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Summary:

Powder technology is used to immobilize nuclear waste (MLW,HLW) in sintered glass. By in-can hot pressing (temperature <1000 K; pressure <1 MPa; heating rate ∿ 100 K/h; cooling rate 5 K/h) glass products containing simulated HLW and MLW (20 wt.%) have been produced in stackable steel cans (< 300 mm diameter). High densities (∿ 93% TD), bulk integrities and homogeneities for the waste element distributions are realized. The advantages of powder technology as, for example: (i) no segregation due to solid state vitrification, (ii) low evaporation losses and no compatibility problems due to low densification temperatures (sinter temperature ∿ 0.6 softening temperature of glass), (iii) production in easily arrangeable and interchangeable stacking units at modest pressures adequate especially for the use in hot cells under remote handling conditions, all together hold for the process which therefore is appropriated for high level waste, medium level waste and - as expected now - for HLW/MLW common vitrification as well.

Zusammenfassung

Pulvertechnologische Verglasung von mittel- und hochradioaktivem, nuklearem Abfall durch Drucksintern

Beschrieben wird die pulvertechnologische Konditionierung von nuklearem Abfall (MLW, HLW) in Sinterglas durch Drucksintern (Temperatur <1000 K; Druck <1MPa; Erhitzungsgeschwindigkeit ~100 K/h; Abkühlungsgeschwindigkeit 5 K/h; Abfallanteil 20 Gew.%; Gebindedurchmesser <300 mm). Die Verwendung stapelbarer Stahlhüllen mit - wahlweise in wechselnder Folge - mittel- oder hochaktivem Abfall eröffnet die Möglichkeit, die Wärmeproduktion eines Gebindes zu variieren. Hochdichte (~93% TD), rißfreie und - bezüglich der Verteilung der Elemente des nuklearen Abfalls - homogene Produkte werden hergestellt. Die vorteilhaften Betriebsbedingungen der pulvertechnologischen Methode

- schlossen Segregationen aus, da kein flüssiger Aggregatzustand eintritt;
- vermieden hohe Abdampfverluste (Sekundärabfall) und Verträglichkeitsprobleme, da die Sintertemperatur bei Zweidrittel der Erweichungstemperatur des Glases liegt;
- ermöglichten eine Produktion von leicht handhab- und austauschbaren, stapelfähigen Einheiten bei niedrigen Drücken, wie sie für den Betrieb in heißen Zellen besonders geeignet erscheint.

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POWDER TECHNOLOGICAL VITRIFICATION OF MEDIUM-LEVEL WASTE BY IN-CAN HOT PRESSING *

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Powder technology is used to immobilize medium level nuclear waste (MLW) in sintered glass. By in-can hot pressing (temperature 923 K; pressure 0.4 MPa; heating rate ≈100 K/h; cooling rate 5 K/h) glass products containing simulated MLW (20 wt%) have been produced in stackable steel cans (⩽ 300 mm diameter). High densities (≈ 93% TD), bulk integrities and homogeneities for the waste element distributions are realized. The advantages of powder technology as, for example: (i) no segregation due to solid state vitrification, (ii) low evaporation losses and no compatibility problems due to low densification temperatures (sinter temperature ≈ 0.6 softening temperature of glass), (iii) production in easily arrangable and interchangeable stacking units at modest pressures adequate especially for the use in hot cells under remote handling conditions, all together hold for the process which therefore is appropriated for high level waste (HLW), medium level waste and HLW/MLW common vitrification as well.

1. Introduction

As recently demonstrated, powder technology has a significant number of advantages compared with melting technology in nuclear waster conditioning [1,2]. Specially, in-can hot pressing was successfully applied for the immobilization of—simulated—high-level waste in sintered borosilicate glass [3,4]. Endeavouring common vitrification of high level (HLW) and medium level waste (MLW) as well by powder technology as a final objective, the next experimental step had to assure that also medium level waste may be immobilized in sintered glass by in-can hot pressing. This is the content of the present report.

2. Materials

The glass frit used in this study was slightly modified compared with the one used in former investigations [4] in order to demonstrate:

- that powder technology as a procedure is not very sensitive to the type of glass and
- that the glass type may be adapted to special waste forms and problems.

