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Recent Experiments on Fixation of High Activity Wastes in Karlsruhe

by

W. Guber, L. Kahl, J. Saidl

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Zusammenfassung

Für die Verfestigung der zu erwartenden hochradioaktiven Abfallösungen aus einer großen deutschen Wiederaufarbeitungsanlage für bestrahlte Kernbrennstoffe wurde ein titanoxidhaltiges Borosilikatglas entwickelt, in welches mehr als 20 Gew. o/o Glührückstand der Abfallösung homogen eingeschmolzen werden können.

Neuerdings ergab sich die Notwendigkeit, die Aufnahmefähigkeit dieses Glases für weitere Ballaststoffe wie Gd_2O_3, Sulfate, Chloride und Fluoride zu überprüfen. Die Untersuchungen zeigten, daß neben den 20 o/o Spalt- und Korrosionsproduktoxiden noch etwa 11 o/o Gd_2O_3 im Glas inkorporiert werden können ohne daß sich dessen Eigenschaften wesentlich verschlechtern. 1,25 o/o Sulfat, 1,1 o/o Chlorid und 5,5 o/o Fluorid können maximal im Glasprodukt unter Beibehaltung seiner Homogenität eingebettet werden. Der Anteil an Gd_2O_3 scheint sogar die Ausscheidung der leichtlöslichen Molybdatphase aus der Glasschmelze zu behindern.

Neben dem Borosilikatglas wird eine Glaskeramik auf Borosilikatglasbasis auf die Verwendbarkeit zur Fixierung von hochradioaktiven Abfallösungen untersucht und beschrieben.

Summary

A titanium dioxide containing glass in which more than 20 w. o/o of HAW oxides can homogeneously be incorporated has been developed for the solidification of the highly active waste solutions from the future large german reprocessing plant.

Recently, investigations on the capacity of this glass for further ballast matter as Gd_2O_3, sulphate, chloride and fluoride became necessary. Results show that besides the 20 w. o/o of HAW oxides about 11 w. o/o Gd_2O_3 can be integrated in the system without substantial deterioration of the final product properties. 1,25 o/o sulphate, 1,1 o/o chloride and 5,5 o/o fluoride represent maximum amounts when a homogeneous glass product shall be maintained. Moreover, Gd_2O_3 seems even to hinder the separation of the soluble molybdate phase from the glass melt.

In addition to the work on borosilicate glass a similar glass-ceramic composition has been investigated which is described in view of its applicability for the fixation of highly active waste solutions.

Introduction

At Gesellschaft für Kernforschung mbH, Karlsruhe, work has been performed for several years on the laboratory-scale development of a boronsilicate solidification matrix as well as on the technical-scale development of process technology and the technology underlying the solidification process in glass of high level wastes. More than 20 wt.% of HAW oxides could be incorporated into the titatium oxide containing boronsilicate glass developed here and homogeneously vitrified.

Last year the requirement was imposed on the flowsheet of the large German reprocessing plant for irradiated fuel elements that for reasons of criticality gadolinium in the form of Gd_2O_3 is added as a neutron poison during the process of fuel element dissolution. Gadolinium cannot be separated chemically during the reprocessing campaign so that in addition to the fission and corrosion products Gd_2O_3 will be present in the high level waste solution to be vitrified. According to the calculations 15 kg Gd/t of fuel will be incorporated, corresponding to a concentration of Gd_2O_3 in the waste solution of about 25 g/l. In total, this is a higher amount by about 50% compared with the initital content of solids in the solution. This implies that in addition to 20 wt.% of the oxide content of fission and corrosion products in the solidified glass product approximately 10 wt.% of Gd_2O_3 should be integrated into the glass. Following US calculations (6) the Gd_2O_3 content of the waste solution will even amount to 30 g/l.

However, knowledge of investigations of glasses containing gadolinium is rather poor, so that no predictions can be made on the influence exerted by relatively high amounts of Gd_2O_3(about 2 mol%) on the properties of glasses containing solidified waste. Since Gd_2O_3 is not a vitrifying agent, the complexity of the multi-component glasses implies that unpleasant surprises have to be anticipated with respect to the properties so far strived for in the waste glasses, i.e. maximum capacity for fission and corrosion products, meltability around 1100 - 1200°C, good heat conductivity, high chemical and mechanical stability, low tendency to devitrification and to phase formation.

In addition to investigations of the glass improvements of the solidification matrix were studied. The structure of the glass which is metastable by its nature, may devitrify in case the system is fed with the necessary activation energy in any form - heating, irradiation - which may strongly change the chemical and mechanical properties of the product. A more stable type of the solidification product can be obtained by specific programmed recrystallization of the appropriate system, taking the molten rocks or glass ceramics as an example.

A product similar to glass ceramics was synthesized which can be molten below 1200°C, takes up more than 20 wt.% of HAW oxides, and can still by recrystallized effectively in a specific way.

It became necessary to investigate glasses and glass ceramics previously conceived for HAW waste fixation in order to determine how the incorporation of Gd_2O_3 into the structure of the matrix influences the properties indicated. Since very differing glasses were proposed in several countries for waste solidification, it must be anticipated that one or the other system (inclusive of glass ceramics) proves to be inadequate and must be adapted to the gadolinium problem.

