KERNFORSCHUNGSZENTRUM

KARLSRUHE

Juni 1975

KFK 2162

Experimental Studies on the Possibility of Using a Ceramic Matrix for Fixing the High Level Radioactive Wastes

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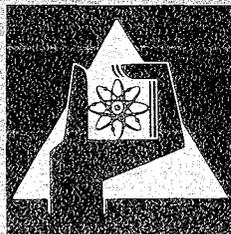
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KFK-2162
PWA 1/75

Abteilung Behandlung radioaktiver Abfälle

Experimental Studies on the Possibility of
Using a Ceramic Matrix for Fixing the High
Level Radioactive Wastes

by
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Abstract

A ceramic product has been developed to fix high level radio-
active wastes for storage and final disposal. In the present
experiments some of the properties, e.g. visual change, change
in size or shape, change in weight, change in structure, density
and leachability, are studied for the long term stability of
the product under heat and radiation treatment. The properties
are not severely affected by radiation or by heat treatment.
The leaching property is slightly affected due to heating.
From the results it appears that the heating has a dominant
effect over the radiation on the properties of the ceramic
product.

Zusammenfassung

Zur Fixierung hochradioaktiver Abfälle für Lagerung und Besei-
tigung wurde ein keramisches Produkt entwickelt. In den hier
beschriebenen Versuchen wurden einige von dessen Eigenschaften,
z.B. Aussehen, Ausmaße und Gestalt, Gewicht, Struktur, Dichte
und Auslaugbarkeit, im Hinblick auf die Langzeitbeständigkeit
des Produktes unter der Einwirkung von Wärme und Strahlung un-
tersucht. Diese Eigenschaften werden durch eine Behandlung mit
Wärme oder Strahlung nur unwesentlich verändert; lediglich die
Auslaugbarkeit wird geringfügig vergrößert. Die Ergebnisse
zeigen, daß die Eigenschaften des keramischen Produktes durch
Wärmeeinwirkung stärker verändert werden als durch Strahlen-
einwirkung.

Contents

1. Introduction

The hazard inherent in the highly radioactive fission products from reprocessing nuclear fuels requires that their final disposal be preceded by a step of fixation into a solid medium. Various solidification methods have been discussed so far; incorporation into borosilicate glass has found the most general acceptance. One of the possible alternatives is the use of a thermite reaction to produce a solid material containing highly active fission products [1,2,3]. In this line, however, no extensive work has been done so far.

A solidification process making use of the thermite reaction is under investigation in the Karlsruhe Nuclear Research Center. In laboratory experiments a ceramic product has been developed which is generated in the reaction of aluminium with manganese dioxide and which appears to have certain advantages over glass [4]. Investigations are continuing to fully explore all safety aspects of this product. Some results relating to its thermal and irradiation stability are presented in this report.

2. Computation of Cumulative Radiation Doses

The solid medium containing high level radioactive wastes must maintain its integrity during long term storage. The continuous irradiation from decaying radioisotopes causes an energy deposition and also a rise of temperature in the medium which may affect the physical and chemical properties of the product itself. The cumulative doses from this radiation have been calculated as varying from 10^{10} to 10^{12} rads for glass medium; the value of 10^{12} rads, e.g., has been obtained by ELLIOT [5].

A computation of cumulative doses expected in ceramic material from the thermite reaction is shown in Figure 1. The values are computed for LWR fuel, a burn-up of 33,000 MWd/t and an activity concentration in the ceramic material of 10,000 Ci/litre. This activity concentration corresponds approximately to the following concentrations of fission product oxides:

Cooling time 150 d   - 75 g/l of fission product oxides
    "   365 d - 160 g/l   "
    "   730 d - 330 g/l   "
    "   1830 d - 751 g/l   "

The ceramic material described in the following sections has a fission product oxide concentration of about 580 g/l. For calculating the actual radiation dose to this product, a proportionality between concentration and dose may be assumed to exist. In these calculations it is assumed that $100^{\circ}/o$ of the significant fission product elements, not including actinides, are incorporated in the ceramic matrix. Curves I, II, III and IV represent fission products aged 150 days, 1, 2 and 5 years, respectively, age meaning the interval between withdrawal from the reactor and fixation into the solid medium. From these calculations it is seen that there will be the maximum absorbed dose of $9 \cdot 37 \times 10^{11}$ rads in the solid block when fission products aged 5 years are incorporated and stored for an infinitely long time, assuring complete decay.
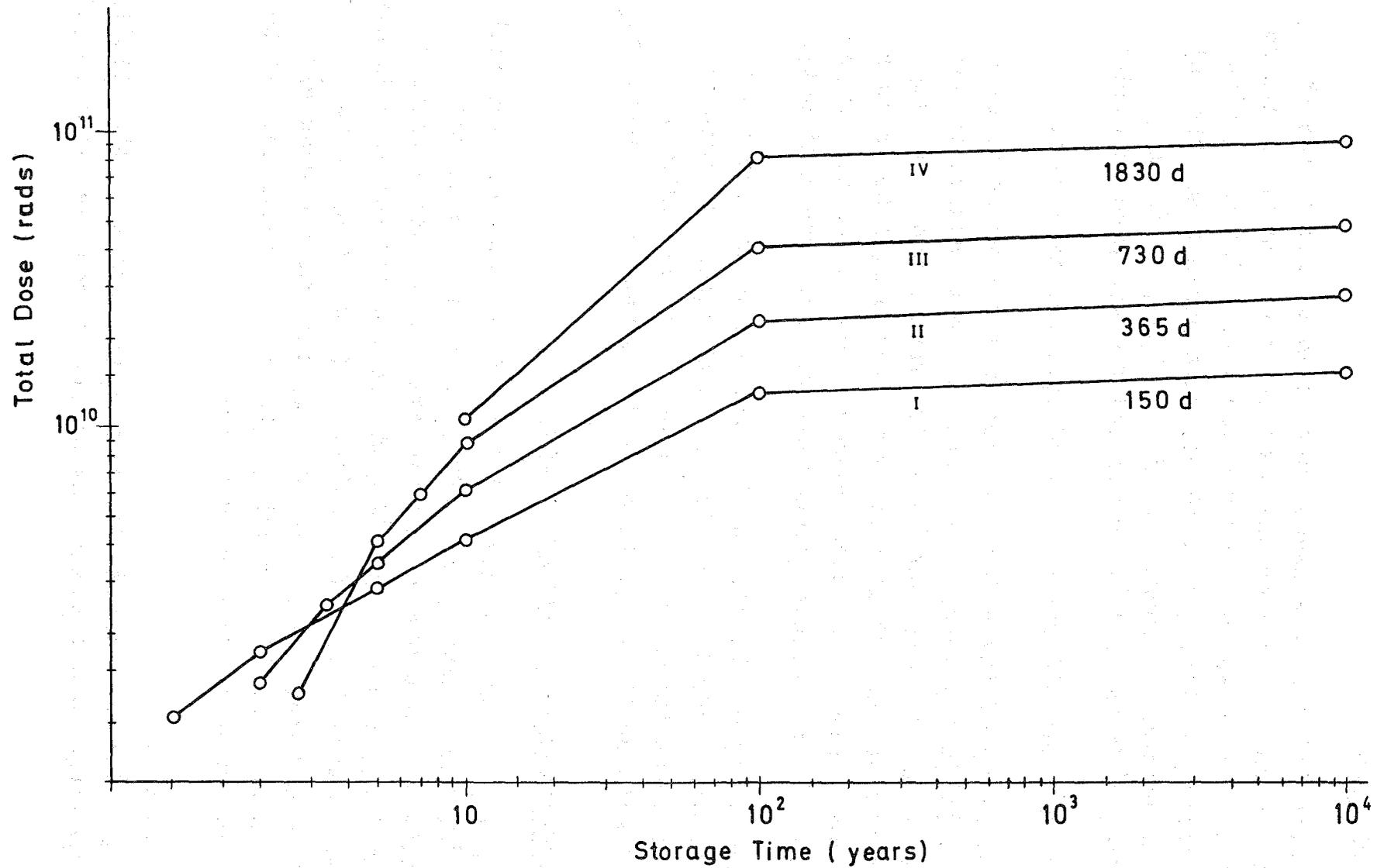
Fig. 1 Variation of Total Absorbed Doses with storage time of the ceramic block containing fission products of different age (specific initial activity: 10^4 Ci/l)

