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Projekt Wiederaufarbeitung und Abfallbehandlung

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Investigations on the Long-Term Radiation Stability of Borosilicate Glasses against Alpha-Emitters

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Abstract

By accellerated experiments with Cm-242 doped HLW glasses the long-range behaviour of borosilicate glasses during final disposal has been simulated. To cover those questions concerning long-term safety aspects the properties of these glasses have been investigated on a time-lapse scale corresponding to 10.000 years storage of real HLW borosilicate glasses. The effects of radiation on structure, helium build-up, mechanical strength, energy storage and leachability of the glasses have been studied.

Zusammenfassung

Untersuchungen zur Langzeitstrahlenbeständigkeit von Borosilikatgläsern gegenüber Alpha-Strahlern

Durch Zeitrafferexperimente mit Cm-242-haltigen hochaktiven Gläsern wurde das Langzeitverhalten von Borosilikatgläsern während der Endlagerung simuliert. Um die mit der Langzeitsicherheit in Zusammenhang stehenden Fragen zu beantworten, wurden die Glaseigenschaften im Zeitraffermaßstab entsprechend 10.000 jähriger Lagerung echter hochaktiver Borosilikatgläser untersucht. Die Strahlungseinflüsse auf Struktur, Heliumaufbau, mechanische Festigkeit, Energiespeicherung und Auslaugung dieser Gläser wurden bestimmt.

Résumé

Des recherches sur la stabilité des verres borosilicate aux émetteurs alpha à longue échéance

Dans des expériences accélérées avec des verres de hautes activités, fondus avec Cm-242, le comportement des verres borosilicate à longue échéance pendant le stockage final est simulé. La qualité des verres est examinée dans une période accélérée correspondant à 10.000 années de stockage des verres de hautes activités typiques en réponse à la question posée sur la sécurité pendant de longues périodes de temps. Les influences d'irradiations sur la structure, la formation d'hélium, la résistance mechanique, les énergies emmagasinées et la lixiviation de ces verres sont étudiées.

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1. Introduction

At present, glass-systems are considered as the most convenient solidification products for the final disposal of high-level wastes arising from the reprocessing of spent nuclear fuel. The process technology for the immobilization of high-level waste in glass is most advanced and just demonstrated in some countries.

The basic glass compositions have been optimized for different types of high-level wastes and different types of technological processes aiming at the incorporation of a high percentage of waste oxides into glass. At the same time a series of requirements are expected from the final glass products with respect to final disposal safety considerations. In this context leachability, mechanical and physical properties are of particular interest, and special attention is paid to the long-term integrity and stability of the HLW glasses.

This report presents some appropriate procedures and results on HLW glass behaviour over 10.000 years, that has been simulated by time-lapse experiments.

2. General Aspects of Radiation Effects in Borosilicate Glasses during Final Disposal

There is the question, what might happen to HLW glasses within thousands of years due to the bombardement by α-and ß-particles or x-rays or recoil nuclei. A quantitative evaluation performed on the basis of theoretical calculations {1} demonstrates that the number of atomic displacements following α-disintegration of the long-lived actinides takes more than 95% of the total number of atomic displacements caused by all particle interactions in the HLW glass matrix. Therefore it seems to be a good approach that only the actinides are taken into account when any radiation damage in the glasses would occur.

As the lifetimes of the interesting actinides esp. americium and plutonium exceed those of human beings by some orders of magnitude it is obviously necessary to start with accelerated experiments on realistic models of HLW glasses doped with short-lived actinides.

From the point of view of their solubility in glass and their availability the curium-242 and curium-244 isotopes are specially favoured to achieve similar α-decay yields on curium spiked glass specimens within months as on real HLW glasses within centuries {2}

3. Simulation of Long-Term Irradiation, Preparation of Test Specimens

As indicated in chapter 2 the most realistic assessment to the long-range stability of HLW glasses will be met by accelerated experiments carried out on curium doped glass samples with the proper composition of HLW glasses and similar preparation techniques.

A detailed description of the preparation procedure and the composition of the specimens which are subject of the post-irradiation studies reported below is given in lit. (2). Table 1 shows a compilation of some relevant chemical, physical and irradiation properties of the three different types of specimens.

The curium spiked specimens, prepared in January 1975, were analyzed on their properties at certain irradiation intervals. After one years storage at room temperature the cumulative number of α-disintegrations and the total absorbed α-dose were corresponding to 2.300 years and 4.000 years disposal respectively when compared to real HLW glasses, and after two years storage of the specimens the quivalent disposal periods of HLW glasses would be 8.500 years or 13.000 years respectively.

Thus, the results of the post-irradiation investigations on these α-emitter doped samples are representative for those effects that might happen during final disposal of HLW glasses due to the α-decay of actinides within about 10.000 years. This disposal period has to be considered as the very important one in view of the decrease of the α-toxity of HLW glasses with respect to the α-toxity of naturally occuring 3% uranium ore (2): the relative α-toxity is decreasing by about three orders of magnitude to a level only slightly above that of uranium ore.

kind of specimen	composition (wt.%)	density (g/cm^3)	α-activity (Ci/g glass) initial	after 1 year	after 2 years	cumulative number of α-disintegrations after 1 year	after 2 years
basic glass "98"	95,1 "98" (1) 4,9 $(Am,Cm)O_2$	2,58	2,63	0,67	0,25	$1,64 \cdot 10^{18}$	$2,12 \cdot 10^{18}$
HLW glass "98"	78,5 "98" 16,6 HLW-oxides (2) 4,9 $(Am,Cm)O_2$	2,74	2,63	0,67	0,25	$1,64 \cdot 10^{18}$	$2,12 \cdot 10^{18}$
HLW-Gd glass "98"	69,0 "98" 16,6 HLW-oxides 9,5 Gd_2O_3 (3) 4,9 $(Am,Cm)O_2$	3,06	2,63	0,67	0,25	$1,64 \cdot 10^{18}$	$2,12 \cdot 10^{18}$

(1) basic glass composition, "98" (wt.%): 50,5 SiO_2, 4,2 TiO_2, 1,4 Al_2O_3, 13,6 B_2O_3, 2,8 CaO, 27,5 Na_2O

(2) HLW-oxides composition: 87,9 wt.% f.p.-oxides from LWR-fuel (burn-up 33.000 MWd/t), 8,4 wt.% Fe_2O_3, 2,4 wt.% Cr_2O_3, 1,3 wt.% NiO

(3) Gd_2O_3 is added in the form of Gd-nitrate solution as homogeneous neutron poison during dissolution of spent nuclear fuel.

Table 1: Data Sheet on Curium Doped HLW Glass Specimens

4. Post - Irradiation Investigations

4.1 Effects of Radiation on Structure, Microscopy

The surface of polished discs of the glass cylinders was observed through the light microscope (fig. 1,2,3). Supplementary photographs of artificially produced crack areas were taken by the scanning electron microscope (fig. 4).

All together the microscopic observation of the specimens as a function of α-disintegration shows no significant radiation effects on the glass structure even in the sphere of metallic inclusions which may be expected as nucleation centers.

4.2 Effects of Radiation on Composition, Autoradiography

Alpha-Autoradiographs taken from polished samples after different decay periods of the actinides dissolved in the glass specimens are demonstrating the unaltered homogeneous distribution of these α-emitters (fig. 5,6,7).