Investigations were performed with the glass and the product similar to glass ceramics developed in Karlsruhe with the objective of observing the influence of Gd_2O_3 on the capability to adsorb HAW oxides, the meltability, the tendency to devitrify, and phase formation. The maximum amounts of Gd_2O_3 were found which can be absorbed by the systems without having negative impacts.

- 3 -

In addition, the capability of glass was studied to absorb the thermally stable anions SO_4^{2-}, F^- and Cl^-.

Besides laboratory work just mentioned, an inactive pilot plant was built for development of the solidification process. This plant serves to verify the results derived from the development of the solidification matrix in the light of process and general technology and to test them on a technical scale. The investigations will result in the design and construction of a high active plant with a troughput of 30 l HAW-solution per hour and will be terminated by the construction of a large-scale solidification plant with a capacity of 150 l HAW-solution per hour.

Investigations of Glasses

The solidification matrix was developed on the basis of the boronsilicate glass of the general formula

$$SiO_2-Al_2O_3 - B_2O_3 - CaO - Na_2O$$

following work with the natural silicate raw materials such as nepheline syenite, basalt and Filtrolit. The results obtained were mainly satisfactory as regards the capability to take up ballast oxides, the resistance to leaching and the very significant prerequisite technically of a sufficiently low melting temperature of the base glass and the solidified final product. To increase the capability to absorb ballast oxides without having to raise the melting temperature, TiO_2 was incorporated into the system, which lowered the volatility of cesium during melting and improved the resistance to leaching of the product. It was already reported about these glasses (1). Part of them were tested in the inactive pilot plant and found to be adequate for use (2).

After the necessity of using gadolinium had become known and the amount was calculated to be about 15 kg Gd/t of fuel, the percentage in the waste solution shown in Table 1 was derived.

- 4 -

The current technical literature on silicate yields but moderate information about the behavior of major percentage of rare earth oxides in the silicate glass and no data have been found for Gd and Gd_2O_3, respectively. Previous knowledge of and experience on the use of Ce, Pr, Nd and other elements, to cite a few examples, the use of which is above all known in conditioning the optical properties of the glasses (3,4), did not provide an indication for the studies because only fractions of mol percentages are added. When solidifying the high-level waste much higher amounts, more than 2 mol % Gd_2O_3 (about 10 wt.%) in addition to about 20 wt.% of HAW oxides, should be incorporated without deteriorating the properties and increasing the melting temperature.

The composition of the base glasses used is evident from Table 2. The VG 38 type was developed prior to facing the Gd problem. The incorporation of Gd_2O_3 and HAW oxides + Gd_2O_3, respectively, led to phase formations with the generation of a heavier phase which was enriched in Gd_2O_3. The composition of VG 38 was therefore modified. It became obvious that an increase in the alcalioxide fraction, above all of Li_2O and K_2O, will suppress phase formation. The modifications VG 98, 100 and 101 (Table 2) can absorb as much as 22 wt.% of HAW oxides + 11.5 wt.% of Gd_2O_3. They can be molten at approximately 1100°C and form a homogeneous product. These products were investigated for their suitability for recrystallization and the results obtained are represented in Fig. 1,2. A good idea of the meltability of glasses and their products is provided by the viscosities of the melts exhibited in Fig. 3. It is very interesting in this context that the development of viscosities in the range of temperatures under consideration between 700 and 1100°C was practically not subjected to changes.

Preliminary examinations have shown that the VG 98 glass is apparently the most appropriate for absorbing at least 20 wt.% of HAW oxides and 10% Gd_2O_3. Therefore, this glass was selected for an in-depth investigation of the influence of gadolinium on the properties of glass which are relevant to waste solidification as well as on other important properties, such as the tendency

- 5 -

to recrystallize and the resistance to leaching.

Starting with the base glass DTA investigations were performed of glasses containing different combinations of Gd_2O_3 and HAW oxide fractions. As can be seen from Fig. 4 no definite exothermal peak can be found. Despite the total 30% of ballast oxides (corresponds to about 10 mol%) the low tendency to devitrification thus indicated is confirmed by examinations with the scanning electron microscope, the microprobe and the X-ray diffractometer of tempered samples (800°C, between 140 and 180 hours) of the same glasses as used in DTA investigations. In only one of these glasses definite crystal phases could be detected. The element distribution shows that gadolinium is distributed in a very homogeneous manner. The incorporation of up to 11 wt.% Gd_2O_3 in addition to HAW oxides abviously does not result in a higher thermodynamic instability of the glasses under consideration. This is confirmed by investigations of the tempered samples of the same glasses (550°C, 115 hours). Here also, no separate phases were found and it seems that Gd_2O_3, up to an amount of 11 wt.%, takes the function of a network forming agent in the glasses under consideration. A change of its function still waits for thorough investigation. Molybdenum was found to be homogeneously distributed in the matrix in all samples, which is due to the favorable impact of Gd_2O_3 on the retention of the yellow phase which is very rich in molybdenum.

