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LAB-SCALE R + D WORK ON FISSION PRODUCT SOLIDIFICATION BY VITRIFICATION AND THERMITE PROCESSES

by

G. Rudolph, J. Saidl, S. Drobnik, W. Guber,
W. Hild, H. Krause, W. Müller

Gesellschaft für Kernforschung Karlsruhe

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Kurzfassung

Mehrere Arten von Glasprodukten, die simulierte hochaktive Abfälle enthielten, wurden hergestellt und ihre physikalischen und chemischen Eigenschaften studiert, insbesondere diejenigen, die für die Verarbeitung und Handhabung der Produkte und für die Endlagerung wichtig sind. Diese Untersuchungen führten zur Auswahl einer Glassorte für die praktische Anwendung bei der HLW-Verfestigung.

Eine Anlage im Labormaßstab wurde gebaut und mit inaktivem und hochaktivem Material getestet.

Als potentielle Alternative zur Verglasung wird ein Thermitprozeß für die Verfestigung hochaktiver Spaltproduktlösungen entwickelt. Modellversuche mit inaktiven Materialien zeigten die besten Ergebnisse bei Thermitmischungen, die kalzinierte Spaltprodukte, Mangandioxid, Aluminium und Siliciumdioxid enthielten.

Abstract

Several kinds of vitrified products with incorporated simulated high-level wastes were synthesized and their physical and chemical properties were studied, especially those important for processing and handling of the products and for secular storage. From the investigations a glass type has been selected for practical application in HLW solidification.

A laboratory-scale plant was built and tested with inactive and high-level material.

A thermite process for the solidification of high-level fission product solutions is under development as a potential alternative to vitrification. Model tests with inactive materials produced the best results with thermite mixtures containing calcined fission products, manganese dioxide, aluminium, and silicon dioxide.

1. INTRODUCTORY REMARKS

The German concept of handling highly active fission products from fuel reprocessing includes solidification and final storage in a salt mine. This paper describes the present status of the laboratory work on two solidification processes, namely the incorporation into borosilicate glass, the more advanced procedure, and the incorporation into ceramics by a thermite reaction, which may replace it in the distant future. The construction of a pilot vitrification plant is subject of a different paper of this conference [1].

2. FUNDAMENTAL INVESTIGATIONS ON THE INCORPORATION OF FISSION PRODUCTS INTO GLASS

2.1 Objectives of the investigations

The vitrification process described here is specifically designed to handle the wastes arising from the German reprocessing plant WAK and to provide a solid suitable for final storage in a salt mine.

2.2 Simulated high level waste solutions

The laboratory experiments were performed using simulated fission product solutions of the following types [2]:

Type 71/2, used for laboratory experiments, resembles the HAW from fast breeder fuels without Tc, Pm, transuranium elements and trace quantities of others.

Type 71/1 a, used for pilot tests, is more simplified with the noble metals omitted and all rare earths substituted by Ce.

Type 71/1 b, as before, with all rare earths substituted by Ca.

2.3 Glass melting experiments

Table I shows the composition of some "basic glasses" and of two glasses with incorporated fission products.

All of them contain approximately the same quantity of TiO_2 (for Cs retainment) and comparable quantities of SiO_2. A decreasing content of Al_2O_3 causes a small decrease of density and of melting temperature. An increasing quantity of B_2O_3 in the glass melt lowers in general the melting temperature. Up to some 8 wt.o/o, B_2O_3 in glass causes an increase of the chemical stability. After fission product incorporation, the chemical stability of the glass product in general did **not** change for the worse.

The "degree of saturation" of the glass, i.e. the quantity of components of the waste solutions which can safely be incorporated into the glass, was investigated for the basic glasses. Particularly, the amounts of MoO_3 and Cr_2O_3 are limited and dependent upon **the** composition of the vitrified product. The mean permissible fraction of these two oxides was found to be 2.5 wt.o/o for each. The glass melts examined so far have shown that it should be possible to incorporate up to 3o wt.o/o of Purex waste oxides.

2.4 Fission product volatilization

Since some of the fission products, especially cesium and ruthenium, may be volatilized during thermal treatment, measures **must** be initiated to reduce the losses from the glass melt by volatilization. As demonstrated in Fig. 1 for cesium, this was shown to be possible by adding substances to the melt which form thermally stable compounds with Cs_2O (titanates, molybdates, borates).

As can be deduced from Fig. 2, the volatility of Ru (as RuO_4) can effectively be reduced by denitration of the waste solution by means of formic acid prior to the calcination and glass melting. A detailed description of this denitration process which has been developed especially for HAW vitrification is given in a separate paper of this conference [4].