4.3 Helium Buildup and Helium Release Rates

By electron capture the α-particles from actinide decay are converted into uncharged helium atoms. The solubility and diffusion coefficients of helium in borosilicate glasses are unknown. Therefore sometimes an influence of helium generation on the mechanical strength of HLW glasses is discussed {3}.

In order to get an idea on the helium permeation rate the leakage of helium from the three curium doped glass specimens was measured by gas chromatography. The glass cylinders (Ø 10 mm, average weight 5g) were confined in welded stainless steel capsules. After 530 days storage at room temperature these samples were inserted into the gas chromatography measuring assembly. The whole system was evacuated and afterwards the capsules tapped and rinsed with argon for helium measurement.

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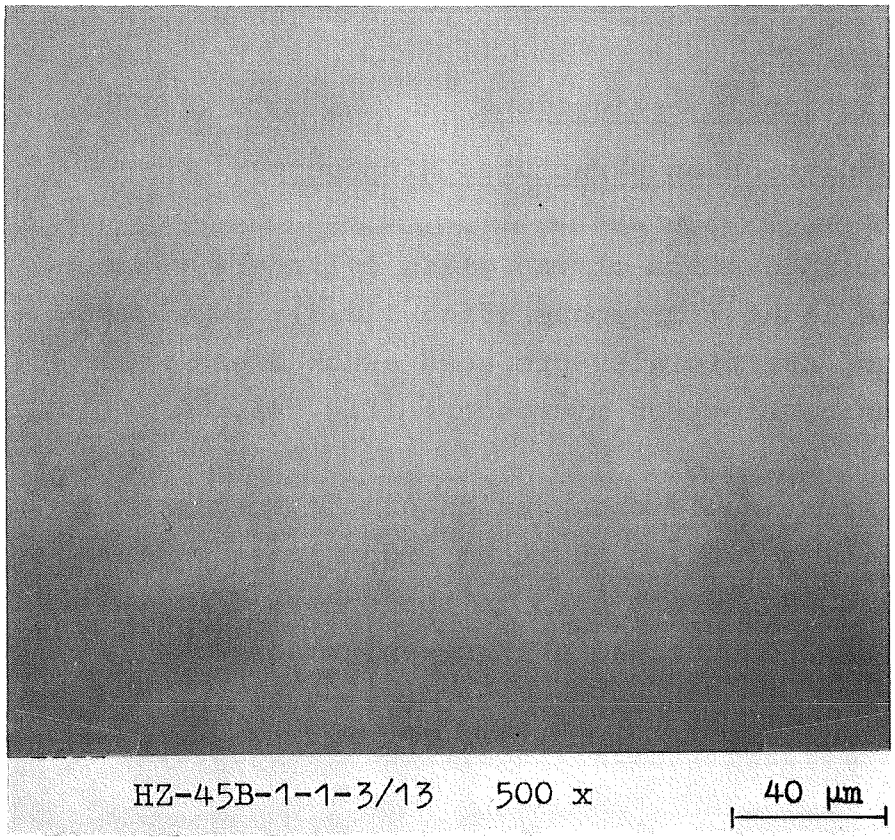
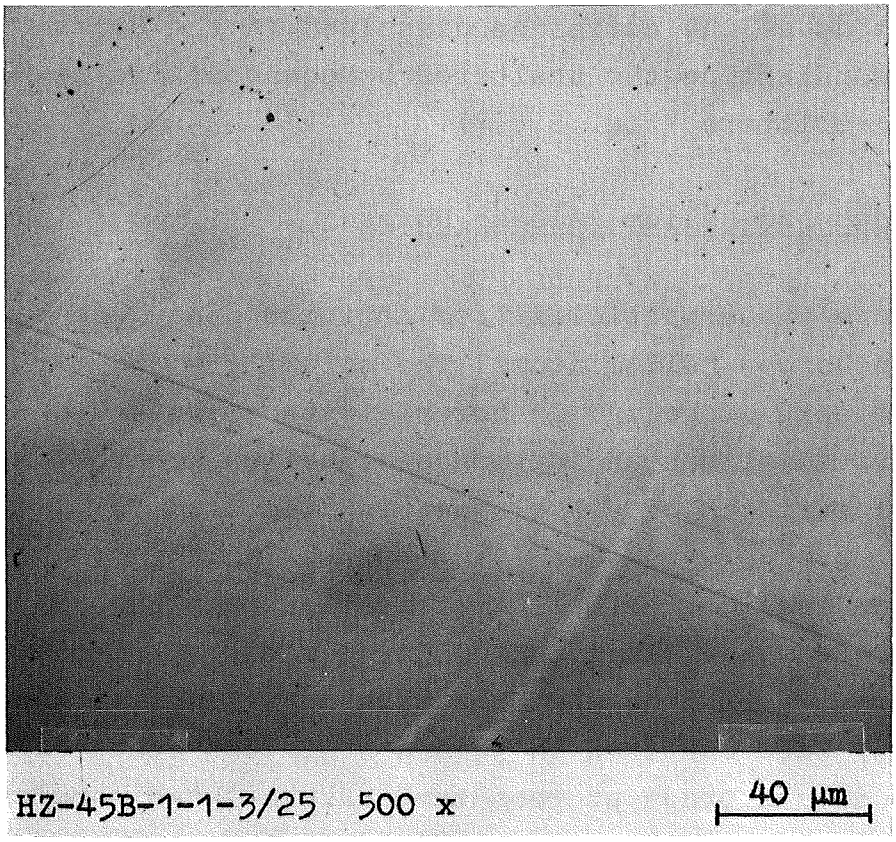