The assumption of an increased molybdenum retention capability in glasses due to Gd_2O_3 seems to be confirmed in the investigation of a high melting boronsilicate glass in the absence of TiO_2 but in the presence of a relatively high Al_2O_3 content (14 wt.%). Following tempering at 900°C extending over several days this glass shows crystal phases of $CaMoO_4$ as was exhibited by the X-ray-diffraction analysis (5). Under the same crystallization conditions the addition of 10 wt.% of Gd_2O_3 also leads to the separation of a crystal phase. However, this crystal phase contains no more molybdenum which remains fixed in the

- 6 -

matrix. The crystal phase has not yet been indentified but it exhibits strong enrichment in gadolinium. The hydrolytic classification of this glass changes from 1 to 3.

Similar to this glass, the resistance to leaching of glasses based on VG 98 is not adversely affected by incorporation of 10% Gd_2O_3. However, knowledge previously obtained with a high Gd_2O_3 content cannot be generalized. It was shown for glasses containing zinc and proposed by BNWL that Gd_2O_3 increases the meltability and raises the tendency to devitrify at the very moment when it is taken from the melt. Consequently, general investigations and examinations of glasses intended for the solidification of high-level waste solution are very appropriate and necessary under this aspect (6).

Glass Ceramics, Products Resembling Glass Ceramics

The idea of improving the properties of the solidified products by micro-recrystallization originated in the experience gathered by industry with molten rocks. It was throroughly investigated and described (7,8). The preparation of glass ceramics for this purpose was not investigated until a later date (9). The underlying research principles have been described elsewhere (10,11). Both methods distinguish themselves by the products which are much more stable in the long run as far as the thermodynamic aspect is concerned. This is very important above all with respect to the safe ultimate disposal of the solidified product during the millenium required for its decay.

The use of basalt and of the other natural substances was not successful for two reasons: first because of the excessive content of balast in the raw material itself limiting the capacity for HAW oxides, and second because of the excessive melting temperature (about 1300 - 1350°C). Temperatures as high as 1400°C and more are required to fabricate the glass ceramics known so far.

In Karlsruhe tests were conducted which aimed at a considerable reduction of the melting temperature of the product subjects to specific recrystallization. A series of the products of the type

SiO_2-TiO_2-Al_2O_3-B_2O_3- CaO-MgO-Li_2ONa_2O-K_2O

were molten and loaded by up to 20 wt.% of HAW oxides. The basic product and the product containing HAW oxides were recrystallized and their properties examined. The results can be seen in Figs. 6,7 and in Tables 3,4 (12). The main crystalline phase has been indenitified as perovskite.

Also in this case the attempt was made to settle the problem of additional Gd_2O_3 incorporation. The products first developed (VC 15) took up Gd_2O_3 but unsatisfactorily in addition to HAW oxides and phase separations occured. Of the modified compositions (see Table 3) VC 15 k has so far exhibited the best results. Although work has not yet been terminated, it seems that high-level waste can also be effectively solidified in this way.

When modifying the glass compositions for Gd_2O_3 incorporation a problem was touched which might adversely influence the vitrification of high-level waste. It relates to the thermally stable anions sulphate, fluoride, and chloride. Sulphate and chloride can be present only as non-typical pollutions in the high-level wastes of the Purex type. By contrast, fluorides can be introduced into the waste solution from the Purex process as a result of HF addition intended to improve the extraction of U and Pu. Only very restricted amounts of sulphate and chloride can be dissolved in the glass. It was stated experimentally that 1.25 wt.% of SO_4^{2-} and 1.1 wt.% of Cl^-, respectively, can be taken up by the VG 38 glass without phase formation. This value was 5.5 wt.% for F^-, with turbidity effects in the glass product observed already after short-term tempering (about 3 hours at 500°C).

During the melting process volatilization of these anoins is noticed as a white smoke. All three anions produce strong corrosion effects on the construction material (F^- and Cl^- in general, SO_4^{2-} on the Inconel melting crucible). Summarizing, it can be stated that their influences on the vitrification of high-level wastes are negative and result in a complication of the process.

Tab. 1

Chemical composition of the high active waste solution (KEWA standard)

mean burn-up 33.000 MWd/t, spec.volume 700 l/t of fuel

element	g/l	residue on ignition	g/l
Rb	0,5	Rb_2O	0,55
Cs	3,9	Cs_2O	4,13
Sr	1,3	SrO	1,54
Ba	2,0	BaO	2,23
Y	0,7	Y_2O_3	0,89
La	1,8	La_2O_3	2,11
Ce	3,8	Ce_2O_3	4,45
Pr	1,7	Pr_2O_3	1,99
Nd	5,6	Nd_2O_3	6,53
Pm	0,04	Pm_2O_3	0,05
Sm	1,3	Sm_2O_3	1,51
Eu	0,24	Eu_2O_3	0,28
Gd	0,16	Gd_2O_3	0,18
Zr	5,2	ZrO_2	7,02
Mo	4,9	MoO_3	7,36
Tc	1,2	TcO_2	1,59
Ru	3,2	RuO_2	4,21
Rh	0,6	Rh	0,6
Pd	1,9	Pd	1,9
Te	0,8	TeO_2	1,0
U	1,4	U_3O_8	1,65
Pu	0,06	PuO_2	0,07
Np	1,1	NpO_2	1,25
Am	0,4	AmO_2	0,45
Cm	0,03	CmO_2	0,03
Fe	3,0	Fe_3O_4	4,15
Cr	0,5	Cr_2O_3	0,73
Ni	0,5	NiO	0,64
	49,63		61,20
Gd	21,42		24,61
	71,05		85,81

cooling period 300 d, spec.activity 3600/l, total 1050 m^3/y
loss of U and Pu according to project data of KEWA