The powder characteristics is given in table 1, where the adaptation to MLW from a chemical point of view mainly consists in its ability to transform the

Table 1
Lead–borosilicate glass BBS-10 (producer BATELLE Frankfurt; supplier DEGUSSA Hanau) used for solidification of medium-level waste

Composition (wt%)		Al_2O_3	6.7
		B_2O_3	12.0
		CaO	1.8
		MgO	0.9
		PbO	36.0
		SiO_2	42.0
Transformation temperature [K]			793
Softening point [K]			1023
Softening interval [K]			160
Density (g/cm^3)			3.1
Particle size distribution (wt.%)	> 100	mesh	5.3
	63–100	mesh	21.5
	< 63	mesh	73.2

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* Dedicated to Prof. F. Thümmler on the occasion of his 60th birthday.

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Table 2
Composition of the simulated medium-level waste (MLW)

	CeO_2 [1]	MoO_3	Ni [2]	Sb_2O_3	"SS"	Zry
Composition (g/t heavy metal)	138	620	28	20	104	856
Particle size distribution (mesh)	32–6	32–63	≈10	32–100	≈150	⩽ 4 mm see text

[1] substitutes UO_2, PuO_2
[2] substitutes Inconel

Table 3
Metal chip characterization after cladding tube chopping (unpublished results by C. Bauer, Kernforschungszentrum Karlsruhe)

Sieve fraction K (mm)	Metal chip fractions (g)				Cumulated metal chip fractions (g)		
	Zircaloy	Inconel	Steel	Total	Total	Per cut	Per ton UO_2
$K > 5$	n.d. *	376	n.d. *	740	905.5	75.5	7858.6
$5 > K > 4$	31.2	4.6	6.3	42.1	165.5	13.8	447.1
$4 > K > 3.15$	36.5	6.2	2.4	45.1	123.4	10.3	479.0
$3.15 > K > 2$	40.3	5.0	2.0	47.3	78.3	6.5	502.3
$2 > K > 1$	20.9	0.5	0.2	21.6	31.0	2.6	229.4
$K < 1$	n.d. *	n.d. *	0.5	9.4	9.4	0.8	99.8

* n.d. = not determined.

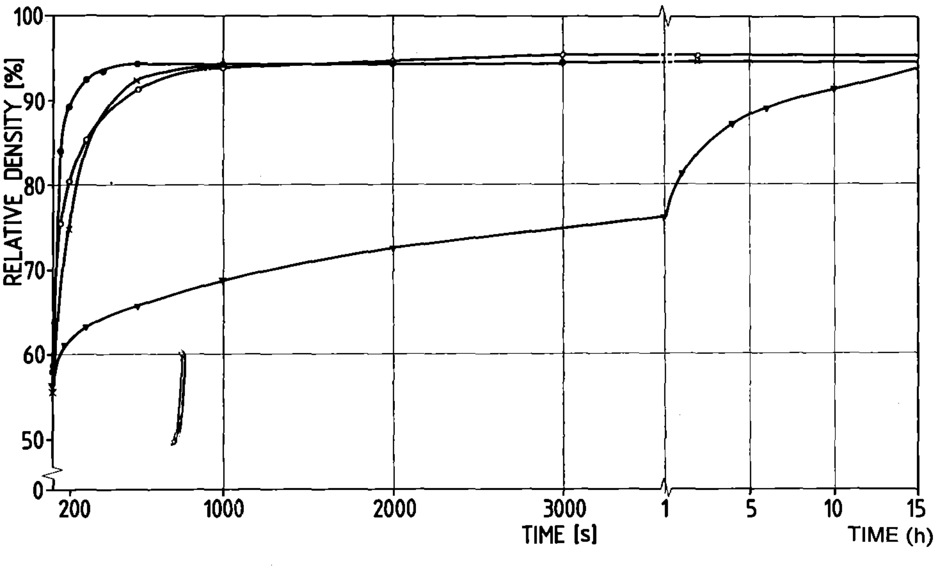

Fig. 1. Relative density-time plot for uniaxial pressure sintering (sintering temperature 923 K; pressure: ▼ 0.2; × 0.4; ● 0.7; ○ 1 MPa).