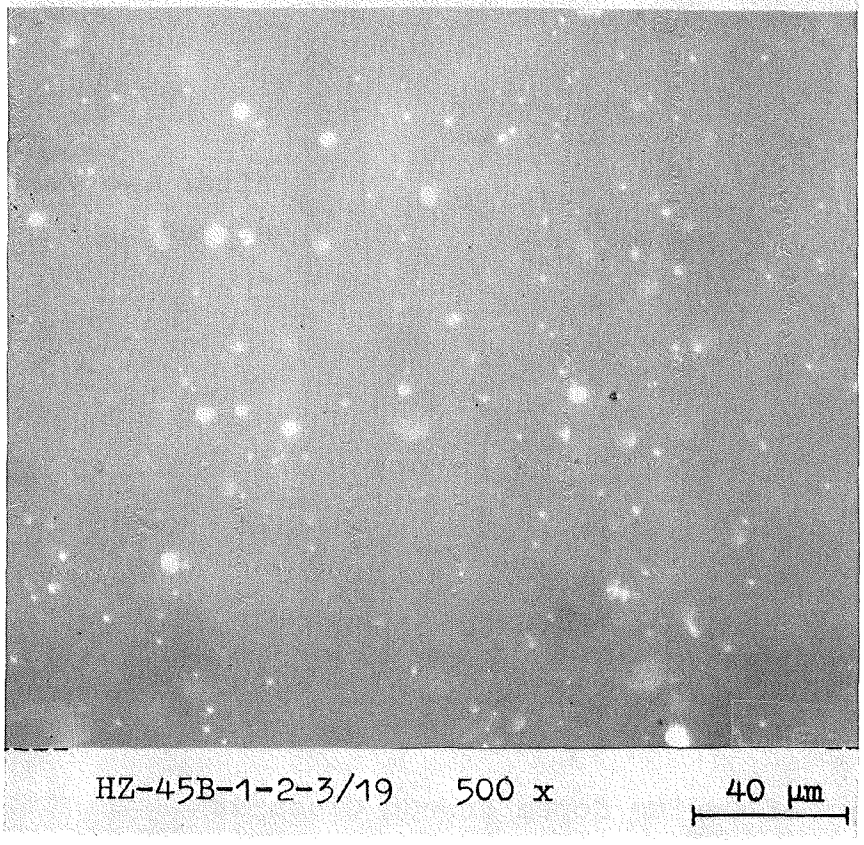
at start of experiment



after two years storage

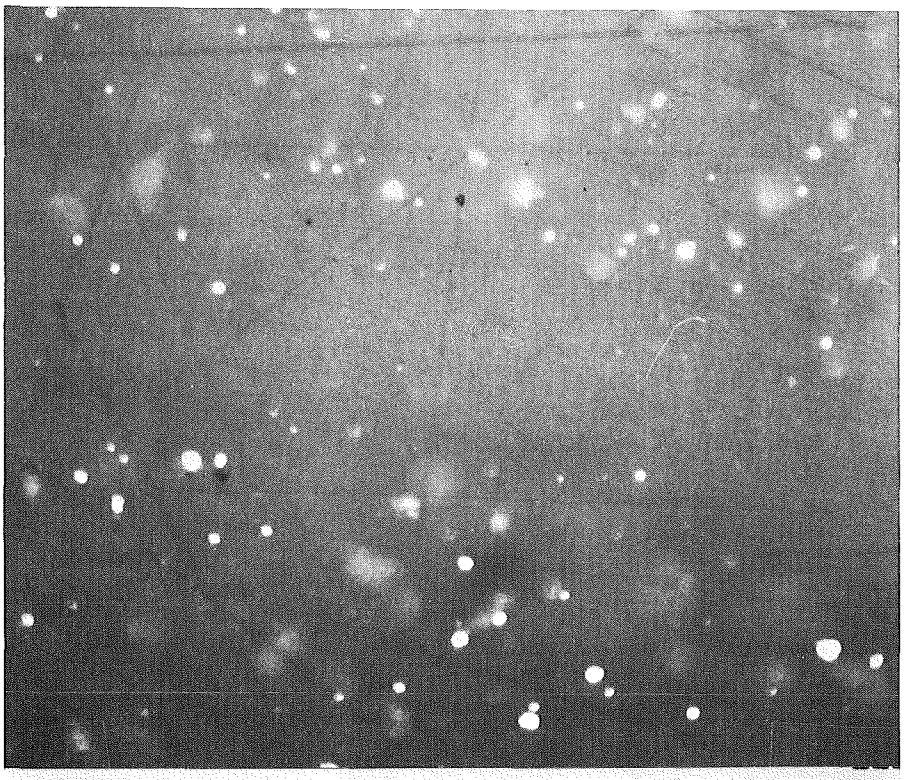
Fig. 1: Microscopy of Curium Doped Basic Glass "98"

as start of experiment



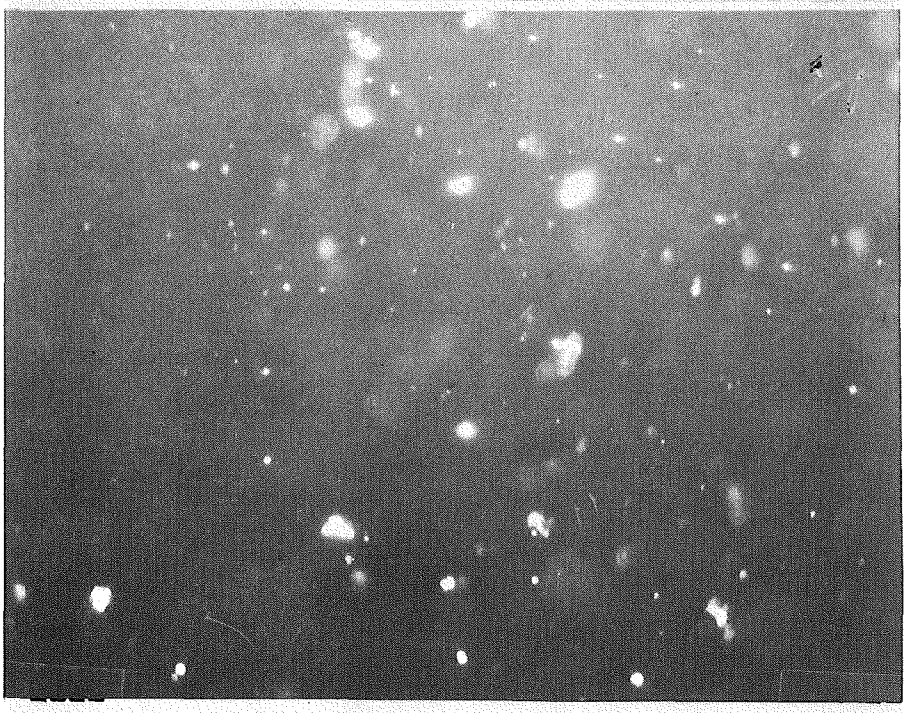
after two years storage

Fig. 2: Microscopy of Curium doped HLW Glass "98"