3. Experiments

The samples for the experiments have been prepared from the ceramic blocks produced by the thermite reaction of aluminium, manganese dioxide and silicon dioxide with addition of simulated fission product oxides [4,6]. This product has the following approximate composition: $50^o/o$ Al_2O_3, $15^o/o$ SiO_2, $15^o/o$ MnO, $3^o/o$ Na_2O, $17^o/o$ simulated fission product oxides.

The experimental program is divided into two main parts:

(a)   The study of the effect of time on the samples of ceramic product maintained at constant temperatures in the range of 400^oC to 1000^oC. It is assumed that the temperature during actual long term storage will be in this range. This is to investigate the effects on the properties of the ceramic product due to heat treatment only.

(b)   The study of the effect of radiation on the samples of ceramic product for different total absorbed doses at different energies of radiation. This will show the effects on the properties due to radiation treatment only.

3.1. Experiments on Heating Effects

Rectangular or cubic samples of 5 or 10 mm diameter were kept at 400^oC, 600^oC, 800^oC, and 1000^oC for 55 and 75 hours*, respectively, in a small electric oven. This oven attains a maximum temperature of 1000^oC with its lid on. For experiments at lower temperatures, the desired temperature has been attained by using a transformer. Temperatures are measured by thermocouples. After heating, the sample blocks were allowed to cool down to room temperature.

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* these times were chosen for easy comparison with the effects of irradiation which requires similar times (see section 3.1.2)

3.2. Experiments on Radiation Effects

From Figure 1 it is seen that the maximum radiation energy absorbed by beta and gamma radiation during storage for thousand of years is 9.4×10^{11} rads for fission products aged 5 years and 4.8×10^{11} rads for fission products aged 2 years. Hence the experiments were designed to irradiate the samples to a total absorbed dose of about 10^{11} rads. Total absorbed doses of about 10^{10} rads were also used to investigate the dose dependence of the property changes. For similar reasons different energies of radiation were used, i.e. electrons of 5 and 10 MeV. It should be noted that the actual decay energies of fission products are in a much lower range; however, 5 MeV is the lowest energy attainable in the linear accelerator used for the irradiation.

The samples are cut to rectangular blocks of 5 mm thickness and 30 mm length or to cubes of 10 mm with a diamond saw for irradiation with a 5 and 10 MeV electron beam, respectively. This is sufficient to absorb the nominal dose almost homogeneously throughout the entire thickness [7]. The average dose rates for 5 and 10 MeV electron beams are 0.225×10^8 rads/minute and 0.30×10^8 rads/minute, respectively. Thus for a total absorbed dose of 10^{10} rads the irradiation times are about 7.5 and 5.5 hours, respectively, and ten times these values for a total absorbed dose of 10^{11} rads. In the latter case it is not possible to irradiate the samples by a continous run of the linear accelerator.

During irradiation the samples become heated. Although an exact temperature measurement is not possible during irradiation, the temperature may be estimated by extrapolation. Sample blocks of about 10 mm thickness were irradiated for 5,15,30,60 and 120 minutes at 10 MeV electron beam energy with an average dose rate of 0.30×10^8 rads/minute. Just after the irradiation, the temperature on the surface of the samples was measured by a contact thermometer at intervals

of 1/2 minute while cooling down to room tempearature. Figure 2 shows the results obtained. From this figure the maximum temperature of the sample is extrapolated and gives a value of approximately 160°C. In another experiment of irradiating the sample for 5.5 hours, the surface temperature measurements of the sample also gave a maximum temperature of 160°C by extrapolation. Therefore it may be assumed that the surface temperature of the samples during irradiation will not exceed 160°C, regardless of irradiation time.
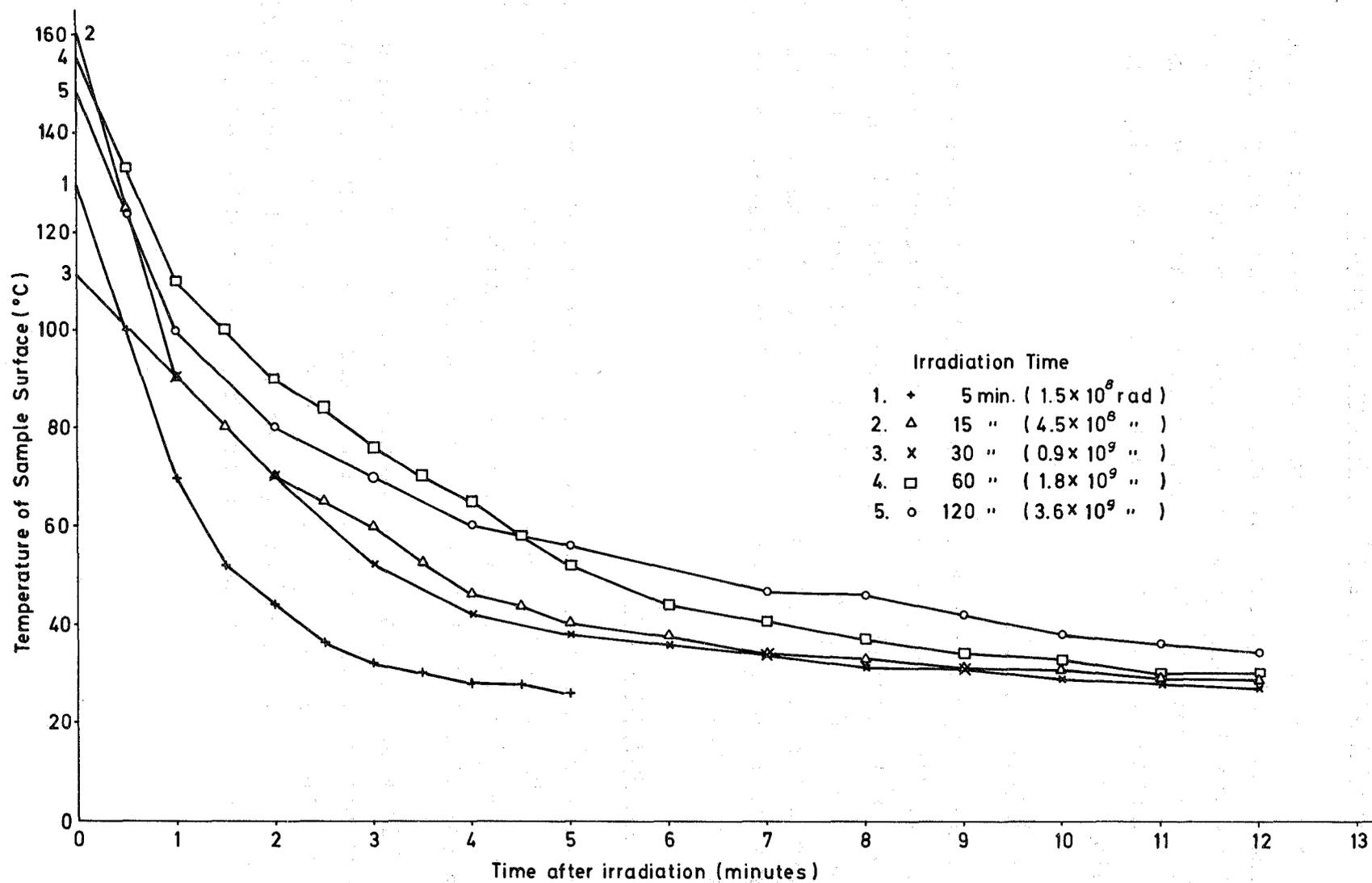
Fig. 2 Extrapolation of the temperature on the sample surface during irradiation