2.5 Physical and chemical properties of theglasses

The physico-chemical properties of the glass products are determined mainly by the chemical composition, the process of generation and the annealing procedure. All examined glasses are rather soft and of medium chemical stability; a better quality would imply other disadvantages.

The densities and softening points of some selected types of glass are given in Table I; in Figs. 3, 4 and 5 the temperature dependence of viscosity, thermal and electrical conductivity is plotted.

The most desirable viscosity curve of a glass melt would show a very steep slope in the transformation area ("short" glass). However, for fission product fixation this objective could not fully be achieved because the transformation interval extends between approximately 47o° C and some 9oo° C. Yet, glass of this type has a rather low melting point.

Table II shows the relative leaching tests according to DIN 12111 of basic glasses and glass products. As mentioned, the glasses are not very stable against hydrolysis, but their stability is sufficient to fulfill the safety requirements for salt disposal as well as during transportation and any intermediate storage that may preceed.

2.6 Fission product migration

Since the high-level glass blocks will be firmly enclosed by the surrounding salt already a very short time after the burial, fission products could be released only through migration processes from the glass into the salt and through the salt. To evaluate such processes of dissipation, the migration of fission product nuclides such as cesium, cerium, strontium and ruthenium was investigated in glass, rock salt and through the glass/rock salt phase boundary at temperatures above 4oo° C assumed to prevail during the initial storage period.

Migration through the glass/salt interface was studied on glass spherules homogeneously labeled with radioisotopes pressed into NaCl powder. The migration in the glass and in the salt was observed on cylindrical samples labeled with radioisotopes at the front surface.

Evaluation of the results shows the migration to occur at roughly the same rates in glass and in common salt. Table III demonstrates the excellent agreement with similar values found in the literature.

From the diffusion coefficients D, the mean depth of penetration $\bar{x}$ of the respective isotope can be calculated by

$$\bar{x} \approx 2\sqrt{Dt}.$$

Thus, the following values of the mean depth of penetration correspond to the diffusion coefficient at 6oo° C for a period of $1o^{1o}$ seconds (32o years):

	D (cm^2/s)	$\bar{x}$ (cm)
^{9o}Sr	$1o^{-9}$	6.4
^{137}Cs	$1o^{-11}$	o.6
^{144}Ce	$1o^{-12}$	o.2

3. BENCH SCALE GLASS MELTING UNIT FOR HIGH ACTIVITY OPERATION

In order to verify the inactive results in high activity tests, a complete glass melting installation for a semicontinous pot process with a throughput of 2 l fission product solution per batch was built and tested under active conditions.

The installation is located in two small hot cells. A third cell will be used for physico-chemical investigations of molten high level glasses. The flowsheet of the installation is shown on Fig. 6. The main part consisting of an HAW feed tank, a dosage pump, denitration system and one melting and two annealing furnaces is located in the first hot cell. The off-gas cleaning system is composed of two condensers, four scrubber columns, absolute filters and the respective collection tanks for intermediate-level liquid waste; it is housed in another hot cell.

The finished glass blocks are taken out through a tank flanged onto the rear wall of the cell or transferred through a conveyor system into the neighboring cell for measurements.

The unit operates as follows: In the inactive tests, the basic glass was pulverized and added batchwise to the melting crucible of the unit. The simulated HAW solution, after denitration with formic acid (3 hours), was metered in portions into the glass powder at 10-minute-intervals and evaporated there (5 to 6 hours per 2 l-batch). After that, the temperature in the melting crucible was raised to 1,100° C, the glass was molten and refined (approximately 3 hours), then discharged into the graphite mold preheated to 600° C, raising its temperature to 700° C during casting. The finished glass was cooled overnight at a cooling rate of 7o degrees per hour.

After the inactive operating phase, the installation was successfully tested in two active experiments with some 2o,ooo Ci of ^{56}Mn per batch which after dissolution was added to the simulated fission product solution. The tests showed the necessity for a few conversions in the glass melting cell which are due to be finished in the near future.

Later, the cell will be used to investigate possible applications of glass blocks containing highly radioactive fission products.

4. SOLIDIFICATION OF FISSION PRODUCTS BY A THERMITE PROCESS

4.1 General remarks

In order to have available an alternative which in the future may replace vitrification, a thermite process for solidifying fission products is being developed.