HZ-45B-1-3-2/4 500x 40 µm

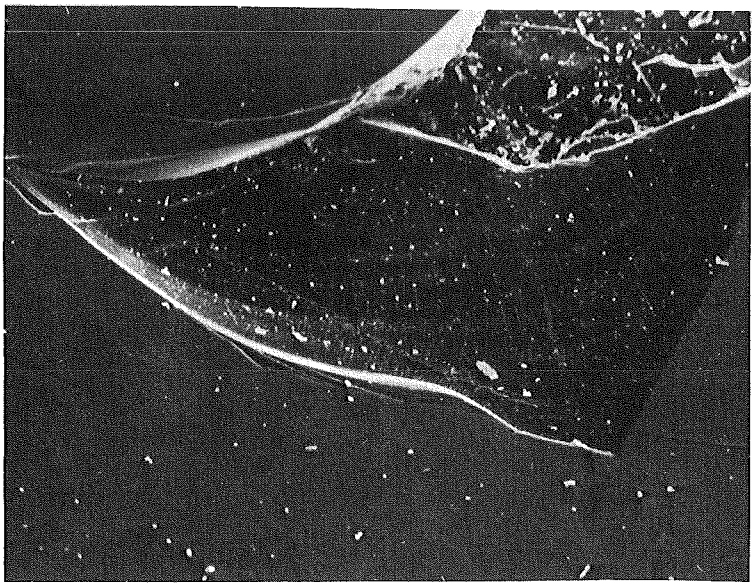
at start of experiment



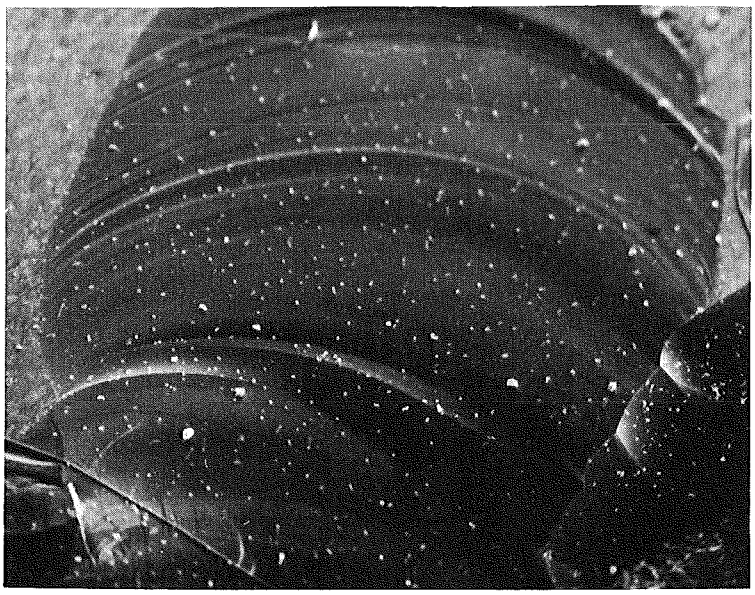
HZ-45B-1-3-3/25 500x 40 µm

after two years storage

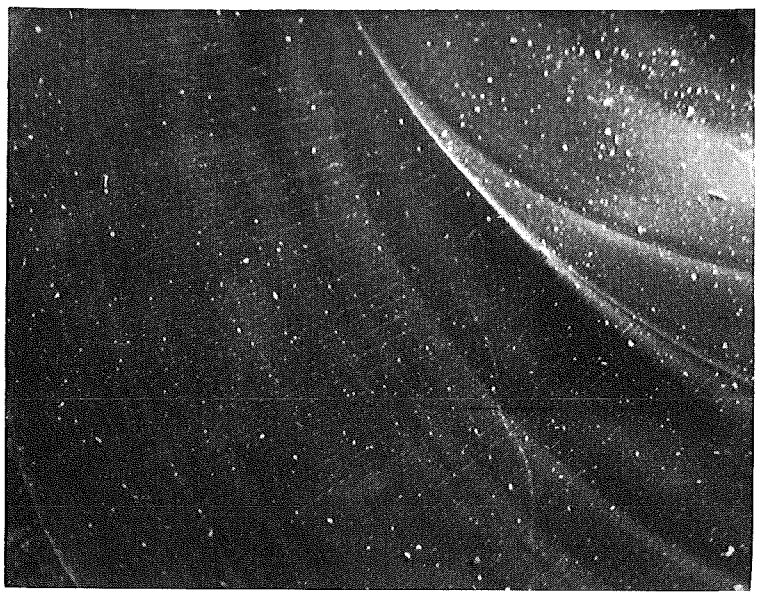
Fig. 3: Microscopy of Curium doped HLW-Gd Glass "98"



basic glass

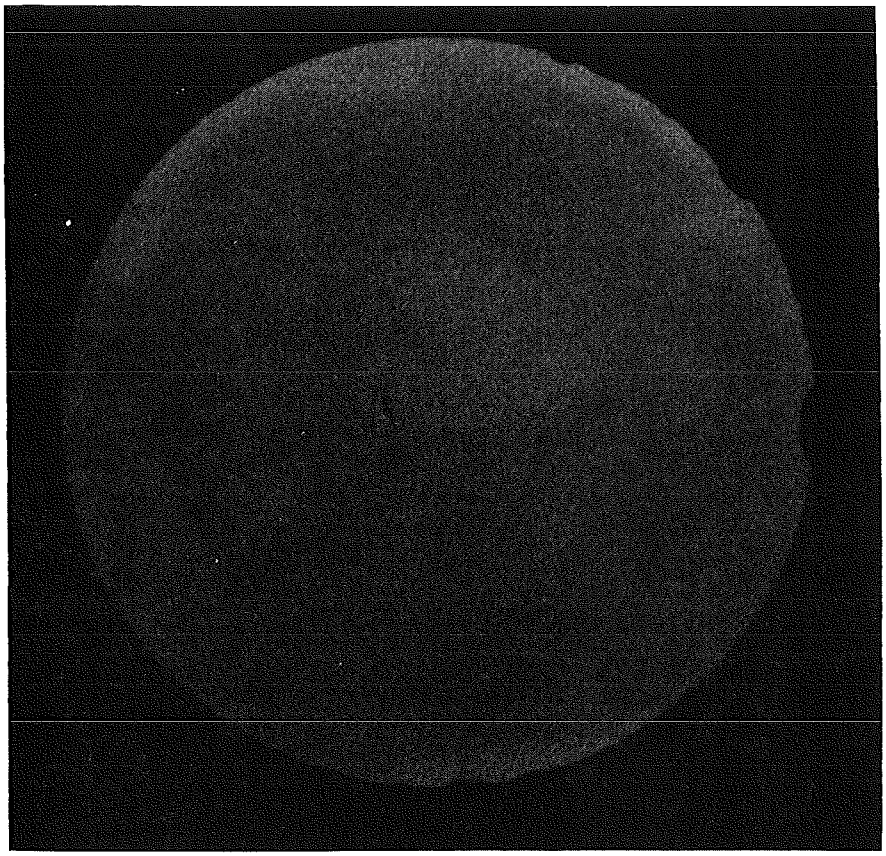


HLW glass '98'



HLW-Gd glass "98"

Fig. 4: Scanning Electron Microscopy on Cracks at Curium Doped Specimens after two years storage