4. Results and Discussion

4.1. Discussion of Results on Heating Effects

Each group of experiments is carried out with samples from the same batch of ceramic product. After the heat treatment at different temperatures for different periods of time, the samples are examined for visual change, change in size and shape, change in weight, change in structure, density, and leaching rate.

4.1.1. Change in Color

The color of the samples changes on heating from greenish yellow to dark brown. This color change is merely superficial and does not proceed into the interior of the samples. It is assumed to be due to oxidation to the tetravalent state of the manganese contained in the product which has been left in a lower state of oxidation after the aluminothermic process of preparation.

4.1.2. Change in Weight

There is a slight gain in weight when the ceramic samples are heated to higher temperatures. After 168 hours, for example, the weight of 5 samples has increased by an average of $2 \cdot 10^{-3}$ grams per square centimeter of surface area at $1000^{\circ}C$.

From this value it may be estimated how far the oxidation process proceeds into the product. Assuming a reaction according to $MnO + 1/2\ O_2 \rightarrow MnO_2$, a content of MnO of $15^{\circ}/o$ and a densitiy of $3.4\ g/cm^3$ of the product, a weight increase of $2 \cdot 10^{-3}\ g/cm^2$ corresponds to a depth of penetration of 0.017 cm.

4.1.3. Shape and Size

From visual inspection no change in shape is observed. Dimensional measurements were made with the help of a slide caliper having an accuracy of ± 0.005 cm. There was an increase in the linear dimensions amounting, e.g., to 0.005 to 0.02 cm in the case of samples heated to 1000°C. Also this effect is believed to be due to superficial oxidation since no appreciable change in density is observed (see section 4.1.5.).

4.1.4. Change in Structure

Figure 3 shows X-ray diffraction powder photographs of samples heated to 400,600,800, and 1000°C for various periods of time, each picture containing the untreated sample for comparison. For calibration purposes, elemental silicon has been added to each sample. As can be seen from the photographs, the untreated product gives a large number of lines due to the presence of crystalline phases. The only compound which can be identified is β-Al_2O_3, a hexagonal form of alumina which is stabilized by the presence of small amounts of sodium. The following changes are observed after heat treatment:

1. At 400 and 600°C, one unidentified phase decreases or vanishes.

2. At 800 and 1000°C, after 55,75 and 168 hours, a new phase appears which has been identified to be nepheline ($NaAlSiO_4$).

3. At 800°C after 168 hours and at 1000°C after 75 hours or more, a compound of spinel structure is formed having the formula M_3O_4, possibly with excess oxygen. The lattice constant determined from the photographs is a= 8.2 $\overset{o}{A}$. This corresponds, for example, to $(Fe,Al)_{3-x}O_4$ (a= 8.11...8.22$\overset{o}{A}$) or MgO-Cr_2O_3-Al_2O_3 (a= 8.00...8.33$\overset{o}{A}$), or a mixture thereof.
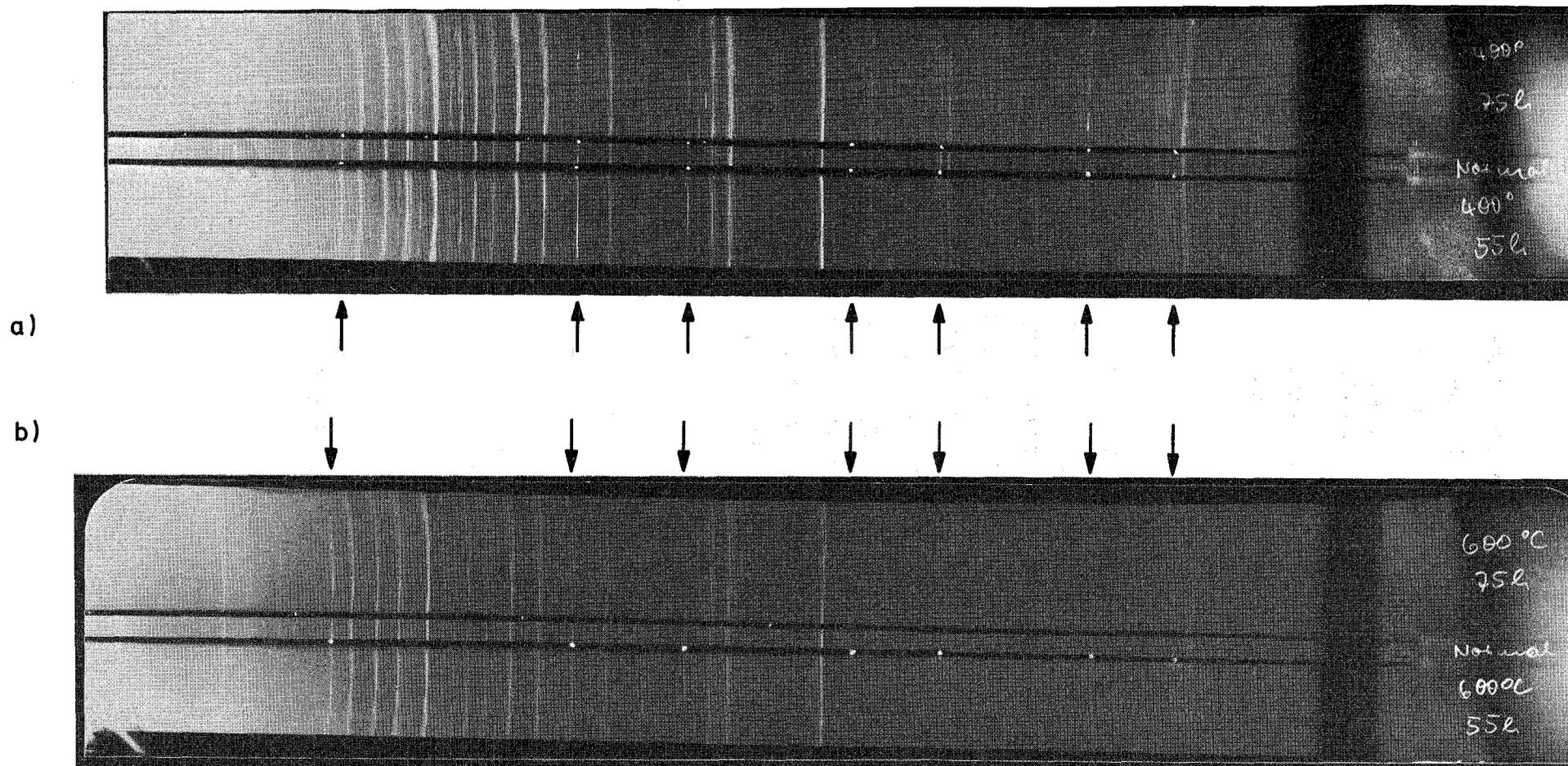
Fig. 3   X-ray diffraction powder photographs of heated and unheated (normal) samples
(GUINIER photographs, $Cu-K\alpha_1$ radiation, silicon added for calibration)