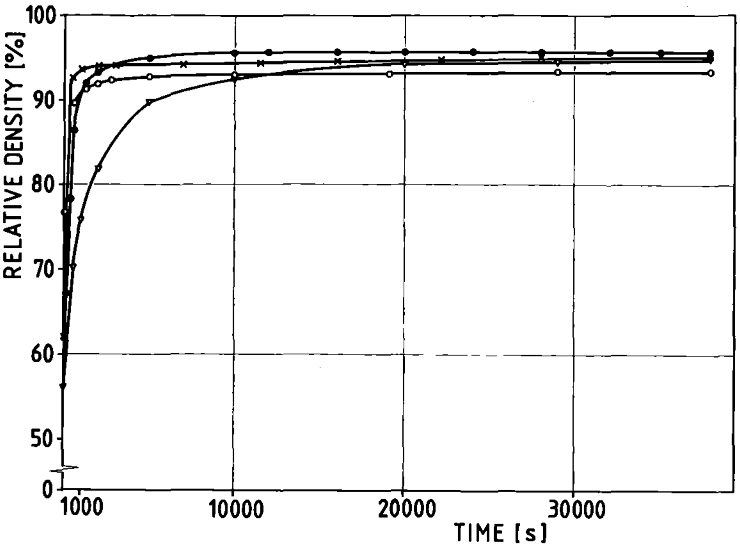

Fig. 2. Relative density-time plot for uniaxial pressure sintering at different temperatures (pressure 0.4 MPa; temperature: ▽ 893, × 923; ○ 948; ● 973 K).

molybdenum content in the waste—which is even higher in MLW than in HLW—into proper compounds ($M^{+2}MoO_4$ e.g. $PbMoO_4$, $CaMoO_4$, $MgMoO_4$) instead of MoO_3 [5]. Furthermore, some components such as PbO and MnO are assumed to reduce the oxidation of Ru/RuO_2 to RuO_4 which is very volatile in air ($\leqslant$ 1300 K) [6].

The simulate waste-solution was prepared with the composition shown in table 2 where special emphasis was put to a realistic simulation of the Zircaloy chips which enter the waste during fragmentation of the fuel element tubes. This simulation of Zircaloy chips in the MLW was based on investigations using dummy fuel rod tubes (Zircaloy-4, length 3.9 m) filled with porcelain and assembled in rod bundles (236 rods per bundle). The tubes were chopped in short sections (length 5 cm) by a steel bundle scissor including cuts through distant holders (Inconel 718) and steel control tubes as well. By magnetic, sedimentative and optical methods the different materials present in the chip mixture could be

Table 4
Initial and final densities (g/cm^3) for uniaxial pressure sintering of leadborosilicate glass together with medium active waste

Pressure (MPa)	Temperature (K)						
	848	873	893	923	948	973	998
0.2				2.16 3.34	2.02 3.33	2.11 3.32	1.93 3.30
0.4			1.97 3.29	2.16 3.35	2.07 3.36	2.05 3.33	
0.7			2.18 3.30	2.09 3.37			
1	2.06 3.33	2.03 3.27	1.98 3.35	1.99 3.29			
2	1.96 3.24						

