet when the isothermal temperature was attained. The lower curve in each graph (Fig. 19) represents the data after correction by subtracting, according to the method of Prill, et. al.⁽²³⁾, the best estimates of the length (l_r) and time (t_r) at the end of the rearrangement stage. The slope (time exponent) is next to each straight line segment of the curves.

Often, there is not a clear cut distinction between the rearrangement and solution-precipitation stages of densification. This is not totally unexpected since both stages undoubtedly overlap and, at best, we hope to identify time periods in which one of the processes dominates.

For the samples hot pressed at 1.03, 2.07 and 2.76 MPa, the time exponent associated with the reduced data (0.54, 0.50, 0.51 respectively) is in good agreement with a dissolution controlled process. The best agreement with the

Figure 19. Corrected and uncorrected isothermal time dependence of the linear shrinkage at pressures less than 4.34 MPa according to the method of Kingery⁽²²⁾ and Prill et. al.⁽²³⁾

same process for the sample hot pressed at 3.52 MPa occurs with the uncorrected data (time exponent = 0.55).

These data show that increasing the pressure does not affect the densification mechanism, but rather, it controls the time at which one mechanism begins to dominate. For example, in these studies, the times associated with the end of the rearrangement stage (t_r) decreased in the order 4, 4, 3 and 0 minutes as the pressure increased from 1.03 to 2.07 to 2.76 to 3.52 MPa respectively. For the sample hot pressed at 3.52 MPa, the particle rearrangement process proceeded to completion as rapidly as the temperature was increased to the isothermal value. At pressures greater than 3.52 MPa, densification occurred so rapidly (≤ 3 minutes) that no agreement with any of the model processes was possible. This is consistent with earlier observations that the samples densified as rapidly as the temperature was increased.

In two cases (Fig. 19, 1.03 and 3.52 MPa), we observed a change in slope which signals the onset of final stage sintering processes. The slopes (time exponents) of these lines are in close agreement with each other and with $n = 1/3$ which is indicative of a process controlled by diffusion through the liquid phase. However, that process is not generally considered applicable during the final stage. Consequently, the significance of the time exponents is not known.

Kingery⁽²²⁾ described the rearrangement stage as a viscous flow process. The densification data for the first ten minutes of the isothermal heat treatment were plotted in Figure 20 according to the theory of Murray, et. al.⁽²⁴⁾. The slopes of the lines were determined from a linear regression analysis of the data. The corresponding composite viscosities are given in Figure 21. The agreement among the composite viscosities calculated during the rearrangement stage is very good. For pressures greater than 2.07 MPa the linear fit

of the data extends over the entire densification range in spite of the detailed behavior observed in Figure 19. Apparently when the data are expressed according to the viscous flow theory the results are relatively insensitive to the differences between the rearrangement, solution-precipitation and final stage sintering processes.

Data from a sample hot pressed at 3.79 MPa (densification time, three minutes) are included in Figure 20. Its composite viscosity is in good agreement with the others in spite of the very short time to densification. This result suggests that at higher pressures, rearrangement (viscous flow) dominates the densification process.

A similar series of experiments were carried out for samples hot pressed under isobaric conditions but different temperatures. The data are plotted as logarithm shrinkage vs logarithm time for temperatures of 900, 950 and 1000°C in Figure 22. Consistent with the isothermal series, the data in Figure 22 exhibit time exponents very close to $1/2$. When a final stage region is present (900 and 1000°C) the time exponent again approximates $1/3$.

The two sets of data at 1000°C show the range of densification behavior observed. In spite of the large differences in time (9 minutes vs 180 minutes), both samples sintered to greater than 99% relative density and both displayed the same dissolution controlled densification process.

The viscous flow analysis is shown in Figure 23. The calculated composite viscosities are given in Table 9. The viscosities decrease with increasing temperature in accordance with expected behavior since the amount of liquid increases with temperature. There is good agreement between the viscosity values of the two samples hot pressed at 1000°C.

The results show that densification of the titanate/wastes occurs by a complex series of processes involving a liquid phase. The initial and largest

Figure 20. Isothermal time dependence of porosity at pressures less than 4.34 MPa according to the method of Murrey, et. al.⁽²⁴⁾

Figure 21. Graph of the composite viscosities for isothermal conditions showing virtually constant values for varying pressure.

Figure 22. Corrected and uncorrected isothermal time dependence of the linear shrinkage at various temperatures according to the method of Kinsary⁽²²⁾ and Prill, et. al.⁽²³⁾

Figure 23. Isothermal time dependence of porosity at various temperatures according to the method of Murray, et. al. (24)

Table 9. Composite viscosities of titanate/wastes as a function of temperature.