   a) Samples heated at $400^{\circ}C$ for 55 and 75 hours
   b) Samples heated at $600^{\circ}C$ for 55 and 75 hours
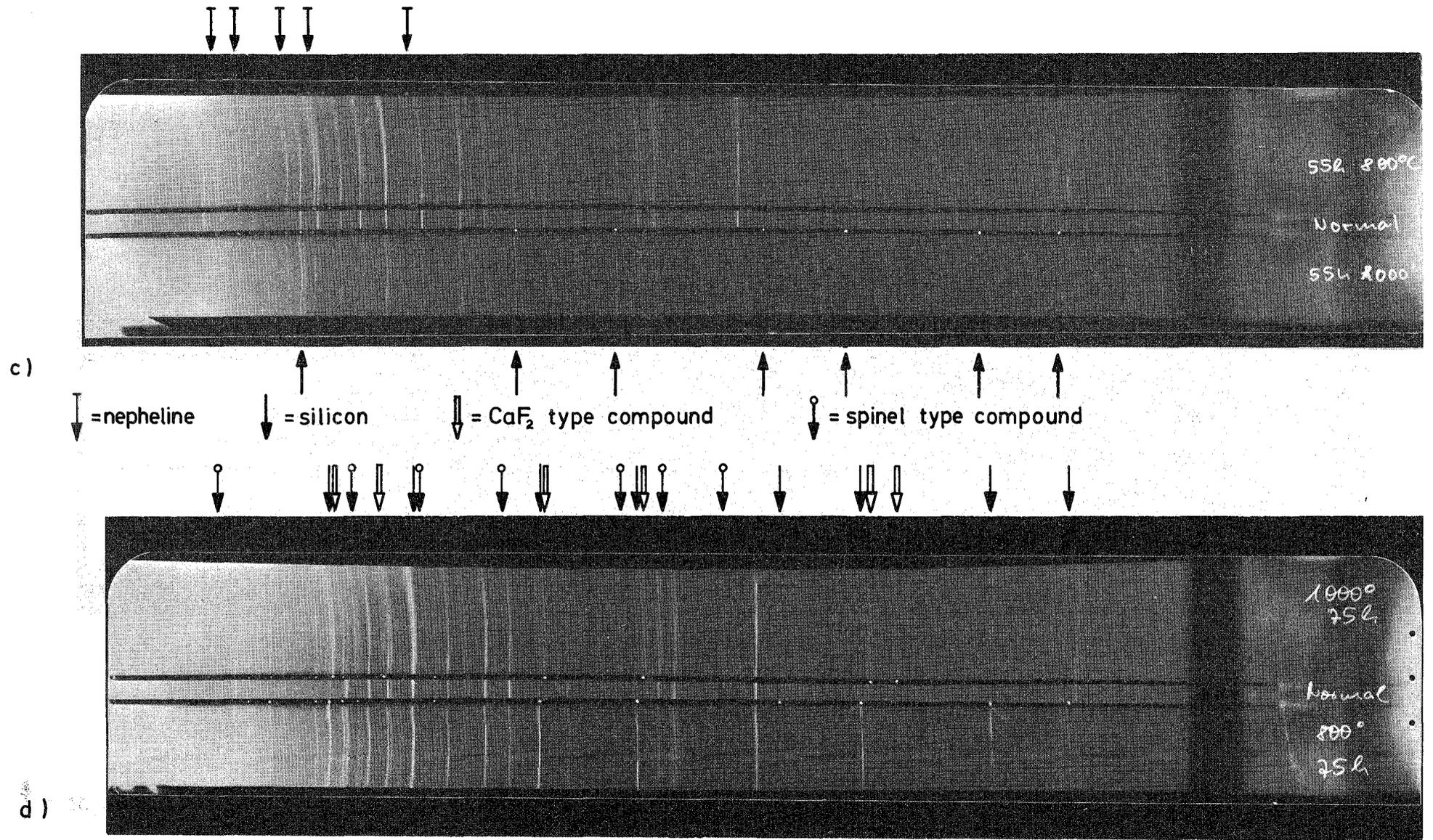
Fig. 3 (cont'd)   c) Samples heated at 800°C and 1000°C for 55 hours
                   d) Samples heated at 800°C and 1000°C for 75 hours
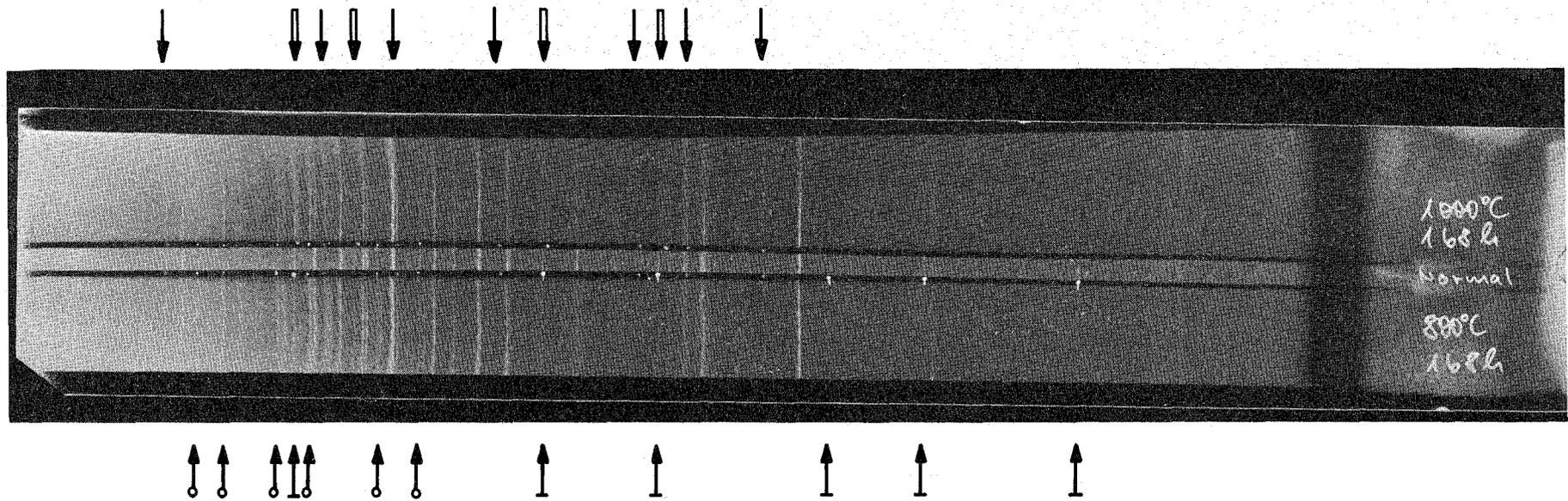
Fig. 3 (cont'd.)