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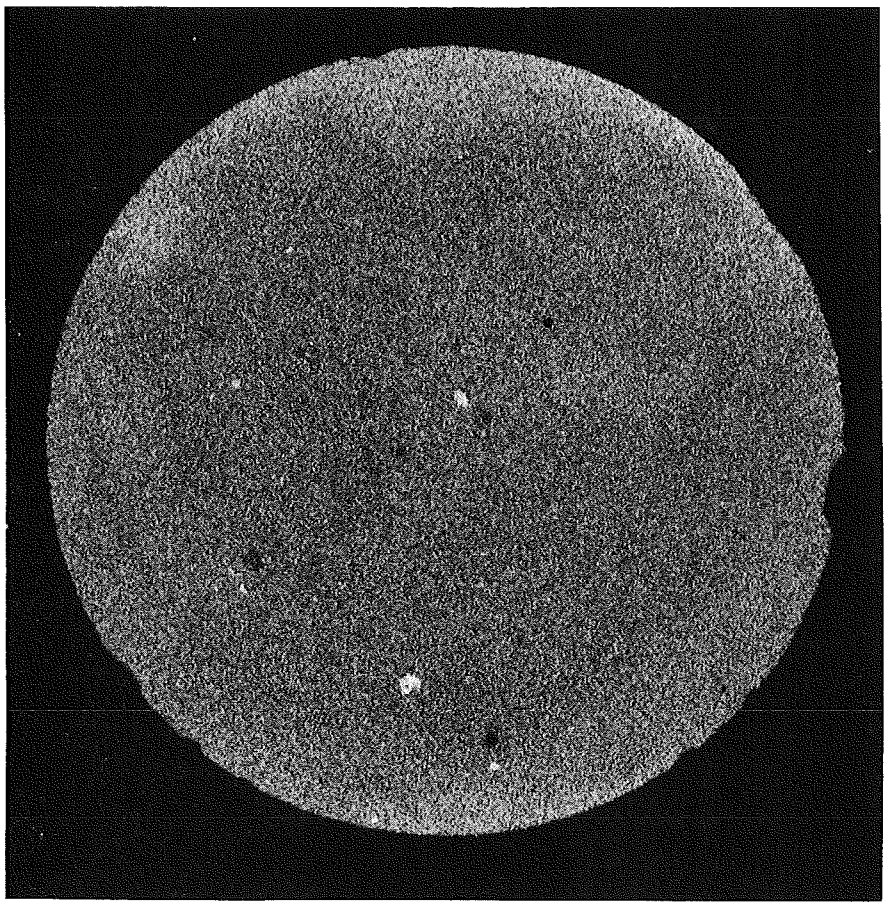
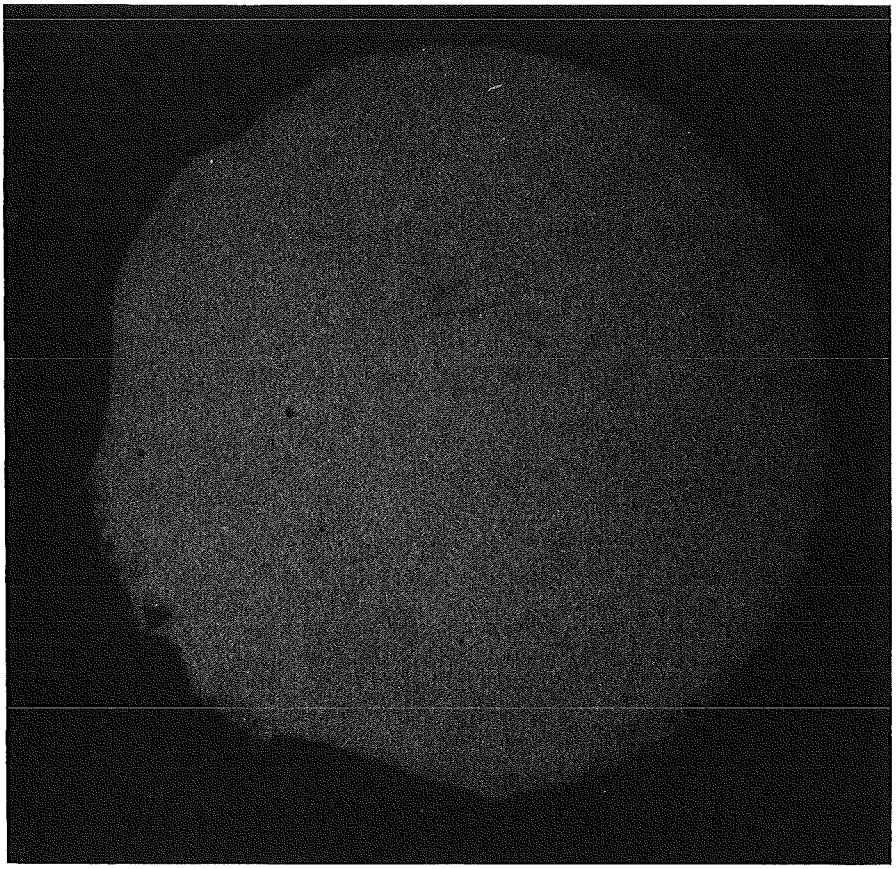
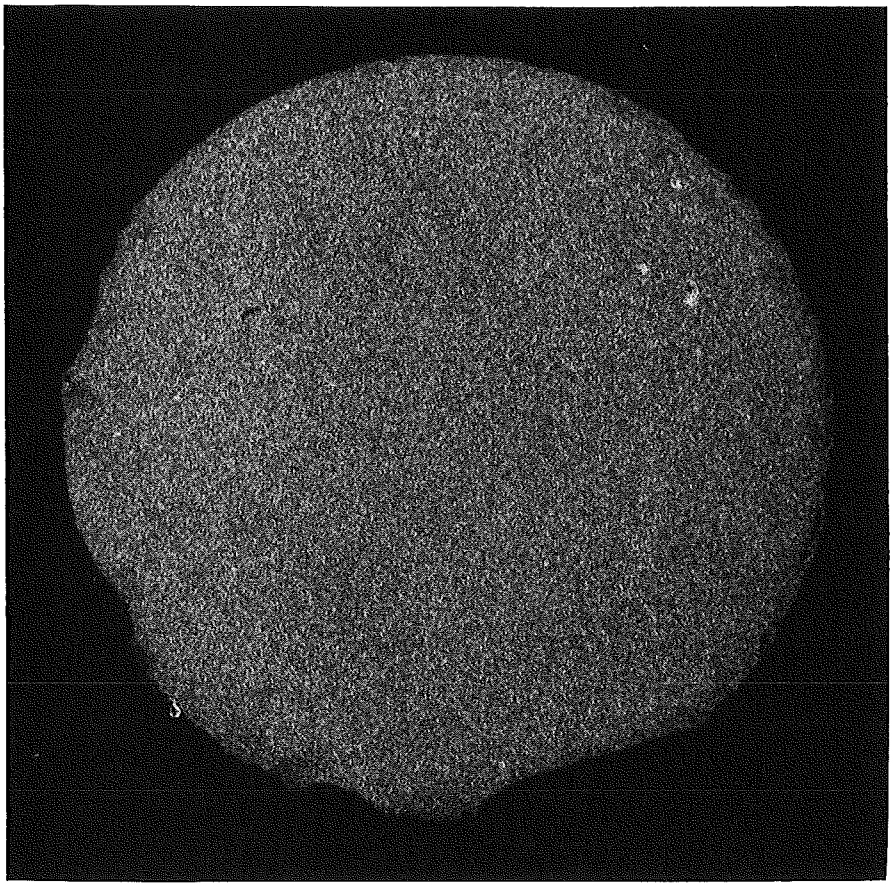


after two years storage

Fig. 5: Alpha Autoradiographs of Curium Doped Basic Glass "98"