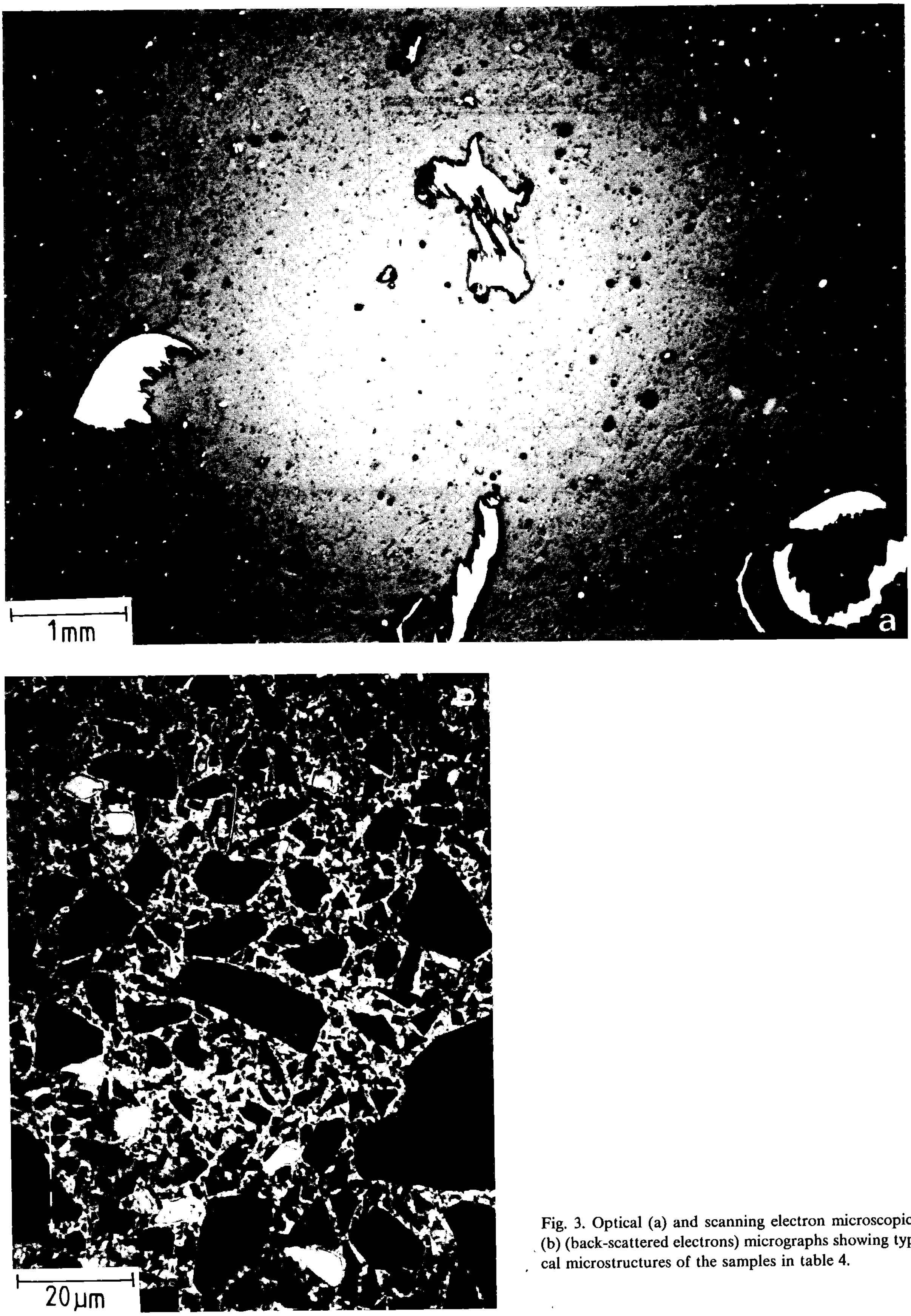

Fig. 3. Optical (a) and scanning electron microscopical (b) (back-scattered electrons) micrographs showing typical microstructures of the samples in table 4.

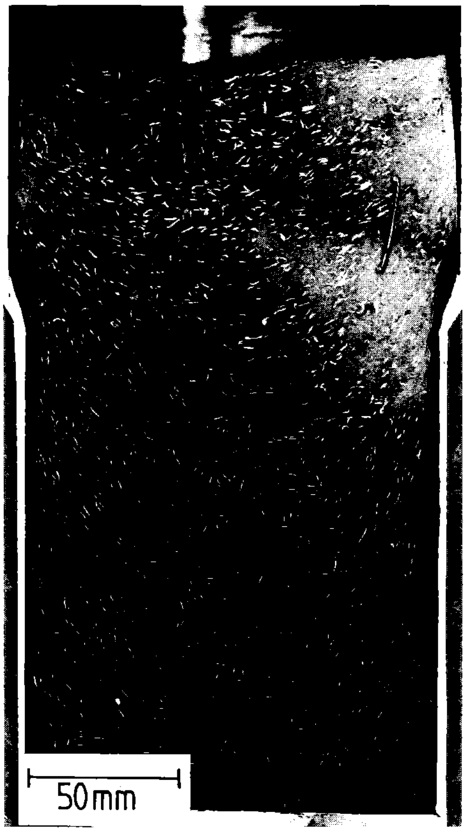

Fig. 4. Simulated MLW containing sinterglass products in steel can (150 mm inner diameter).

separated from each other and subsequently fractionated by sub-sieve analysis. The results for metal chips are given in table 3. As already mentioned in table 2 it was assumed that only small fractions (≤ 4 mm) of the chip material enter the MLW due to the dissolver conditions in reprocessing.