   e) Samples heated at 800°C and 1000°C for 168 hours
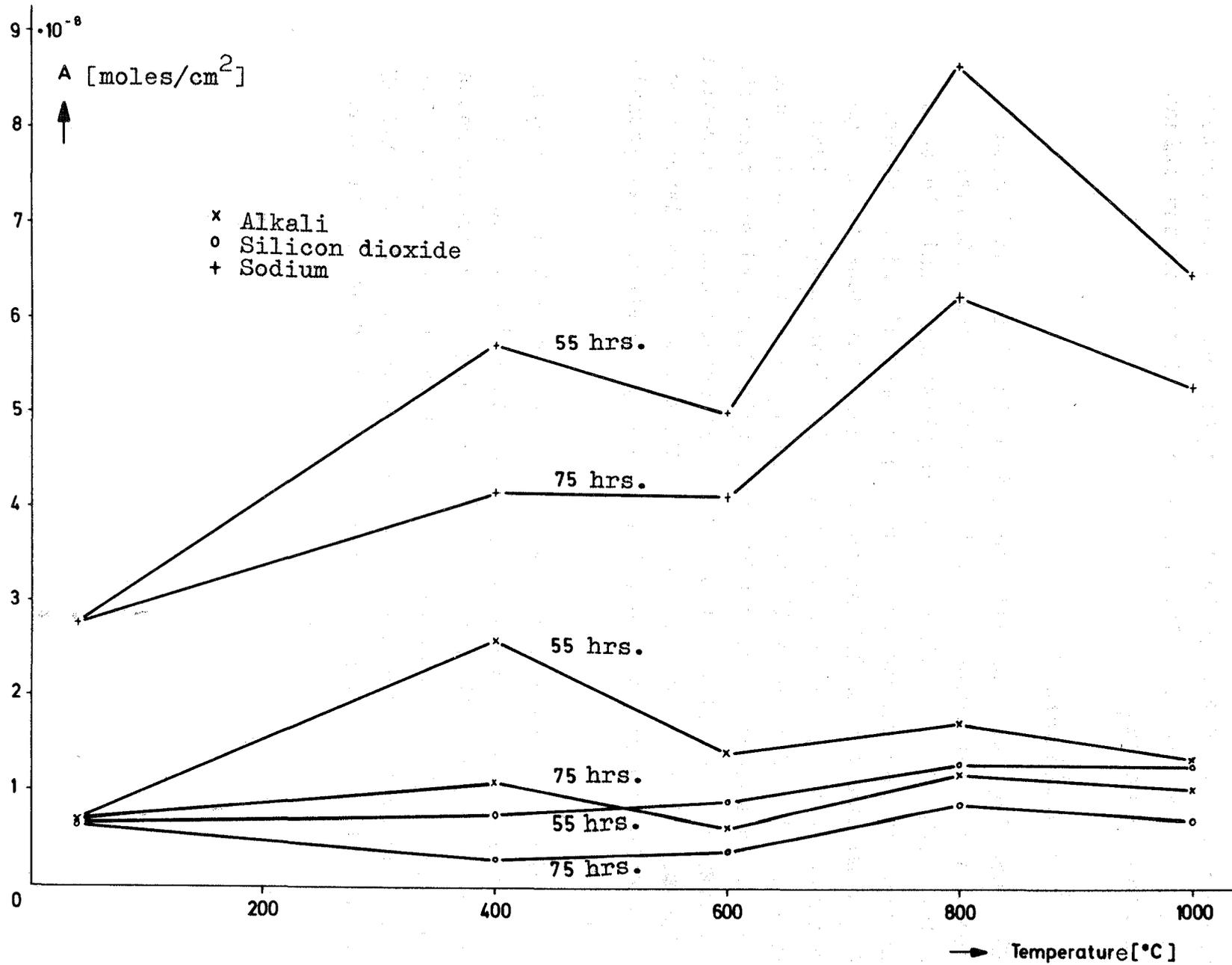
Fig. 4 Leaching rates of samples heated at different
temperatures for 55 and 75 hours

4.1.5. Density

The density of the samples was determined in a pycnometer. The values are given in Table 1. The small variations in these values may be due to variations in the original product. As the densities of the individual samples had not been determined before, it is difficult to say if there is any effect of heating on the density.

4.1.6. Leaching Rates

The leaching rates of silicon and sodium from the heated samples are determined according to the German standard method DIN 12111 which is used for glass material. In this method, the substance is ground to a particle size between 0.315 mm and 0.5 mm. Taking into account the density of the product, 2.73 g are weighed into a 50 ml-volumetric flask which, after filling with distilled water, is heated for one hour in a waterbath of $100^{\circ}C$. From this filtered solution the total amount of alkali leached out is determined by titration with 0.01 N HCl. The amounts of SiO_2 and Na_2O are determined by a colorimetric method and by flame photometry, respectively.

The values of the leaching rates are given in Table 2 along with that of an unheated sample for comparison. From the results it appears that there is an increase in leaching rates for the samples heated at $800^{\circ}C$. This may be due to structural changes as discussed in section 4.1.4. It is interesting to note that the leaching rate is decreased as the heating time is increased (Fig. 4).

Table 1. Results of Density Measurements

Samples heated at $^\circ$C	Heating time (hours)	Density (g/cm^3)
400	55	3·41
400	75	3·52
600	55	3·26
600	75	3·39
800	55	3·44
800	75	3·48
1000	55	3·42
1000	75	3·45
Unheated, Unirradiated, Normal	–	3·43
Irradiated Samples	Irradiation time (hours)	
5 MeV 10^{10}rads	7·5	3·39
5 MeV 10^{11}rads	75	3·40
10 MeV 10^{10}rads	5·5	3·35
10 MeV 10^{11}rads	55	3·41

Table 2. Leaching Rates of the Ceramic Product
According to DIN 12111

Sample Heated at (^{o}C)	Heating Time (Hours)	Leached Substance Alkali SiO$_2$ Na (10^{-8}moles/cm^2)		
400	55	2.60	0.77	5.72
400	75	1.10	0.30	4.15
600	55	1.42	0.90	4.99
600	75	0.63	0.40	4.11
800	55	1.73	1.30	8.65
800	75	1.18	0.87	6.23
1000	55	1.34	1.28	6.45
1000	75	1.02	0.71	5.28
Untreated Sample		0.71	0.66	2.78
Irradiated Samples	Irradiation Time (Hours)			
5 MeV, 10^{10}rads	7.5	0.63	0.32	4.44
5 MeV, 10^{11}rads	75	1.42	0.39	4.39
10 MeV, 10^{10}rads	5.5	0.71	0.50	5.47
10 MeV, 10^{11}rads	55	1.34	0.61	4.23

4.2. Discussion of Results on Radiation Effects

Each group of experiments is carried out on samples from the same batch of ceramic product. After the radiation treatment at different electron energies and for different total absorbed doses, the samples are examined for the following properties as done in section 4.1.

4.2.1. Change in Color

There is a superficial color change of the samples from greenish yellow to brown when irradiated with an electron beam of 10 MeV. This is most probably due to an oxidation at the temperature of $\sim 160^{\circ}C$ developed on the sample surface during irradiation. When the samples are irradiated with an electron beam of 5 MeV, there is not the same rise of temperature and thus no oxidation and no change in color occurs.