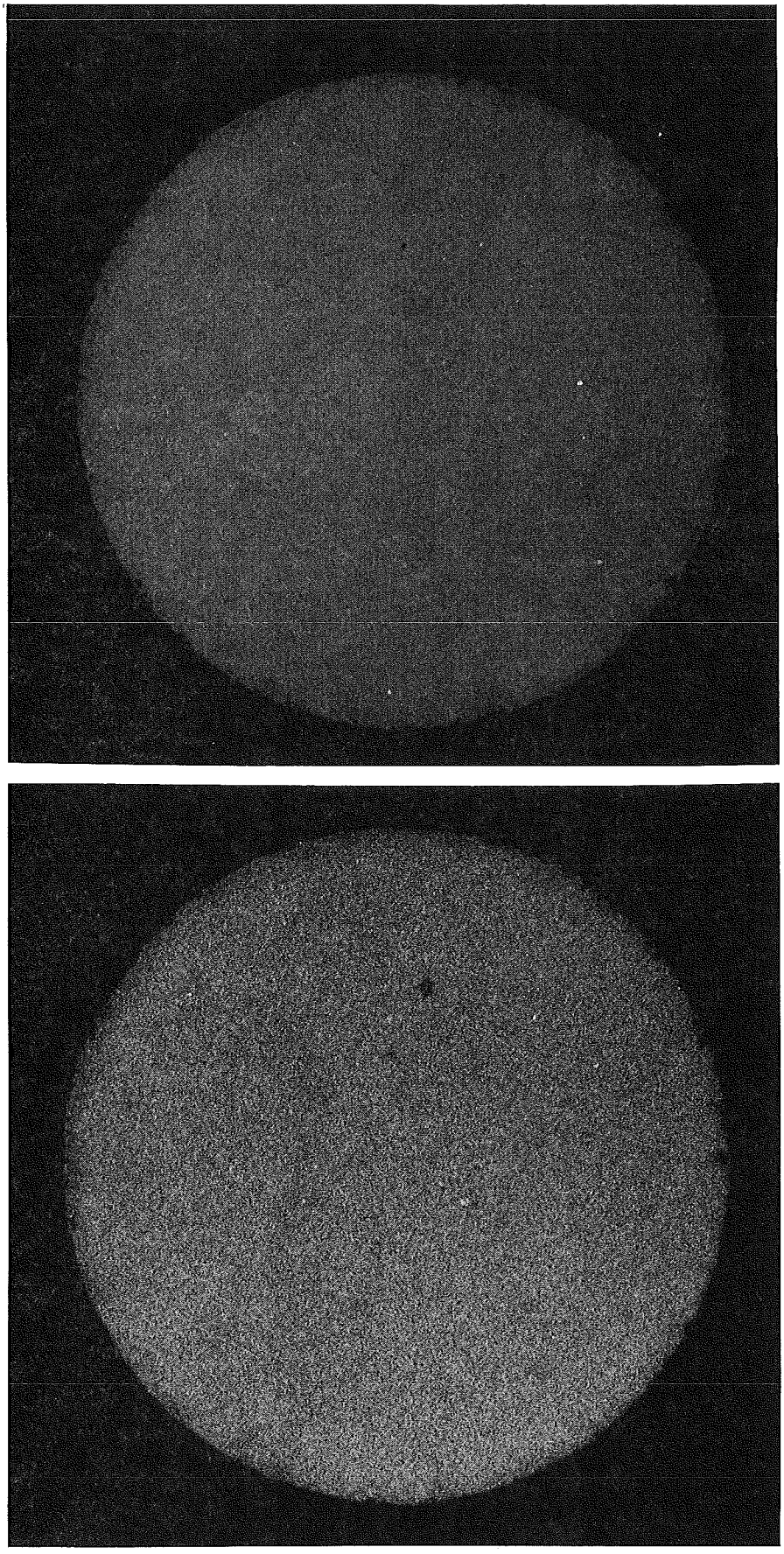


at start of experiment



after two years storage

Fig. 6: Alpha Autoradiographs of Curium Doped HLW Glass "98"



at start of experiment

after two years storage

Fig. 7: Alpha Autoradiographs of Curium Doped HLW-Gd Glass "98"

For all samples no escaped helium could be detected exceeding the sensitivity of the measuring device, which corresponds to a total of 20 mm^3 He per sample.

With the following calculation based on Fick's law an approximate value for the diffusion coefficient of He in the HLW borosilicate glass system has been estimated:

$$\bar{\delta} = \sqrt{2\,Dt}$$

$\bar{\delta}$ mean path length of He atoms {cm}

D He diffusion coefficient $\{cm^2/s\}$

t time {s}

$$\bar{\delta} = r \cdot \frac{a}{\bar{a}_o}$$

r radius of cylindrical sample

a measured He release per g glass

$\bar{a}_o$ average He production per g glass within the time t

$$D = \frac{r^2 \cdot a^2}{2 \cdot t \cdot \bar{a}_o^{\,2}}$$

$r = 0{,}5$ cm

$a < 4\ mm^3/g$ glass

$\bar{a}_o = 46{,}5\ mm^3/g$ glass (see fig. 8)

$t = 530$ days $= 4{,}58 \cdot 10^7$ s

$\underline{D < 2 \cdot 10^{-11}\ cm^2/s}$

From the estimated value for D increasing internal stress in real monolithic HLW glass blocks seems reasonable if the unknown ratio of helium solubility and helium production is low. To answer the question for internal stress and radiation induced changes of the mechanical properties of HLW glasses crack tests have been performed on the irradiated samples - see chapter 4.4 .

4.4 Effects of Radiation on Mechanical Properties, Crack-Test Evaluation

As mentioned above the mechanical properties of the final glass products may be changed by radiation effects during final disposal. There are some common testing procedures for mechanical strength used in glass industry. For these tests it is in any case presupposed that the samples have to undergo very careful preparation, after-treatment and dimensioning prior to testing. But at the expense of these pretreatment procedures only little information is achieved in view of the essential problem.

On the other hand the reasonable objectives are established by the histroy and the future of the products themselves:

- Comparison of different kinds of products
- Intercomparison of products from different processes
- Intercomparison of products before and after irradiation.

An additional marginal restriction has to be taken into account which refers to the more difficult handling of products and equipments in glove boxes or hot cells.

Following these argumentations a simple procedure - the "Crack-Test" - has been elaborated, tested and applied:

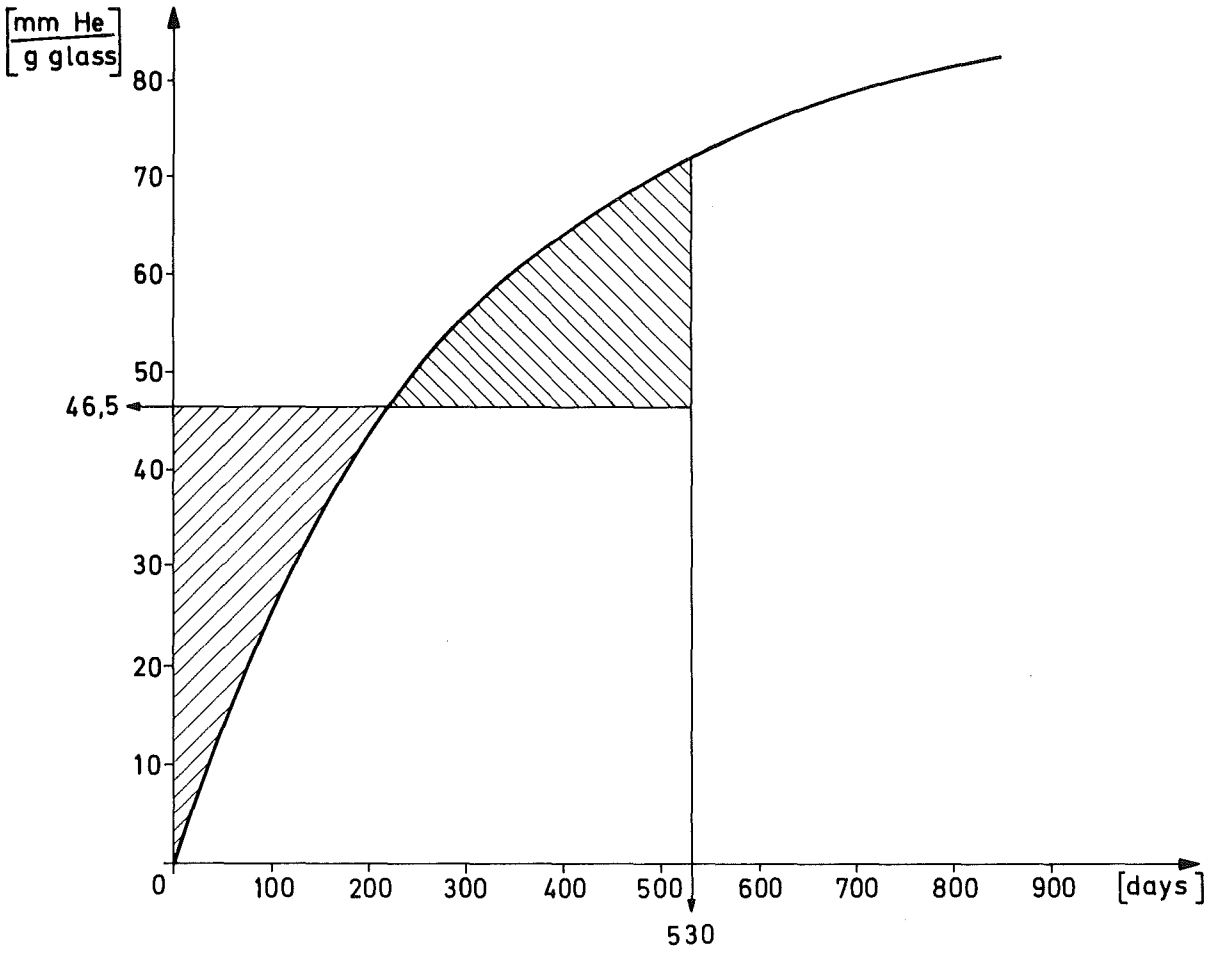


Fig. 8: Helium Generation in Curium Doped Glass Samples

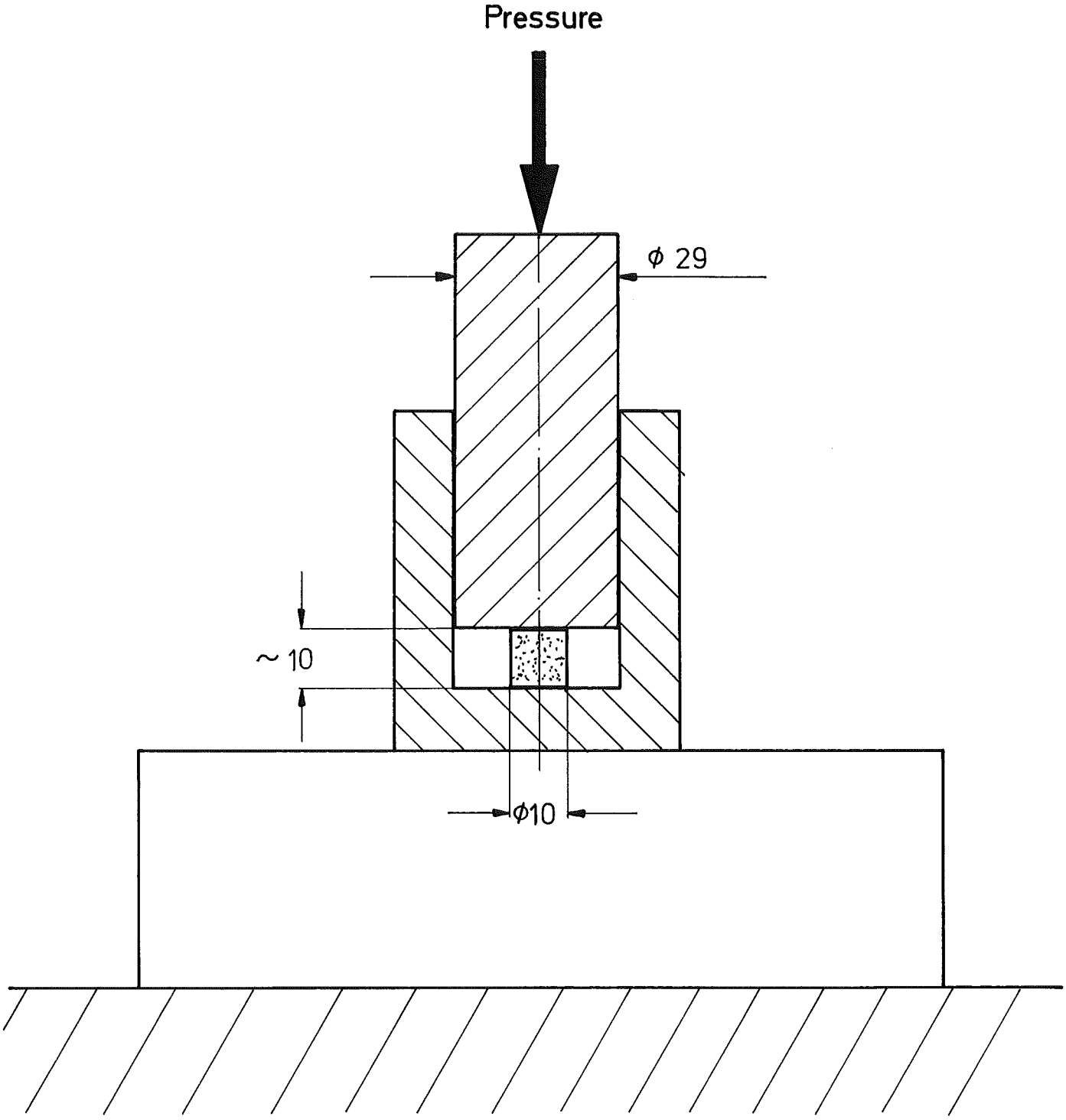
A cylindrical or cube-shaped specimen cut from a bigger sample is inserted into the testing device (see fig. 9) The dimensions of the specimen shall be such that the value of the ratio $\frac{\text{height}}{\text{diameter}}$ shall be about 1. And the value of the ratio $\frac{\text{area of press die}}{\text{area of specimen}}$ shall be about 10.

The specimen and the press die respectively are exposed to a pressure, that shall be ten times larger than the pressure necessary for rupture of the specimen. On the crushed specimen a sieve analysis is performed and evaluated utilizing the RRS-grain size distribution.

For the intercomparison of different types of specimens the average grain diameter $\bar{d}$ has to be standardized to the volume (1 cm^3) of each specimen, since the crushing of the specimen peaces after rupture is dependent on the total particle volume.

In table 2 the results of the crack-tests evaluated on the basis of the RRS plots following the equation $\lg(\lg 100/R) = n \cdot \lg d + C$ are listed (R = weight of cumulative sieving residue in % of total weight, n = expression for the uniformity of grain distribution, d = grain diameter or mesh of the screen).

Apparently the mechanical properties of the Curium doped specimens have changed slightly after irradiation for 2 years (see also table 1) compared to the non-irradiated samples. But their mechanical strength is still in the range of other glass-like products.