3. Procedure and results

The simulated medium level waste is mixed in liquid state with the glass frit in a heatable mixer, dried (≈ 423 K) under continuous blending and treated for sintering in the same way as described recently for glass-HLW-simulate mixtures [4]: the dried powder mixture of glass with MLW oxides is filled into a graphite lined stainless steel can and is uniaxially in-can hot pressed. To find out optimum conditions, test runs were made first with products of smaller inner diameter (35 mm) by variation of pressure and temperature at increasing time at sintering temperature. In table 4 all pressure-temperature-density correlations according to these tests are given. The relative density (calculated theoretical density: 3.53 g/cm^3) is given in fig. 1 as a function of time at one selected temperature (923 K) for different pressures and in fig. 2 as a function of time different temperatures at one selected pressure (0.4 MPa). Typical microstructures by optical and scanning electron microscopy (SEM) are given in fig. 3 in order to illustrate the homogeneous distribution of the waste oxides.

Using one selected temperature (923 K) and pressure (0.4 MPa) larger products (glass frit with 20 wt% MLW: 150 mm inner diameter, 400 mm height; 300 mm inner diameter, 800 mm height) have been produced by heating up in two steps: until 773 K with a heating rate of about 100 K/h without pressure, keeping at constant temperature (773 K) for 24 h without pressure (postdrying) and final heating to 923 K under pressure with the same heating rate. The products were kept at maximum temperature and pressure (923 K, 0.4 MPa) for several hours and subsequently very slowly cooled down (5 K/h) to room temperature revealing bulk integrity, high densities (≈ 93% TD) and homogeneous distribution of the MLW components in the glass matrix as revealed by chemical analyses. A cross section is given in fig. 4. Thus it is demonstrated, that vitrification of MLW by in-can hot pressing results in proper products similar to those obtained with HLW and, therefore, that powder-technologically common HLW/MLW vitrification by in-can hot pressing is promising as the next step for investigation.

Acknowledgement

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IN-CAN HOT PRESSING OF BOROSILICATE GLASS FOR THE IMMOBILIZATION OF HIGH- AND MEDIUM-LEVEL WASTES

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ABSTRACT

The paper presents a method for the immobilization of different waste streams based in the uniaxial in-can hot pressing of a glass frit together with the waste oxides.

The process reported herein offers engineering simplicity in combination with many technological advantages such as significant decrease in temperature, use of small pressure, improved homogeneity of the products, production in easily arrangeable and interchangeable units. Furthermore, the proposed method has also proved to be suitable for treating intermediate-level waste streams containing Zry-4 cladding fragments.

INTRODUCTION

During the last several years a number of vitrification processes for high-level wastes (HLW) based on the melt of glasses have been demonstrated [1,2]. Some of them involve evaporation, calcination of the dried residue and the subsequent dissolution in a glass melt. However, one of the proposed methods,the ceramic melter [2], combines the calcining and melting operations in a single step which operates continuously, simplifying the technology. In any case the immobilization of nuclear wastes by melting involves high temperatures causing evaporation losses as previously reported [3].

The work reported herein was undertaken to develop a method for the immobilization of different waste streams which avoids the melt and is based on the uniaxial in-can hot pressing of a glass frit together with the waste-oxides.

DESCRIPTION OF THE TECHNOLOGY

Fig.1 depicts the flowsheet of the process. In order to assure an intimate mixing the simulated HLW-solution, whose composition is shown in Table I, was fed in denitrated state together with a borosilicate glass frit (Table II), into a heatable mixer for drying during continuous blending. The mixer itself is heated by oil, maintained at the requested temperature (approximately 120 ^{o}C) by a thermostat, allowing the slurry to be slow-dried, minimizing the volatilization of HLW-components. Furthermore, the mixer has the possibility to introduce a desired atmosphere permitting a careful control of the redox state of the mixture during processing.

In order to eliminate solid aerosol particles from the offgas a very simple filter device was developed. A box containing glass beads of the same composition as the glass frit to be processed provides a filtration of the majority of the solids accomplished by sieve and adsorption effects. This arrangement limited to a few ppm the content of the HLW-oxides in two wash columns containing dilute nitric acid and water respectively. Afterwards,the glass beads may be fed by gravity into the mixer in order to be processed with the next charge and obviating the formation of secondary wastes.

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After drying, the resulting powder, comprised of an intimate mixture of HLW-oxides and glass frit, is then fed by gravity into stainless steel canisters shaped for subsequent stacking (Fig.2).
Inside the canisters a graphite textile lining compensates differences in thermal expansion coefficients between the glass product and steel. At the same time this graphite cloth sack has the functions of impeding the loss of radioactive dust during filling of the containers, and of limiting the side wall friction during sintering.