4.2.2. Change in Weight

The weight of the samples is taken before and after radiation treatment. Practically there is no change in weight which means there is only negligible oxidation of the samples.

4.2.3. Shape and Size

From visual inspection no change in shape is observed. Dimensional measurements were made for size determination with an accuracy of $\pm$ 0.005 cm before and after the radiation treatment. At 5 MeV irradiation there is no change in size. At 10 MeV irradiation to 10^{11} rads there is a slight change in size of 0.005 to 0.01 cm perhaps due to oxidation. However, this is within the uncertainty of the measurements. It can thus be concluded that the radiation has no effect in changing the shape and size of the ceramic product used in these experiments.

4.2.4. Changes in Structure

Figure 5 shows X-ray photographs of the product after irradiation. In the samples irradiated to 10^{11} rads a series of additional lines can be detected which lie very close to those of ß-alumina. They have been assigned to a compound of similar structure containing strontium as the stabilizing element and having the composition $SrO \cdot 6Al_2O_3$. These lines are weak or hardly detectable in the untreated samples and those irradiated to 10^{10} rads. No other significant structural changes can be detected after irradiation.

4.2.5. Density

The densities of the irradiated samples are determined as described in section 4.1.5. The values are given in Table 1 along with the value of the unirradiated sample for comparison. Though the samples are prepared from the same batch of the ceramic product the density varies from sample to sample due to some inhomogeneity. It is not possible to detect any change in density due to radiation treatment.

4.2.6. Leaching Rates

The leaching rates of silicon and sodium are determined by the German standard method as described in section 4.1.6. The values of the leaching rates are given in Table 2 along with the value of the unirradiated sample for comparison. The leaching rate for silicon is slightly increased with the increase of radiation energy and/or total absorbed dose, whereas it remains more or less the same for sodium. The leaching rates are almost the same for irradiated and unirradiated samples. Therefore the radiation treatment does not have much effect on the leaching rates of these substances.

↓ = strontium aluminate   ↑ = β-Al₂O₃   ⇓ = silicon
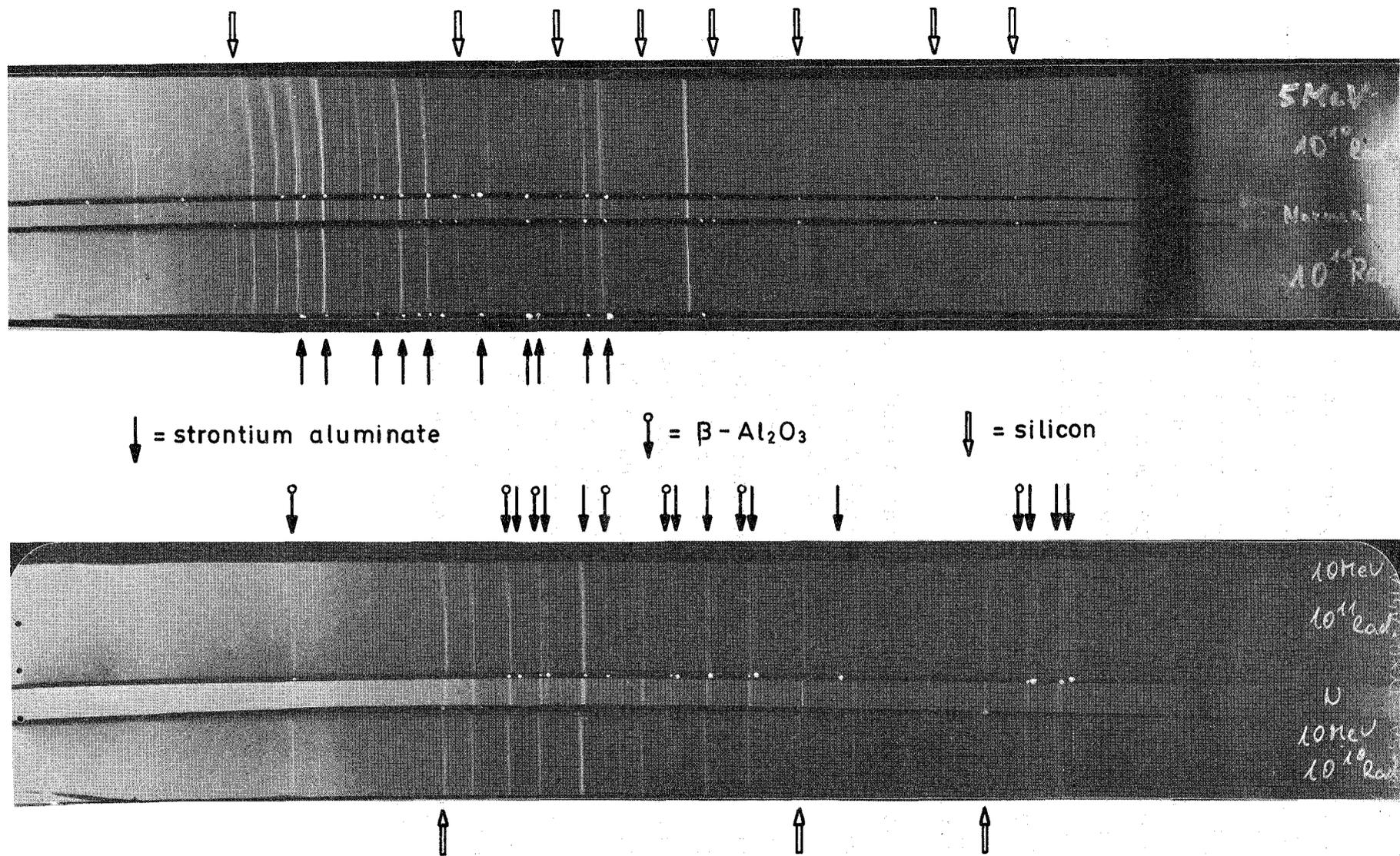
Fig. 5 X-ray diffraction powder photographs of irradiated and unirradiated (normal) samples.
(GUINIER photographs; silicon added for calibration)
a) Samples irradiated to 10^{10} and 10^{11} rads with 5 MeV-electrons (Cu-Kα radiation)
b) Samples irradiated to 10^{10} and 10^{11} rads with 10 MeV-electrons (Cr-Kα radiation)

4.2.7. Microphotographs

Microphotographs of the irradiated and unirradiated samples
have been prepared under a scanning electron microscope (SEM).
From these photographs (Fig. 6) it appears that some holes
have formed in the sample irradiated at 5 MeV and 10^{11} rads
(Fig. 6 (c)). No such damage is seen on the photographs of
other samples. In further experiments it will be attempted
to take SEM photographs of the same position before and after
irradiation in order to fully explore the visible changes due
to irradiation.