Tab. 2

Borosilicate base glasses and melted one-phase final products
weight %

	VG 38	VG 59 1)	VG 80 2)	VG 97	VG 98 3)	VG 100	VG 101	VG 98mod 4)	VG 98mod
SiO_2	52,5	40,0	50,0	58,4	50,5	52,5	50,0	40,5	35,1
TiO_2	10,0	-	9,5	4,1	4,2	4,0	4,0	3,3	2,9
Al_2O_3	2,5	-	2,4	1,4	1,4	1,0	2,0	1,1	1,0
B_2O_3	10,0	40,0	10,0	11,0	13,6	14,0	15,0	10,8	9,5
CaO	5,0	-	8,1	2,8	2,8	5,0	4,0	2,2	1,9
Na_2O	20,0	20,0	13,3	22,3	27,5	22,5	25,0	21,8	19,1
Li_2O			6,7						
w.ox.								-	20,0
Gd_2O_3								13,4	10,5
CeO_2								6,9	

1) three component glass for pilot plant experiments

2) CaO and B_2O_3 present as $Ca(BO_2)_2$ before melting

3) glass modifications for the incorporation of RE oxides

4) examples of the final product after the incorporation

Tab. 3

Ceramics similar products for the incorporation of highly active waste oxides [wt.o/o]

	VC 15	VC 15mod	VC 15 k	VC 15 k mod
SiO_2	50,0	40,0	56,5	38,9
TiO_2	5,0	4,0	5,7	3,9
Al_2O_3	10,0	8,0	6,6	4,6
B_2O_3	5,0	4,0	5,7	3,9
MgO	5,0	4,0	5,7	3,9
CaO	5,0	4,0	-	-
Li_2O	10,0	8,0	14,1	9,8
K_2O	5,0	4,0	5,7	3,9
Na_2O	5,0	4,0	-	-
waste oxides	-	20,0	-	20,0
Gd_2O_3	-	-	-	11,1

Tab. 4

Physical properties of glass and ceramic matrix and products

	1	2*)	3	4	5	6
VG 38	2,55	1,2	0,35	12,9	50	613
VG 38 + HAW ox.(20 %)	2,77			15,6	78	575
VG 98	2,56			18,4	42	542
VG 98 + HAW ox.(20 %)	2,76				50	
VG 98 + Gd_2O_3(10 %)	2,7o				44	609
VG 98+HAW ox.(20%)+Gd_2O_3(10%)	3,00			18,0	58	548
VC 15 glass	2,54	1,5	0,37	9,9	95	500
VC 15 cryst.	2,55	1,8	0,41	8,9		716
VC 15 + HAW ox.(20%) glass	2,81	1,8	0,33	8,9	122	499
VC 15 + HAW ox.(2o%) cryst.	2,85	2,2	0,35	9,7		686

1 - density(g/cm^3) 2 - thermal conductivity(W/m.°C) 3 - heat capacity(cal/g.°C)
4 - thermal expansion(.10^{-6}/°C) 5 - viscosity(poise) at 1050°C
6 - dilatometric softening point(°C)