Thermite processes are reactions of elemental aluminum with an oxidizing agent, e.g. a metal oxide, which, once ignited, proceed through the entire mixture of the components, giving rise to temperatures well above 2,000° C. Their use for the fixation of fission products has first been proposed in 1961 [6]. Attempts to develop a practicable procedure have been reported both from the USSR [7, 8] and the USA [9, 10]; they were, however, considered not suited for our conditions and an own concept was worked out.

4.2 Fundamental investigations

The procedure being investigated in Karlsruhe is designed to start with the calcined fission product oxides produced in the spray calciner of the vitrification plant [1]. In order to obtain a solid fit for final disposal, they are added to a thermite mixture which is then reacted under controlled conditions.

The thermite mixture includes, beside the fission products, basically an oxidizing and a reducing agent and, if necessary, inert components to moderate the reaction and to influence the properties of the final product. While aluminum was used as a reducing agent from the beginning, the selection of an oxidant was more difficult. The idea of using the nitrates contained in the fission products themselves was soon abandoned since the gaseous reaction products cause excessive fume formation with up to 25 o/o of the solids being volatilized. Consequently, a second version of the reaction was studied using metal oxides, preceded by a complete denitration. Examples of such reactions are:

$$\mathrm{Fe_2O_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Fe} \quad \Delta H = -\ 2o2.6\ \mathrm{kcal}$$
$$\mathrm{1.5\ MnO_2 + 2\ Al \rightarrow Al_2O_3 + 1.5\ Mn} \quad \Delta H = -\ 212.4\ \mathrm{kcal}$$

Volatilization is thus reduced to less than 5 o/o of the solids. As can be seen from the equations, a metallic phase is formed in addition to the ceramic slag. If fission products are present, they also are partly reduced and thus distributed according to their chemical behavior. The use of ferric oxide resulted in products of poor quality, so manganese dioxide was preferred, leading to products of better hardness, compactness, and leachability. Table IV gives a comparison of the three oxidants in question.

In the test runs, an inactive model fission product mixture was used. A typical thermite mixture giving satisfactory results has the following composition.

6oo g	model fission product oxides
4oo g	silica (sand)
1,o25 g	manganese dioxide (about 8o o/o MnO_2)
552 g	aluminum
2,577 g	

The product of the thermite reaction is a solid which, according to X-ray studies, contains several crystalline and probably also vitreous phases. Mechanical strength, leachability, thermal conductivity, radiation stability, etc. have been found equivalent to glass.

4.3 Offgas treatment

A major problem is the formation of fumes associated with a thermite reaction. It is caused by the intermediate occurence of lower aluminum oxides such as AlO and Al_2O which, after leaving the reaction zone, are re-oxidized to finely divided alumina. The fume also contains silica which is volatilized by a similar mechanism, and oxides of sodium, molybdenum, manganese and others having low sublimation points. The volatilization is greatly enhanced by the simultaneous evolution of gases as is the case when nitrates are present. Figs. 7 and 8 show typical electron micrographs of fume particles developed in a nitrate and a manganese dioxide reaction, respectively. The differences in size and shape seem to indicate that there are differences in the composition and in the mechanism of formation.

4.4 The reaction apparatus

The reaction apparatus presently used is show in Fig. 9 (1). For carrying out a reaction, a ceramic crucible is preheated to 1,000° C to prevent it from cracking. It is then placed on a support and lifted into operation position in the reaction chamber. The other chamber, originally designed to contain a filter candle, remains empty. The reaction is then initiated by pouring into the hot crucible a thermite mixture as for instance manganese dioxide and silicon having an ignition point below 900° C. By means of a screw feeder the thermite mixture is added continuously as the reaction proceeds. For the batch mentioned above this takes about two to three minutes.

The fume generated in the reaction is drawn off and passes first through a coagulation chamber (2). The fume particles are delayed here to have a chance to coagulate into larger agglomerates which makes them easier to be filtered off. Considerable amounts of solids are already deposited on the drum walls.

The fume is then removed from the gas stream in three steps, viz. a cyclone (3), a container filled with glass wool (4) and an absolute filter (5). The cyclone is not very effective, but aids the subsequent filters when large amounts of fume are to be removed. The most effective part is a cylindrical container loosely filled with glass wool. The final purification is performed by a high-efficiency particulate air filter having an efficiency of 99.998 o/o according to the manufacturer. At the end of the system, there is a fan (6) effecting an air stream of about 45 m^3/h when the filters are fresh.