4.2.8. Thermal Conductivity

The thermal conductivity of the ceramic material was deter-
mined before and after irradiation. The instrument used was
the model TCCGM of the Dynatech Corporation. Cylindrical
samples of 1 in. length and 1 in. diameter were prepared and
irradiated in a linear accelerator with electrons of 10 MeV
to a total absorbed dose of 10^{10} and 10^{11} rads. In Fig. 7, the
thermal conductivity of unirradiated and irradiated samples
is plotted vs. the temperature. While little effect can be
detected at 10^{10} rads, an irradiation to 10^{11} rads causes an
increase in the thermal conductivity by one order of magni-
tude. This leads to the conclusion that, under real storage
conditions, the dissipation of the heat produced by decaying
nuclides will rather be enhanced than impaired by the simul-
taneous action of radiation.
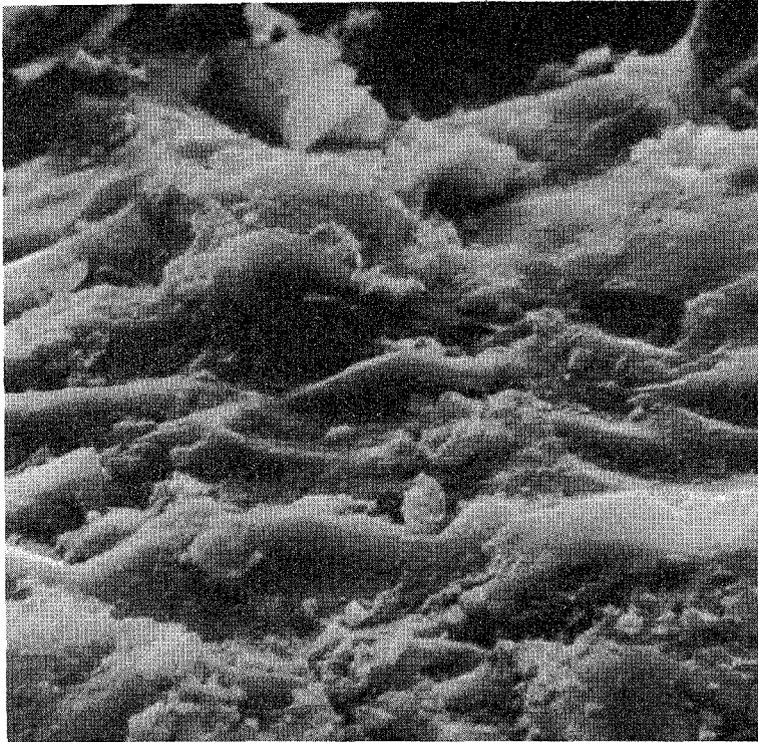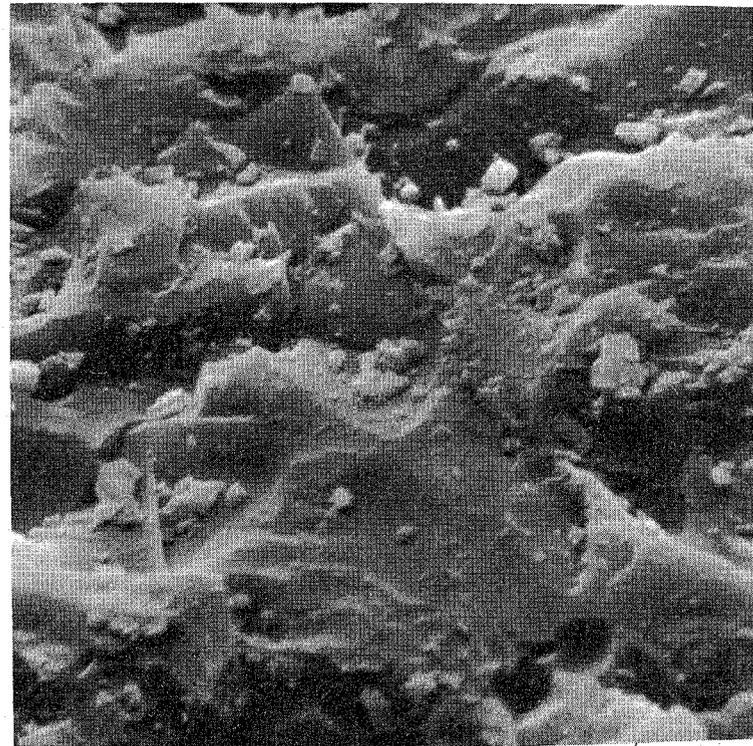
a.   b.

Fig. 6 SEM microphotographs of irradiated and unirradiated samples
        (magnification 2800 : 1)

        a) Unirradiated sample
        b) 10^{10} rads, 5 MeV-electrons
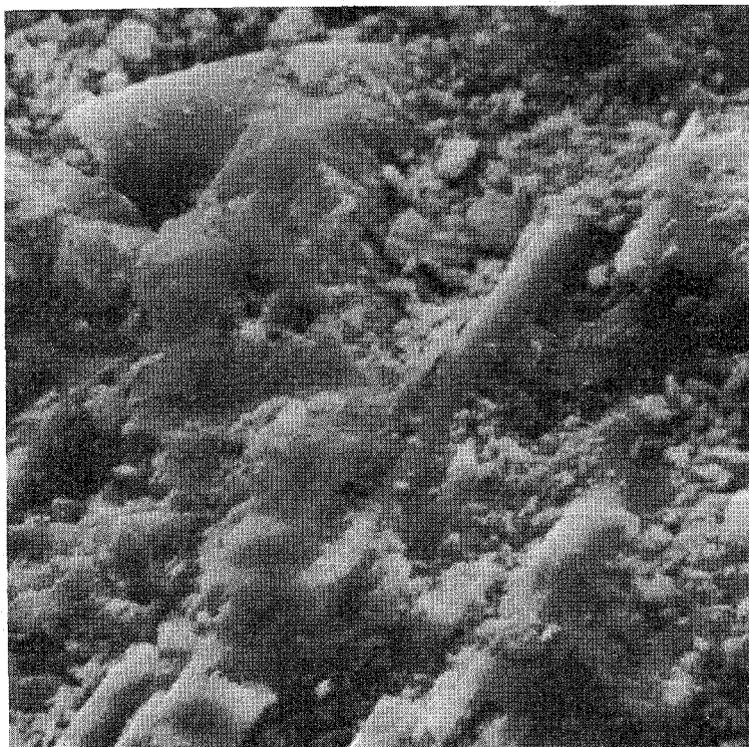
c.
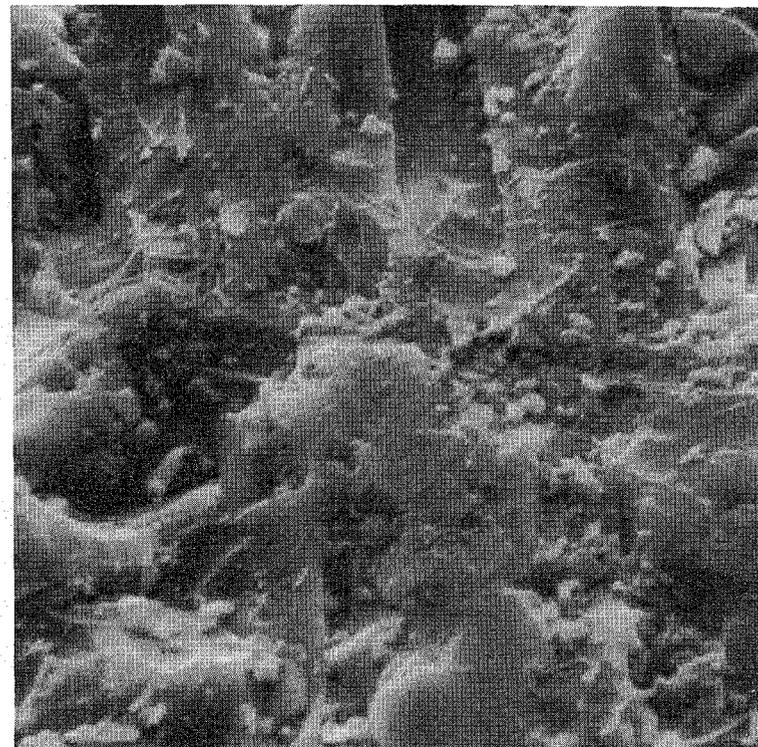
d.