Temperature °C	Composite Viscosity poise
900	2.9×10^9
950	2.7×10^9
1000	$2.1 - 5.0 \times 10^8$

fraction of densification is due to particle rearrangement which can be characterized by viscous flow. While the characteristic composite viscosity is independent of the pressure, higher pressure increases the densification rate and shortens the time interval over which the rearrangement stage dominates. The rearrangement stage is followed by a solution-precipitation stage which is controlled by a phase boundary dissolution process. A final stage sintering region is observed in some cases. However, for the optimized hot pressing conditions established for production of full density titanate/wastes, rearrangement in the presence of a liquid phase is the dominant process.

IV. E. Hot-Pressing High Level, Mixed Fission Product Titanate Waste.

A series of experiments were designed to determine the viability of hot pressing a fully radioactive titanate/waste (radwaste) at Oak Ridge National Labs (ORNL). As described previously, the hot press used for these studies was not designed for research applications. The most serious handicap was the lack of an accurate means of temperature measurement. Originally the hot press was fitted with a glass covered sight port for optical temperature measurements. However, the cover glass broke during several trial runs, consequently, the port was blanked off and the temperature was inferred by the amperage supplied to the heating element.

Only a very rough vacuum was obtainable, 66 cm of mercury as compared to 10^{-4} Torr obtained routinely in the laboratory. Furthermore, the hot press was isolated from the vacuum pump during a run rather than being continuously evacuated as in the laboratory experiments. The ram motion resolution was limited to about 0.4 mm compared with the $25\text{ }\mu\text{m}$ laboratory resolution. And finally, owing to the large thermal mass of the hot press the samples were held at temperature for 1 to 1.5 hours to insure isothermal conditions. In spite of the apparent limitations of the hot press, once a procedure was established the mechanics of every run were trouble free.

The procedures developed with the simulated titanate/waste were adhered to as closely as possible. Prior to the radwaste tests, a series of runs with a well characterized simulated titanate/waste were carried out to check the operation of the hot press and to check the modifications in procedure dictated by the hot press design. These runs were carried out in a laboratory press and in the remotely operated hot press. After some initial difficulties (such as the sight glass breaking), good reproducibility of the previously determined density was obtained. The average value of the density of pellets formed in the remotely operated hot press was 2% lower than the laboratory value.

A total of six 0.5 inch diameter radwaste pellets were remotely hot pressed in the hot cell. The hot pressing pressure (uncalibrated) was 13.8-20.7 MPa (2000-3000 psi). The results are given in Table 10. The densities were measured twice by independent technicians. The first density was measured when the pellet was removed from the die in the Fission Product Development Laboratory (FPDL) where the remotely operated hot press was located. Later, the pellets were transferred to the metallographic (M) facility where they were measured a second time with more accurate equipment. A reference density of 4.14 g/cm^3 was obtained in

Table 10. Densities of high level mixed fission product titanate waste remotely hot pressed at Oak Ridge National Laboratory.

Sample No.	FPDL g/cm	M g/cm
LC2-1	3.89	---
repress	3.86	
LC2-2	3.78	
repress	3.93	3.81
LC2-3	3.95	3.82
LC2-4	3.72	
repress	3.94	3.97
LC2-5	3.92	3.86
LC2-6	3.88	3.81

our lab for a simulated titanate/waste prepared with the same sodium "titanate" exchange material used at ORNL to prepare the high level radwaste. The densities of the radwaste pellets are considerably below the reference value and the first two pellets were replaced in the die and pressed a second time in an attempt to improve their densities. However, it became apparent that the achievable density of the radwaste pellets was well below the reference value and repressing was discontinued except for sample LC2-4 where the density after the initial pressing was undisputably low.

The lower densities of the radwaste pellets could be due to several reasons. The composition of the high level liquid waste (HLLW) stream was virtually unknown, consequently the radwaste composition is unknown which could account for the lower density especially if there is a significant deviation from the simulant composition. In addition, the exchange material was not loaded to capacity in order to prevent breakthrough. Owing to the uncertainties in the HLLW composition, a larger excess of unexchanged material may be present than expected, resulting in a decrease in the final density. Finally, conversations with ORNL staff indicate that for no apparent reason, radioactive materials are generally less dense than their stable counterparts formed under identical conditions.

A typical microstructure for the radwaste is shown in Figure 24. The microstructure is considerably coarser than that obtained for laboratory samples (Figure 8) and most of the metallic silicon appears to have been consumed during processing. Both effects could be due to the long soak times but weight losses during re-hot pressing indicate that higher than expected temperatures may also be involved. In an attempt to reproduce the titanate/radwaste microstructure, a simulated titanate/waste was hot pressed in the laboratory at 1175°C and held at temperature for one hour. The resulting microstructure is included in Figure 24 and is quite similar to the radwaste in the lack of metallic silicon particles. The grain structure is not as well defined but is considerably coarser than typical lab samples. The difference could be due to the additional time the radwaste was at temperature or, more likely, the radwaste was processed at a temperature even higher than 1175°C.