This filtering system can cope even with the large amounts of fume developed in the nitrate reaction. In case of thermite mixtures giving less fuming, the drum and the cyclone may be omitted. In this way, most of the fume will be collec- in the glass wool which may be disposed of by melting down and adding to a subsequent thermite batch when radioactive materials are used in the future.

An advanced version of this apparatus is currently under construction. It will be designed to simulate active operation; therefore, special emphasis will be on offgas cleaning and removal of dust depositions.

3.5 Conclusions

The advantages of this process as compared to vitrification may be summarized as follows:

- The high temperature of the reaction gives great flexibility in the choice of the components.

- The reaction time for a 2 kg-batch is less than 3 minutes; the cooling does not require any special attention.

- The product is equivalent to glass, in some respects superior.

For these reasons the development of this process will be continued with the aim of highly active demonstration in the VERA II engineering prototype plant in 1977/78.

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Table I. Composition of some basic glasses (VG) and glass products (GP) (A - wt.o/o, B - mole-o/o)

Glass Type / Components	VG 32		VG 36		VG 38		VG 39		GP 38	GP 39
	A	B	A	B	A	B	A	B	(wt.o/o)	(wt.o/o)
SiO_2	50	54	55	59	52.5	55.4	54.3	54.5	42.0	44.0
TiO_2	10	8.1	10	8	10	7.9	10	7.5	8.0	8.1
Al_2O_3	10	6.4	7.5	4.8	2.5	1.6	6.9	3.9	2.0	5.4
B_2O_3	5	4.7	7.5	7	10	9.1	9	7.8	8.0	7.3
CaO	5	5.8	5	5.7	5	5.6	-	-	4.0	-
Na_2O	20	21	15	15.5	20	20.4	13.3	13.2	16.0	10.8
Li_2O	-	-	-	-	-	-	6.7	13.1	-	5.4
HAW-oxides (71/2)	-	-	-	-	-	-	-	-	20.0	19.0
density (g/cm^3)	2.62		2.62		2.55		2.55		2.77	2.59
softening point (° C)	737		780		692				760	641

Table II. Leaching rates of glasses and glass products (mg leached/g of substance) according to DIN 12111

Leached substance	Basic glasses			Glass products (with HAW 71/2)		Glass products (with simplified HAW 71/1)		
	VG 32	VG 36	VG 38	VG 38	VG 39	VG 38		VG 39
						71/1 a	71/1 b	71/1 b
SiO_2	0.176	0.183	0.563	0.119	0.206	0.265	0.340	0.514
Na_2O	1.816	0.173	0.586	0.269	0.337	0.192	0.223	0.217

Table III. Apparent diffusion coefficients in polycrystalline NaCl ($cm^2/s \times 10^{-10}$)

temperature (° C)	$^{90}Sr + {}^{90}Y$	$^{144}Ce + {}^{144}Pr$	$^{106}Ru + {}^{106}Rh$
660	31	0.6	0.35
600	13	0.017	0.08
500	5	< 0.01	-
470	-	-	0.01

Diffusion coefficients of Cs-, Sr, and Y-ions in a NaCl-monocrystal according to CHEMLA [5] ($cm^2/s \times 10^{-10}$)

temperature (° C)	Cs^+	temperature (° C)	Sr^{2+}	temperature (° C)	Y^{3+}
721	97.0	705	70	705	39
685	43.0	691	55	691	28
612	8.4	665	34	665	16
575	3.7	623	26		

Table IV. Comparison of the three possible oxidants for the thermite reaction

Oxidant	Number of phases	Amount of fuming	product
$NaNO_3$	1	strong	fair
Fe_2O_3	2	moderate	poor
MnO_2	2	moderate	good

Fig. 1

Loss of ^{137}Cs during melting (1h at 1000°C) in the presence of B_2O_3, MoO_3 and TiO_2