*) at 400° C

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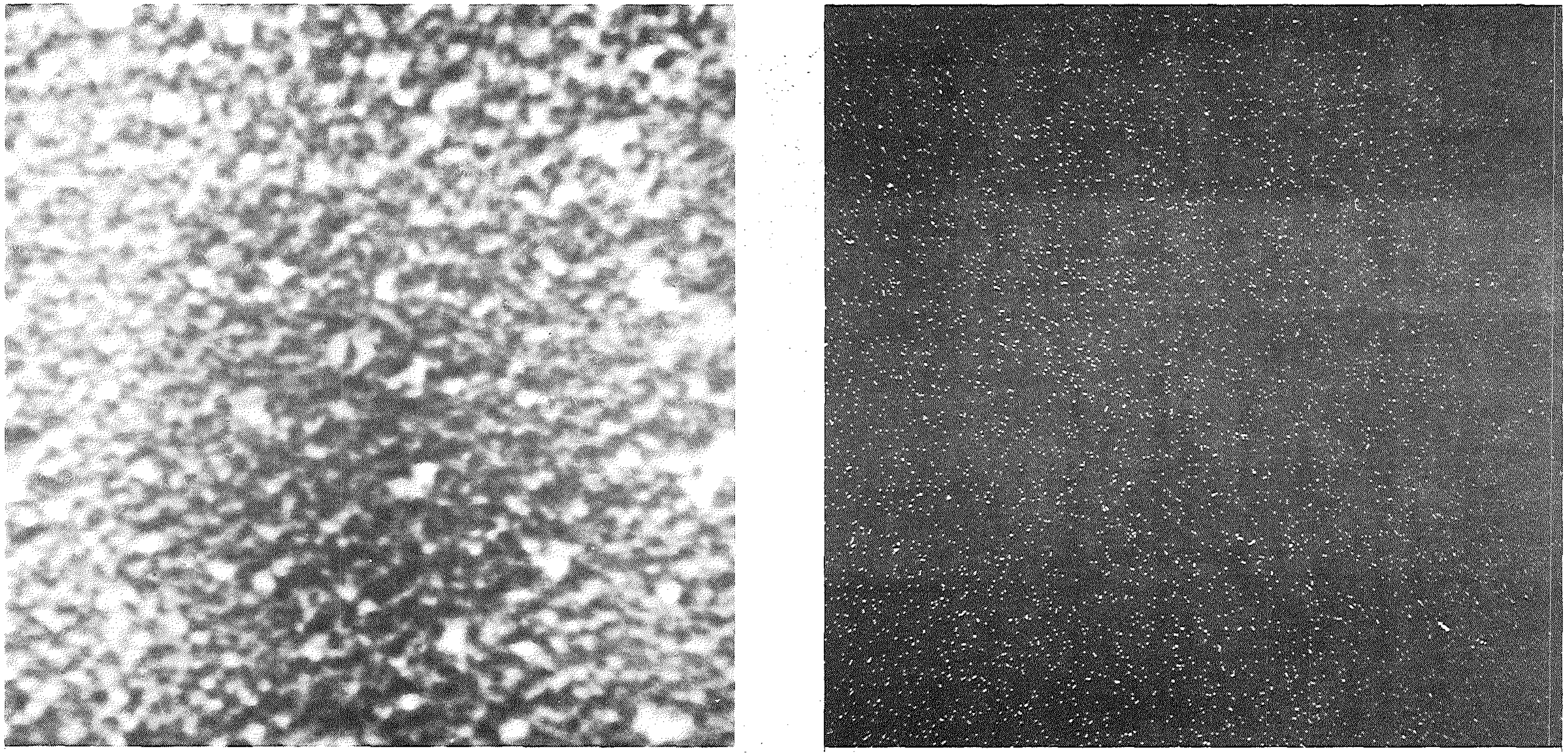
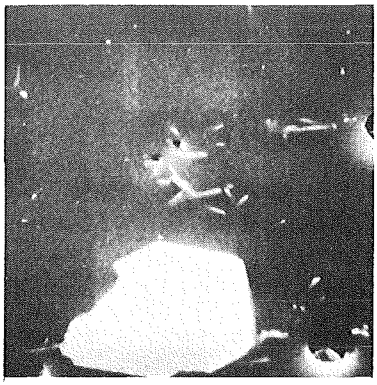


Fig.1 Gd-distribution in the glasmatrix VG 98 + 10 % Gd_2O_3

13.000 : 1

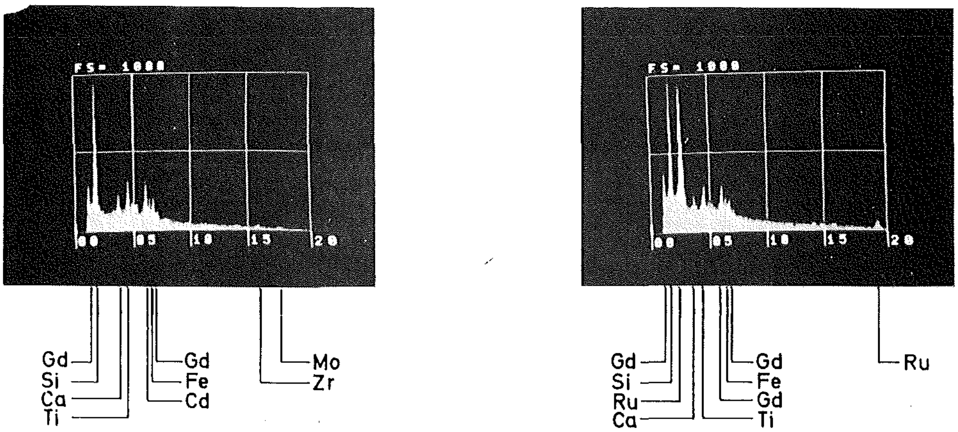


Oversatureted VG 98 Glassmatrix
(22% Wasteoxides + 11% Gd_2O_3)
2100:1

X-ray fluorescenc spectra

Glassmatrix

Needles



White crystal grain

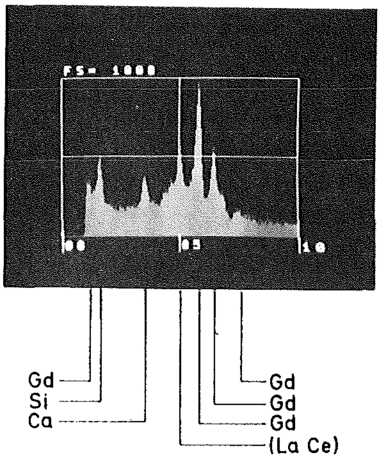


Fig. 2 Gd-distribution in the oversaturated glass matrix VG 98 + 22 % waste oxides + 11 % Gd_2O_3