The ORNL experiments indicate that remote hot pressing of polycrystalline radwastes can be performed on a routine basis. The limiting factor in these experiments was the response time of a hot press that was not designed for these types of studies. In fact, all of the conditions under which these experiments were

Figure 24. Light optical micrographs of (A) titanate/radwaste hot pressed at ORNL and (B) simulated titanate/waste hot pressed at 1175°C for one hour.

conducted were more severe than required by the titanate/radwaste. With a hot press designed specifically for this process along with the associated support equipment it appears that remote hot pressing could be performed on a production basis.

V. Conclusions

1. Hot pressing experiments conducted under very unfavorable conditions using high level mixed fission product titanate/wastes demonstrated the ease and simplicity in which such a process can be executed remotely in a hot cell.
2. The optimum hot pressing conditions for the titanate/wastes are very mild, 6.9 MPa (1000 psi), 1100°C and vacuum. No improvement in the final product is realized by increasing temperature or pressure. The vacuum can be replaced by an inert atmosphere if necessary without affecting the final product. Heating rate and residence time must be determined for the full scale process.
3. Densification during hot pressing occurs by liquid phase sintering. Viscous flow dominates the initial stage, followed by a solution-precipitation process controlled by a phase boundary dissolution reaction. In some cases, an unidentified final densification stage was derived.
4. Densification behavior is relatively insensitive to compositional variations which is desirable since uncontrollable variations in the high level liquid waste stream are expected. However, the final density of the waste is directly dependent on the composition.
5. Significant decreases in the hot pressing temperature - from 1100°C to as low as 900°C - can be realized if glass is added to the waste as a consolidation aid. However, such gains must be weighed against the decrease in volumetric fission product concentration and thermal stability.

6. Semicontinuous hot pressing combined with precalcining the waste appears to be a simple means of increasing the production rate and minimizing the amount of pellet handling prior to encapsulation.
7. Within the scope of these studies, satisfactory consolidation could not be obtained by cold pressing and sintering.

VI. References

1. R. W. Lynch, R. G. Dosch, B. T. Kenna, J. F. Johnstone, E. J. Nowak, Proceedings of the IAEA Symposium on the Management of Radioactive Waste, Vienna, Publication No. IAEA-SM-207/75, p. 361 (1976).
2. W. A. Ross, Pacific Northwest Laboratories, Private Communication.
3. G. T. Noles, Sandia Solidification Process Cumulative Report, SAND-76-0105, p. III. A. 1. C-1 (January, 1976).
4. R. G. Dosch, *ibid*, p. III. D. 1-10.
5. K. J. D. MacKenzie, *Trans. J. Br. Ceram. Soc.*, 74, 127 (1975).
6. R. M. Spriggs and S. K. Dutta, *Sci. of Sintering*, 6, 1, (1974).
7. A. C. D. Chaklader, *J. Can. Ceram. Soc.*, 40, 19 (1971).
8. P. E. D. Morgan, Ultrafine-Grain Ceramics, Edited by J. J. Burke, N. L. Reed, and V. Weiss, Syracuse University Press, Syracuse, New York, p. 251 (1970).
9. A. C. D. Chaklader, *Am. Ceram. Soc. Bull.*, 44, 301 (1965).
10. A. C. D. Chaklader, *Nature*, 206, 392 (1965).
11. A. C. D. Chaklader and V. T. Baker, *Am. Ceram. Soc. Bull.*, 44, 259 (1965).
12. W. D. Kingery, J. M. Woulbroun and F. R. Charvant, *J. Am. Ceram. Soc.*, 46, 391 (1963).
13. T. D. McGee, *ibid.*, 49, 90 (1966).
14. S. K. Guha and A. C. D. Chaklader, *ibid.*, 58, 214 (1975).

15. G. J. McCarthy, J. Matl. Sci., 8, 1358 (1973).
16. G. J. McCarthy and M. T. Davidson, Am. Ceram. Soc. Bull., 55, 190 (1976).
17. W. W. Rhodes and J. Thomson, Jr., *ibid.*, 55, 308 (1976).
18. G. J. Oudemans, Philips Tech. Rev., 29, 45 (1968).
19. F. V. Lenel, AIME Trans., 175, 878 (1948).
20. H. S. Cannon and F. V. Lenel, Plansee Proceedings 1952, Edited by P. Bevesovsky, Metalwerk Plansee, Reuthe, p. 106 (1953).
21. J. Gurland and J. T. Norton, AIME Trans., 194, 1051 (1952).
22. W. D. Kingery, J. Appl. Phys., 39, 301 (1959).
23. A. L. Prill, H. W. Hayden and J. H. Brophy, AIME Trans., 233, 960 (1965).
24. P. Murray, D. T. Livey and J. Williams, Ceramic Fabrication Processes, Edited by W. D. Kingery, Technology Press of Massachusetts Institute of Technology and John Wiley and Sons, Inc., New York, p. 147 (1958).