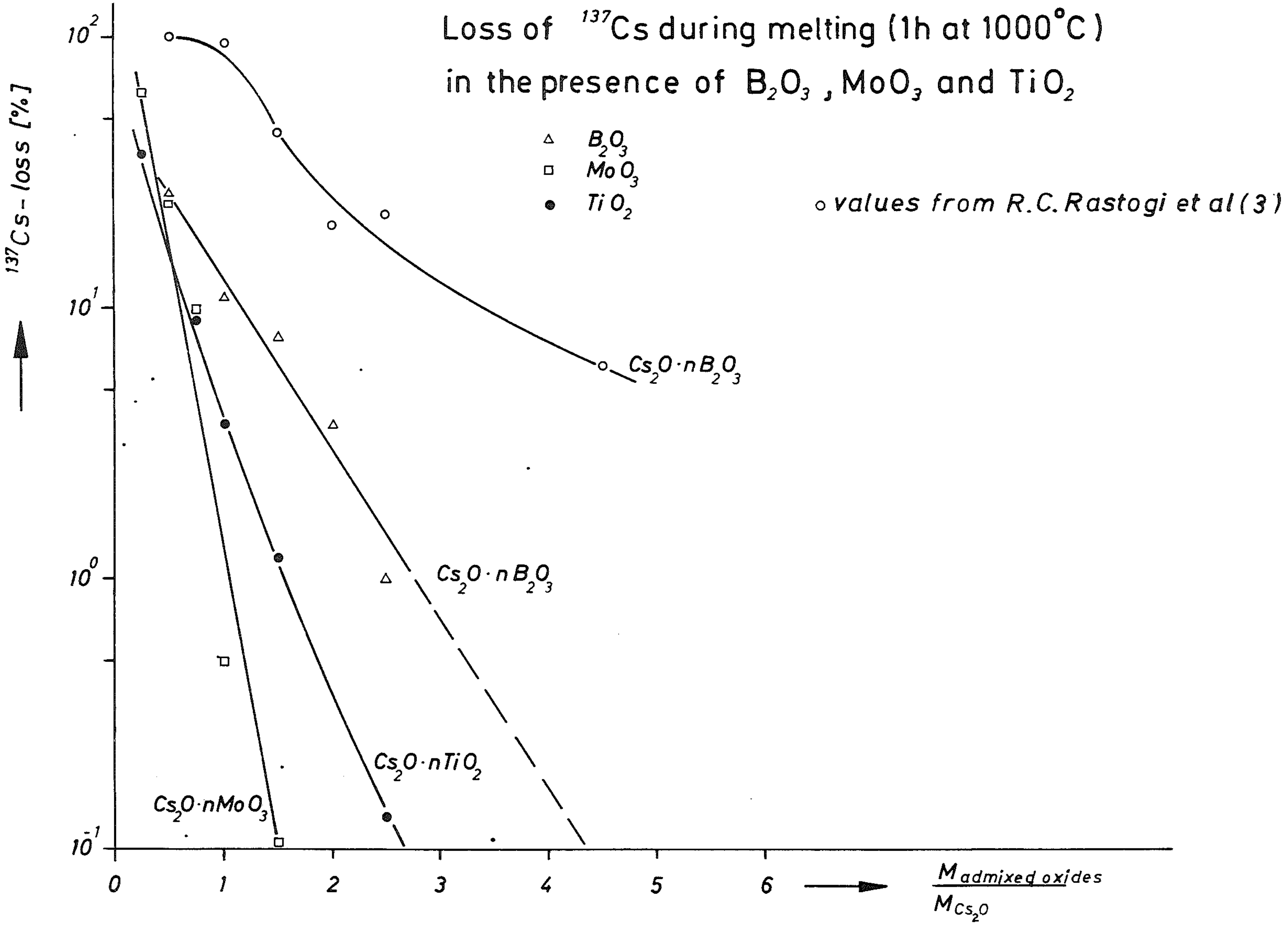


Fig. 2

Loss of ^{106}Ru as