Afterwards, the canisters are pre-heated in an electrical furnace up to approximately 500°C without applied pressure to eliminate the remaining water of the mixture and to thermally destroy some of the residual nitrates. This furnace consists of three coils, where a variable voltage can be applied to each winding.
During densification the temperature was raised, e.g. to 650°C and the pressure normally to less than 1 MPa. The small pressure required was generated by means of a very simple air-pressure device. Subsequently, the products were allowed to cool-down slowly to room-temperature to avoid crack formation.

The same procedure was applied to simulated medium-level wastes (MLW) containing Zry-4 cladding fragments up to 4 mm in diameter.

RESULTS

Fig.2 shows two products manufactured with the described technology. Fig.2a depicts a sample 300 mm in diameter and 800 mm in height, containing about 80 kg of the borosilicate glass (Table II). In a container of these dimensions, loaded with 15% HLW-oxides, approximately 1700 ℓ of concentrated fission products solution can be immobilized.

Fig.2b shows a sample 150 mm in diameter and 500 mm in height, containing approximately 12 kg of a MLW with a high percentage (49 wt.%) of Zry-4 cladding fragments.
Chemical analysis revealed a homogeneous distribution of the oxides in the glass products. Many units can be stacked and welded for sealing, as illustrated in Fig.1, to form a compact cylindrical column for disposal.

EVALUATION OF THE PROCESS

Uniaxial hot pressing is a well established technique for the production of metallic and ceramic parts. In the past it has been successful applied for the immobilization of radioactive waste in glass [6,7] and SYNROC [8]. The essential difference between the present process and that already mentioned is the use of extremely small pressures which are sufficient to assure good densified products and in comparison with SYNROC, the substantially lower temperatures required to accomplish sintering limiting thereby the loss of radioactive nuclides [3]. An additional advantages is the use of the normal atmosphere as the sinter medium.

The employment of a heatable mixer provides the adequate dryness of the mixture for the process obviating the calcination step during which the ruthenium volatility can be as high as 50-100% [9] due to oxidation from RuO_2 to RuO_4.
Since the HLW-oxides are dried together with the glass frit, this process assures an intimate mixture of both components and, hence, a homogeneous distribution of the oxides in the final product.

The different steps of the process are very simple, involve small pressures and relative low temperatures providing that way adequate conditions to be used in hot cells.

SUMMARY AND CONCLUSIONS

A method for the immobilization of different waste streams has been described. The technology proposed has some attractive attributes which make it suitable for remote operation conditions, namely:

- Significant decrease in the manufactured temperature, not only in the sintering phase, but also in the drying process, avoiding evaporation losses.
- The extremely modest pressures needed for a rapidly densification are easily to perform and adequate for the use in hot cells under remote handling conditions.
- Avoidance of the melting and the concurrent segregation problems.
- Production in easily arrangable and interchangeable units.
- Suited for treating both the high- and the intermediate-level waste streams using the same technology.

Further work is underway to test the dissolution behaviour of the products and to fix HLW together with MLW in sinterglass.

TABLE I. Composition of the simulated wastes. HLW concentration approximately 430 ℓ/ton heavy metals a).

Element	HLW (g/ℓ)
Rb	0.91
Sr	2.2
Y	1.2
Zr	10.2
Mo b)	10.9
Tc b)	2.4
Te	1.7
Cs	6.6
Ba	5.0
La	3.6
Ce c)	6.9
Pr	3.3
Nd	11.6
Sm	2.5
Cr	1.1
Fe	4.0
Zr	4.5
Oxides	**MLW (g/ton heavy metals)**
MoO_3	620
Sb_2O_3	20
CeO_2	138
Stainless steel	104
Ni d)	28
Zry-fragments	850

a) The simulated wastes do not include the noble metals Ru, Pd, Rh and the active elements Pu, U.

b) Mo also provides the Tc content.

c) Ce replaces Pu and U.

d) Substitute for INCONEL.