Fig.3 Viscosity of melts

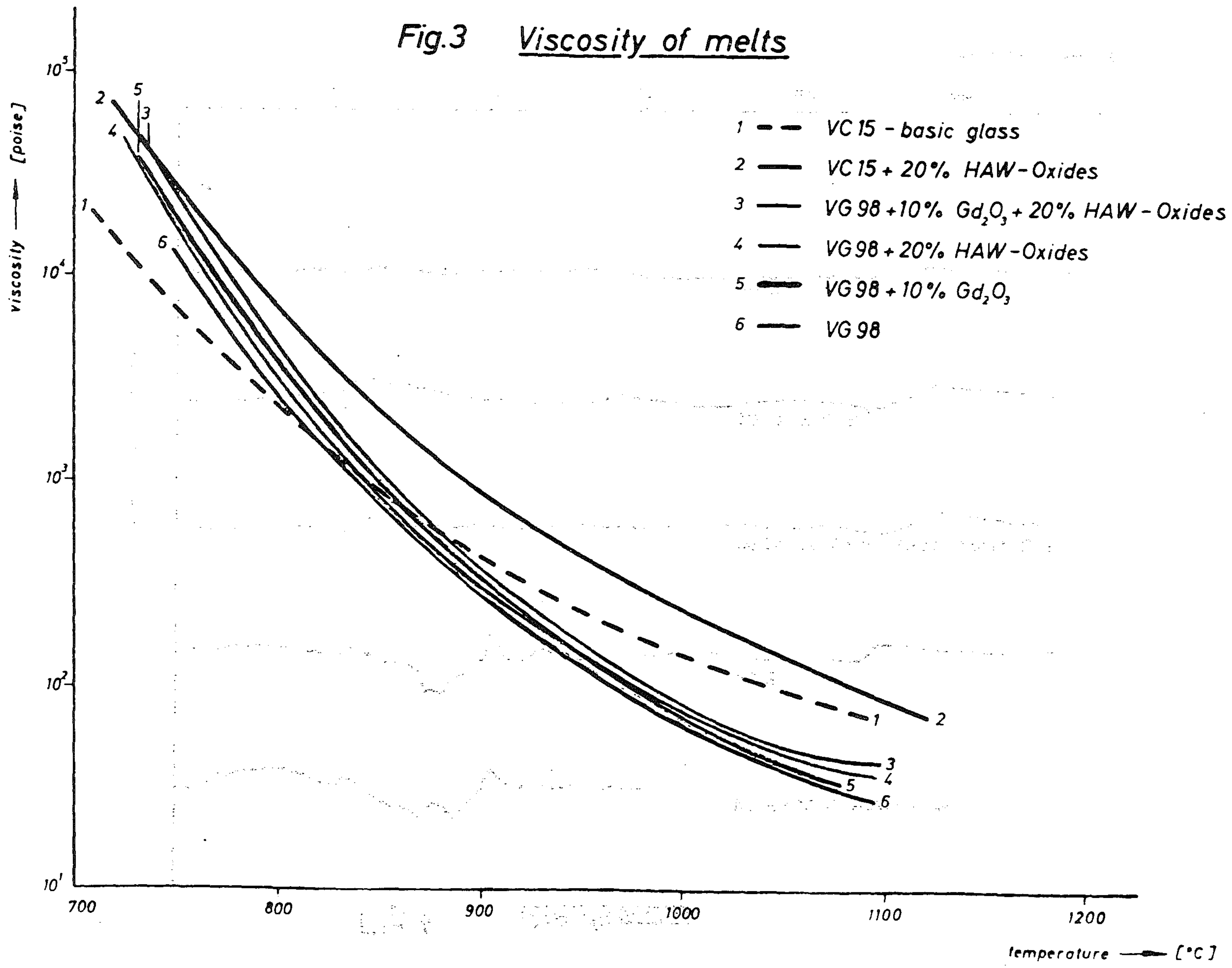
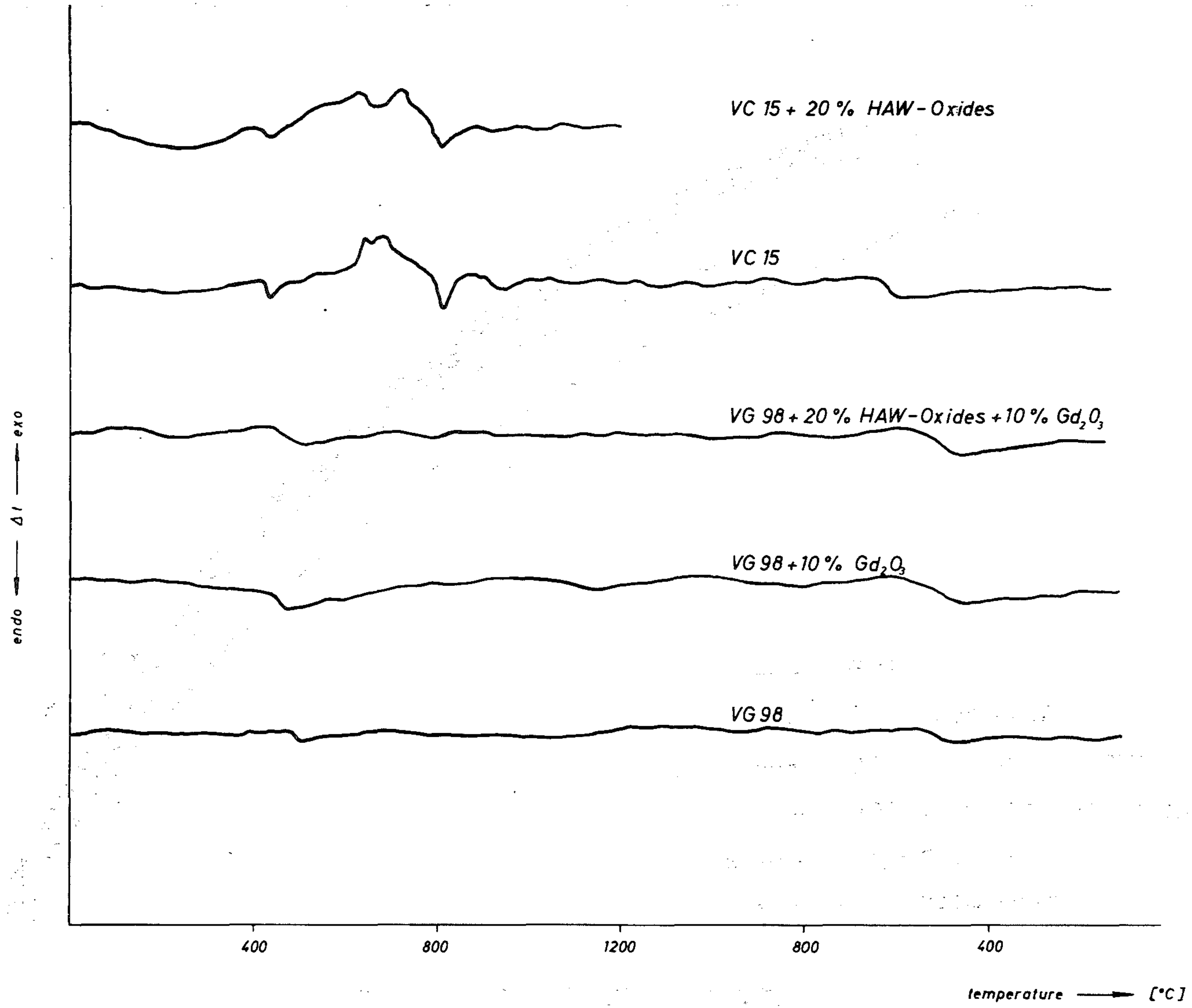