a function of the NO_3^- concentration in the glass melt

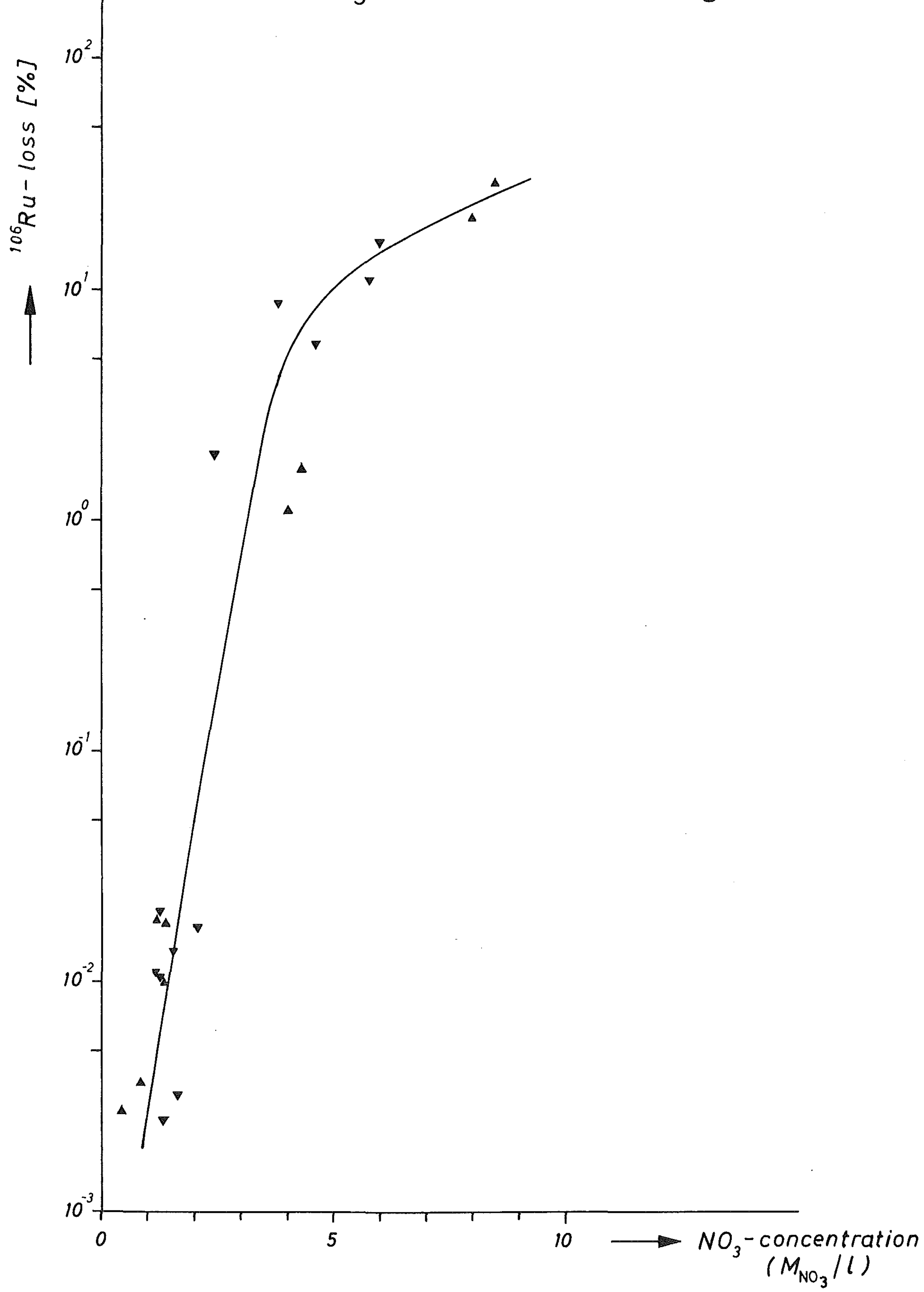
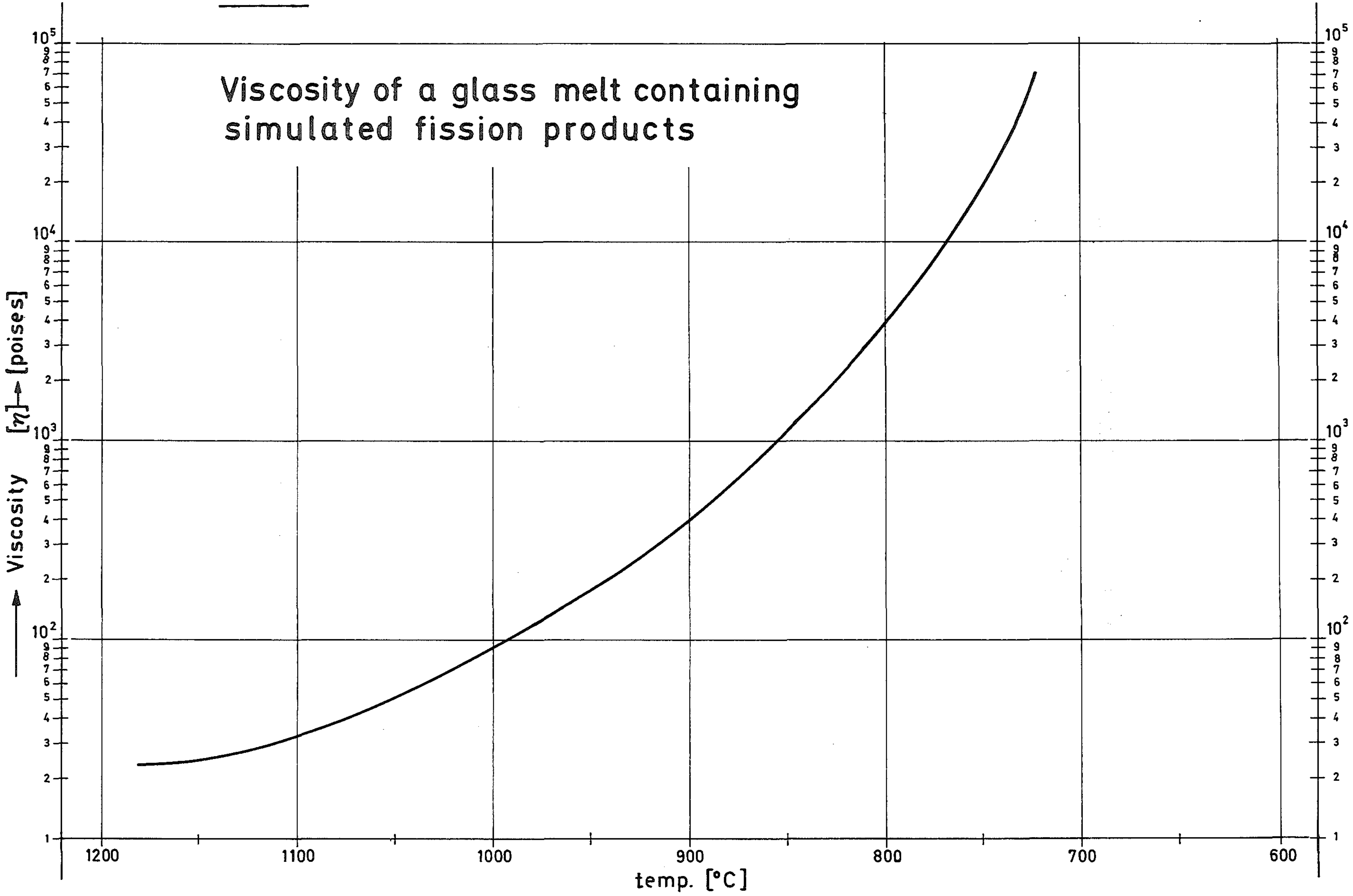