Testing Device for Mechanical Stability

Fig. 9

Specimen	average grain diameter $\bar{d}$ (μ)	degree of uniformity of grain distribution n
basic glass "98"	432	0,75
curium doped basic glass "98" after two years storage	466	0,78
HLW glass "98"	355	0,67
curium doped HLW glass "98" after two years storage	534	0,90
HLW-Gd glass "98"	450	0,74
curium doped HLW-glass "98" after two years storage	500	0,78
commercial DURAN glass	270	0,78
commercial fused silica	260	0,73
commercial sintered alumina ALSINT	5800	0,78
basic glas "98",exposed to a thermo-shock of 400°C	305	0,81

Table 2: Crack - Test Results

4.5 Buildup of Stored Energy

On the samples listed in table 1 energy storage following α-disintegration was measured as a function of the total integrated dose up to a dose equivalent to $2 \cdot 10^{18}$ α-disintegrations/g glass {1}. A saturation value for stored energy is already obtained after about $1 \cdot 10^{18}$ α-disintegrations/g glass{ 1 }. Final values are given in table 3.

Specimen	stored energy (cal/g glass)
basic glass "98"	64 ± 3
HLW glass "98"	83 ± 3
HLW-Gd glass "98"	94,5 ± 2

Table 3: Stored Energy in Borosilicate Glasses after $2{,}12 \cdot 10^{18}$ α-Disintegrations per g Glass

4.6 Effects of Radiation on Leachability, Leach Rates of Actinides

The leaching rates of Curium and Americium were determined in a run of long-term leach tests on the three glass compositions (see table 1).

A somewhat modified leach test when compared to the IAEA-recommended procedure {4} was applied:

Glass specimens were imbedded in Araldite, grinded and polished. The so prepared surface of the specimens was exposed to the different leachants (table 4) at room temperature (23 ± 3°C).

In certain intervals the suspended specimens were withdrawn and introduced into new leachant containers with fresh leachants. The spent leachants were acidified with nitric acid within the leachants containers. Homogenized samples of these leach solutions were taken for α-counting an α-spectrometry for Americium and Curium determination.

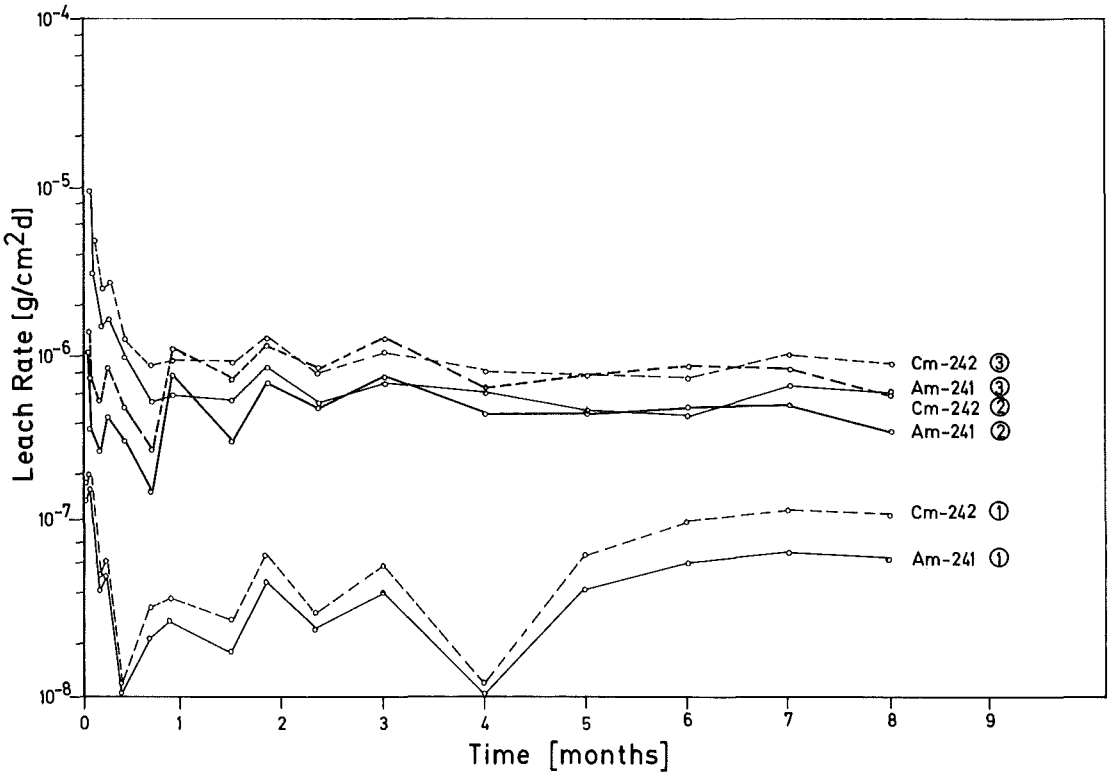
Fig. 10 shows the leaching rate versus time plot from leach tests with demineralized water. Within the total leaching period comprising 8 months the cumulative number of α-disintegrations was increasing up to a value of $1,3 \cdot 10^{18}$ α's /g glass. Nevertheless the leaching rates remained obviously constant indicating that no significant changes of the glass matrix with respect to any leacheability - radiation dose dependence could be detected.

leachant	basic glass "98"	HLW glass "98"	HLW-Gd glass "98"
demineralized water	$3,8 \cdot 10^{-8}$	$5,5 \cdot 10^{-7}$	$6,0 \cdot 10^{-7}$
0,01 M NaCl-solution	$1,4 \cdot 10^{-6}$	$1,4 \cdot 10^{-6}$	$1,4 \cdot 10^{-6}$
1 M NaCl-solution	$1,4 \cdot 10^{-6}$	$4,0 \cdot 10^{-6}$	$22,0 \cdot 10^{-6}$
1 M $MgCl_2$-solution	$0,7 \cdot 10^{-6}$	$0,6 \cdot 10^{-6}$	$1,8 \cdot 10^{-6}$
saturated Carnallite-solution+	$1,8 \cdot 10^{-6}$	$5,7 \cdot 10^{-6}$	$24,0 \cdot 10^{-6}$

+) composition of saturated carnallite solution: 62,83 wt.% H_2O, 2,04 wt.% $MgSO_4$, 34,3 wt.% Mg Cl_2, 0,62 wt.% K Cl, 0,21 wt.% NaCl

Table 4: Leach Rates (g/cm^2d) of Americium from Curium Doped Glass Specimens in different Leachants.

The long-term leaching rates of americium are listed in table 4.



① basic glass "98"
② HLW glass "98"
③ HLW-Gd glass "98"

Fig. 10: Long-Range Leaching Rates for Am and Cm for Curium Doped Glass Specimens (Leachant: Water)

5. Summary and Conclusions

By time-lapse experiments and subsequent post-irradiation studies on Cm-242 doped HLW glasses it has been demonstrated that borosilicate glasses are stable against long-term radiation from α-decay of the long-lived actinides.

The mechanical strength of the glass products is altered slightly but within the limits of mechanical strength for common glass systems. Structure and homogeneity of the borosilicate glasses as well as their leachability are not affected by radiation.

The number of atomic displacements due to α-disintegration is macroscopically indicated by the stored energy in HLW glass. The formation and annealing of atomic displacements gets up to an equilibrium at about 10^{18} α-disintegrations per g glas represented by the saturation values for stored energies. At the values measured, even if a spontaneous release of stored energies would take place, the temperature increase in the glasses would be below 300°C.

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Europäisches Institut für Transurane, (EURATOM), Karlsruhe

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