TABLE II. Borosilicate glass VG 98/12 used for solidification of high-level wastes (HLW).

oxide	wt.%
SiO_2	56.7
TiO_2	4.6
Al_2O_3	2.6
B_2O_3	12.6
MgO	2.1
CaO	4.1
Na_2O	17.5

TABLE III. Lead-borosilicate glass BBS-10 used for solidification of medium-level wastes (MLW)

oxide	wt.%
SiO_2	42.0
PbO	36.0
B_2O_3	12.0
Al_2O_3	6.7
CaO	1.8
MgO	0.9

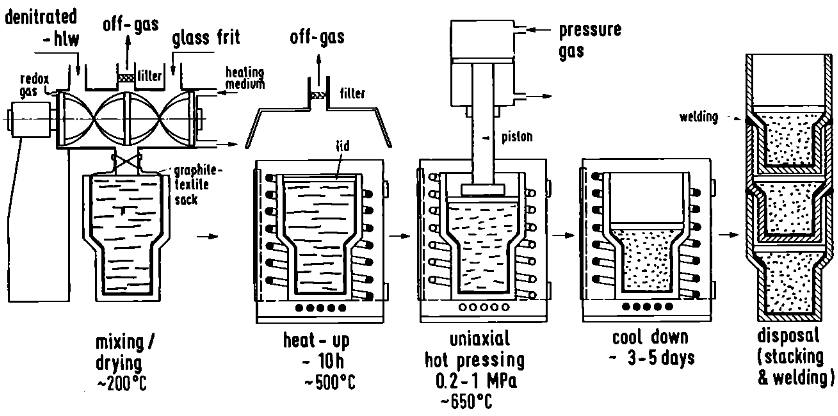

FIG. 1. Conditioning of radioactive waste in glass by powder technology.

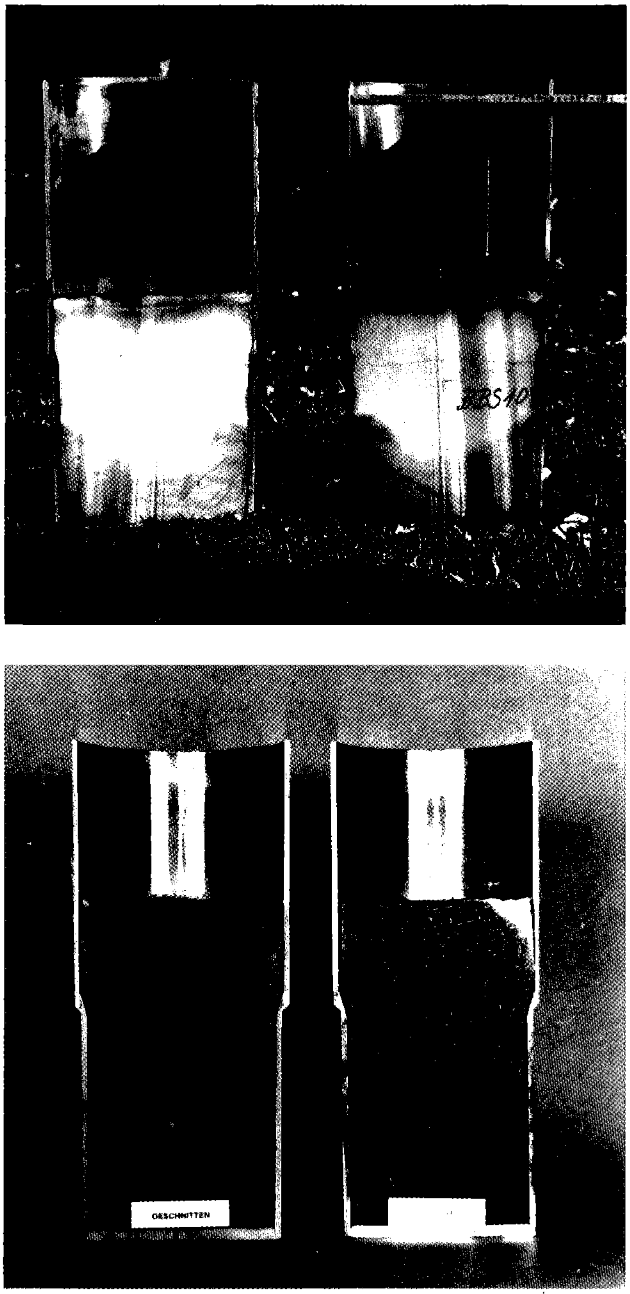

FIG. 2. a) Sample containing 80 kg of the borosilicate glass (Table II).
b) Sample containing approximately 12 kg of MLW with lead-borosilicate glass (Table III).

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