Fig. 4 **DTA diagrams**



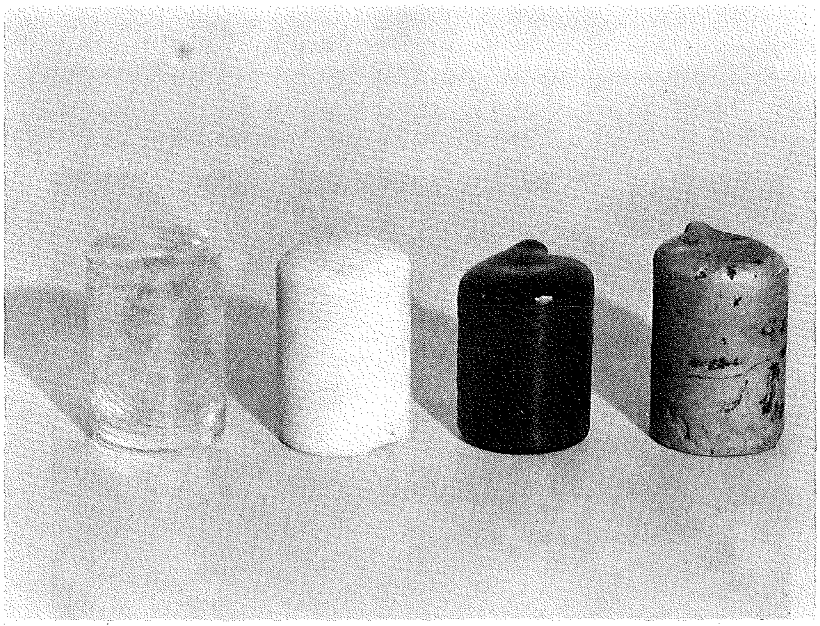


Fig. 5 Blocks of glass ceramics

left to right:
VC 15 glassy, VC15 cryst, VC15+ 20% waste oxides glassy, VC15+20% waste oxides cryst.