Fig. 6 (cont'd.) c) 10^{11} rads, 5 MeV-electrons

d) 10^{10} rads, 10 MeV-electrons
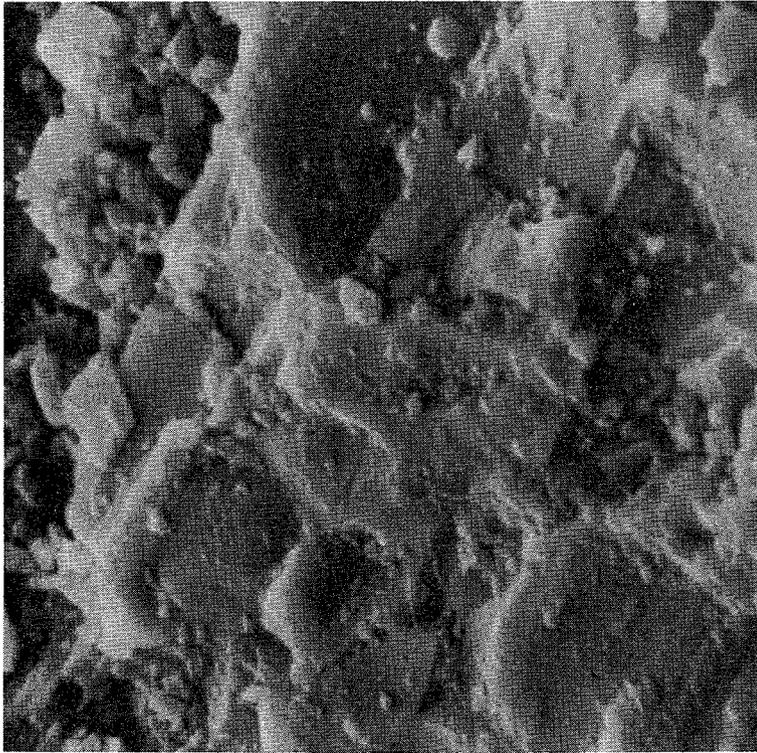
e.

Fig. 6 (cont'd.) 10^{11} rads, 10 MeV-electrons
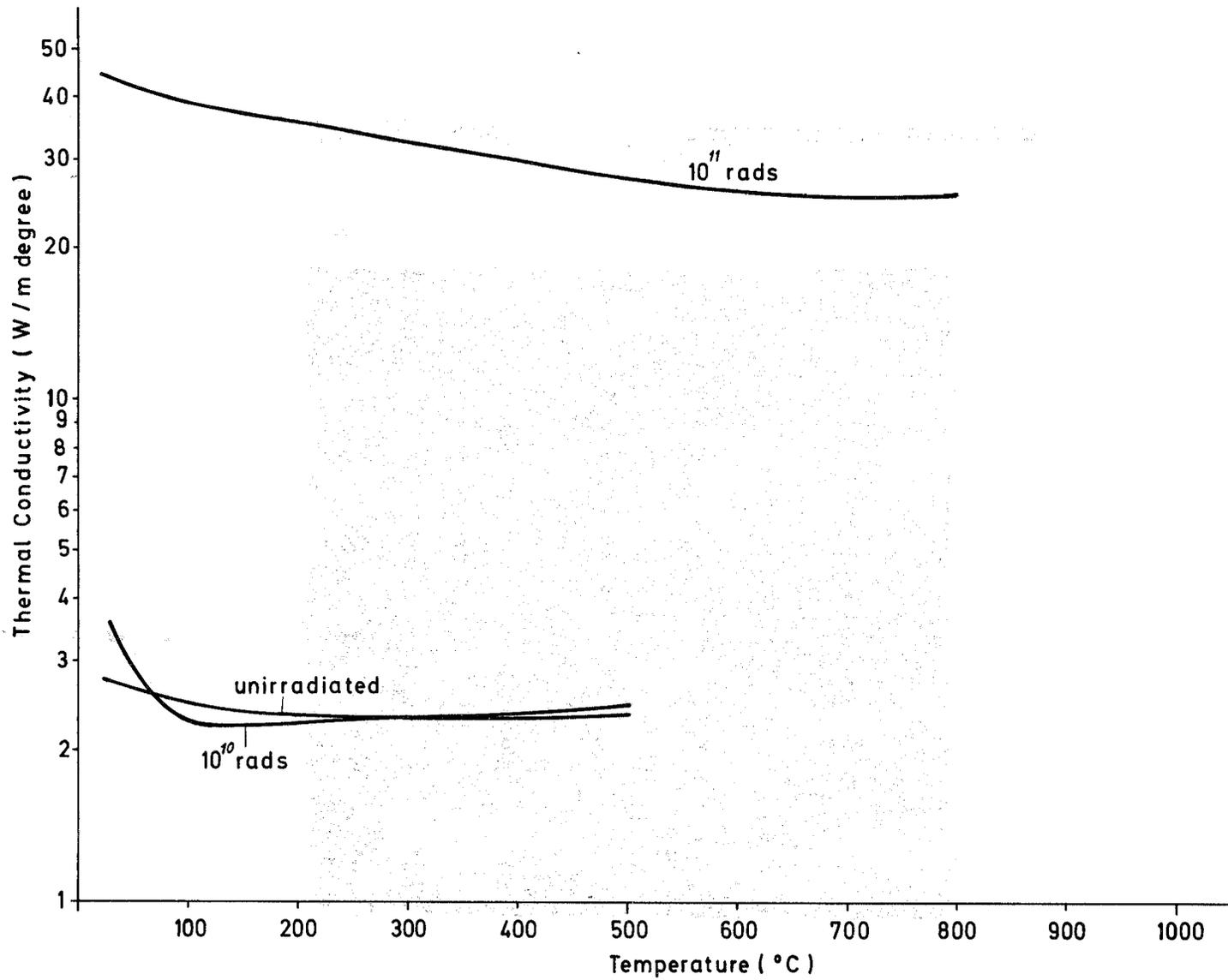
Fig. 7   Thermal conductivity of unirradiated and irradiated ceramic samples

5. Conclusion

The results presented here indicate that the effects of either heat or radiation on the thermite product under investigation can be traced back to two causes, i.e. the formation of an oxidized layer on the surface of the samples and a change in the crystalline structure of the product. The effects of heat are much more pronounced than those of radiation. Other important properties such as density and leaching rate are hardly affected by these changes; the thermal conductivity is even greatly increased.

It is to be understood that the heat and radiation conditions of actual long-term storage are not identical with those used in these experiments; however, it appears that the crystalline product of a thermite reaction is well suited for use as a medium for permanent storage of radioactive wastes. Specifically, the following advantages over borosilicate glass can be pointed out:
- higher melting point,
- higher density and thus lesser volume,
- better leachability and thermal conductivity,
- good stability towards heat and radiation as proved by the experiments described in this report.

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