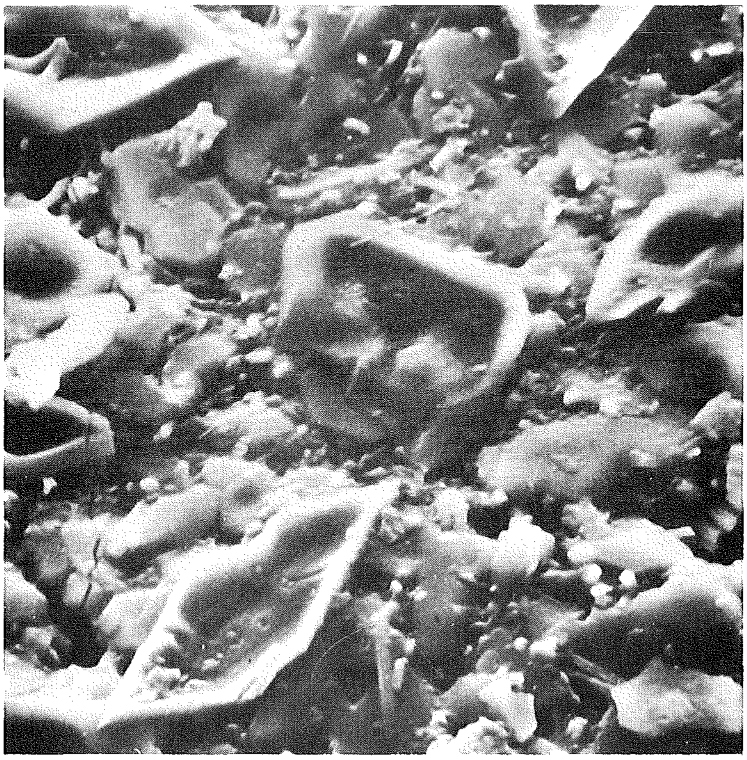


Fig. 6 VC 15 + 20 % waste oxides, cryst.

2400 : 1

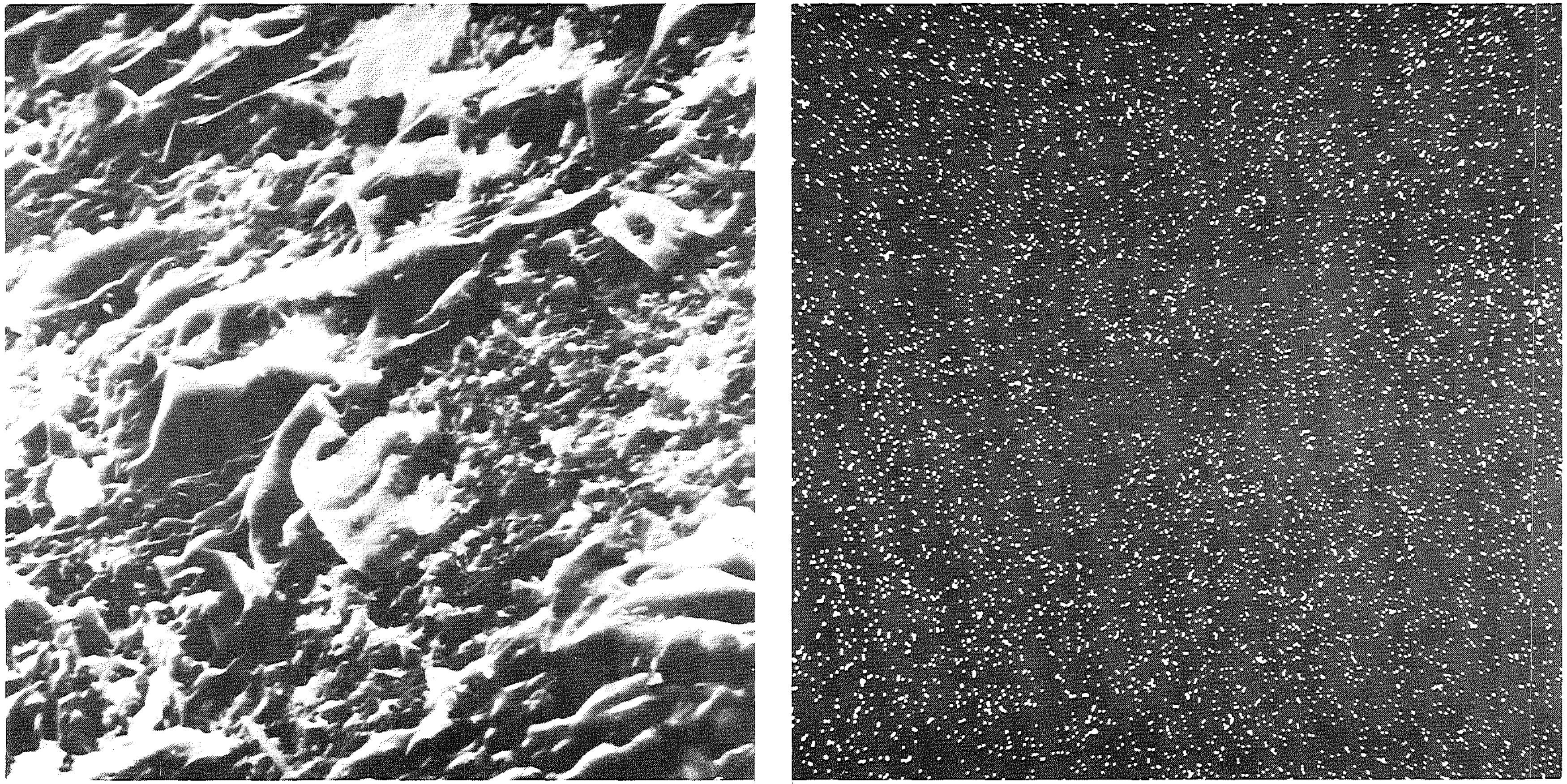


Fig. 7 Ru-distribution in the ceramic matrix VC15+20 % waste oxides
1100:1