Fig. 3



Viscosity of a glass melt containing simulated fission products

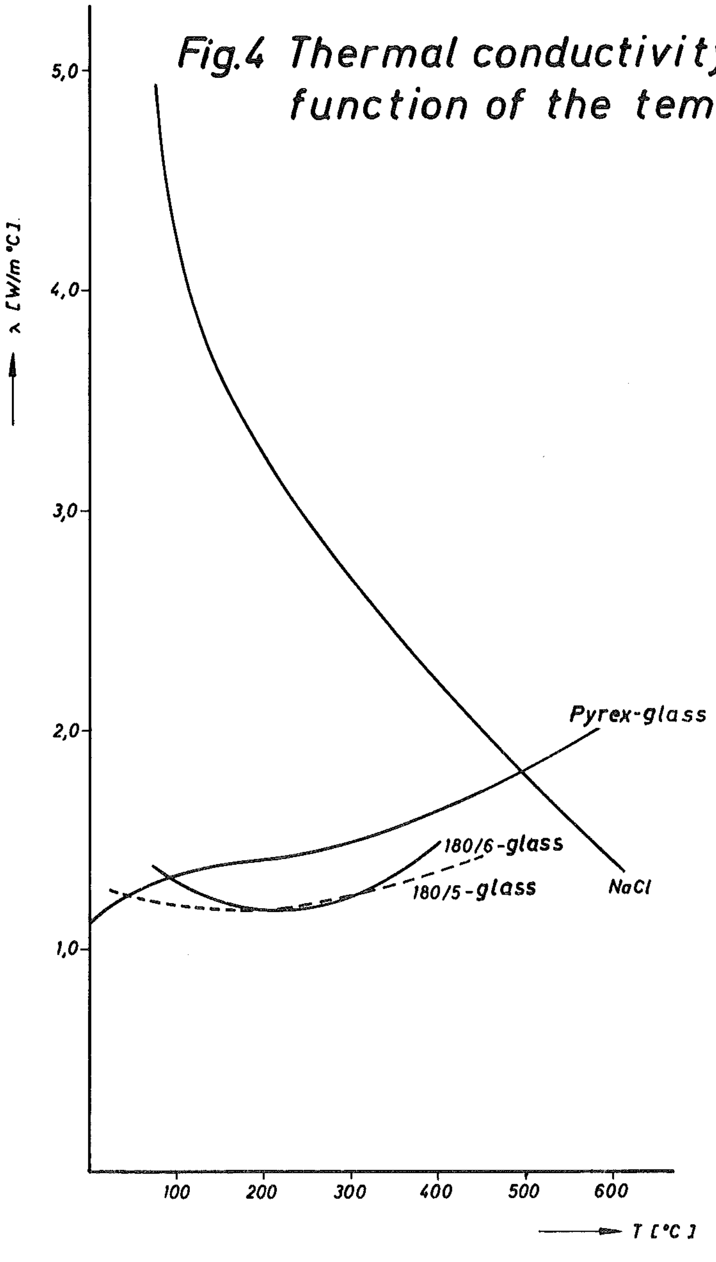


Fig.4 Thermal conductivity as a function of the temperature

Fig. 5. Temperature dependence of the electrical conductivity and diffusion coefficient for sodium in a typical glass

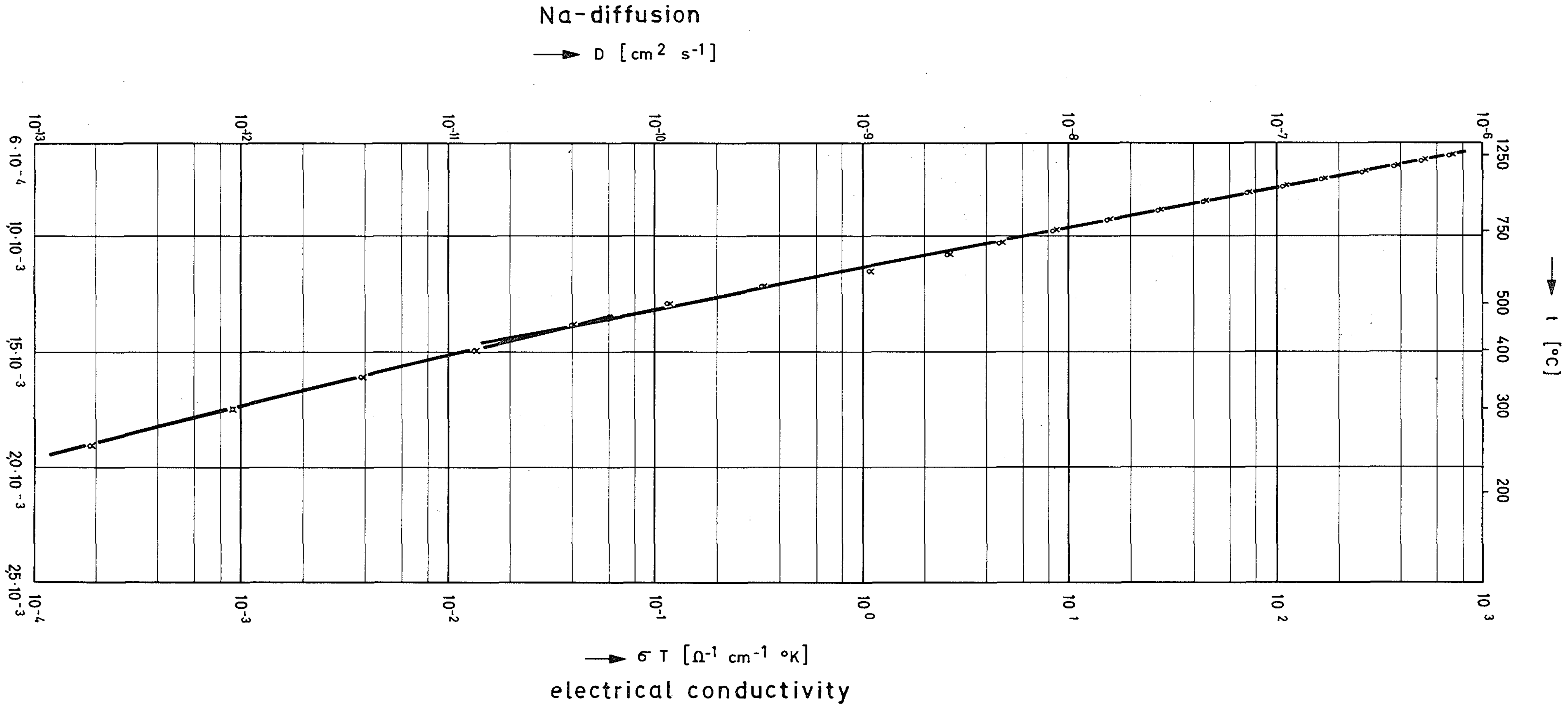
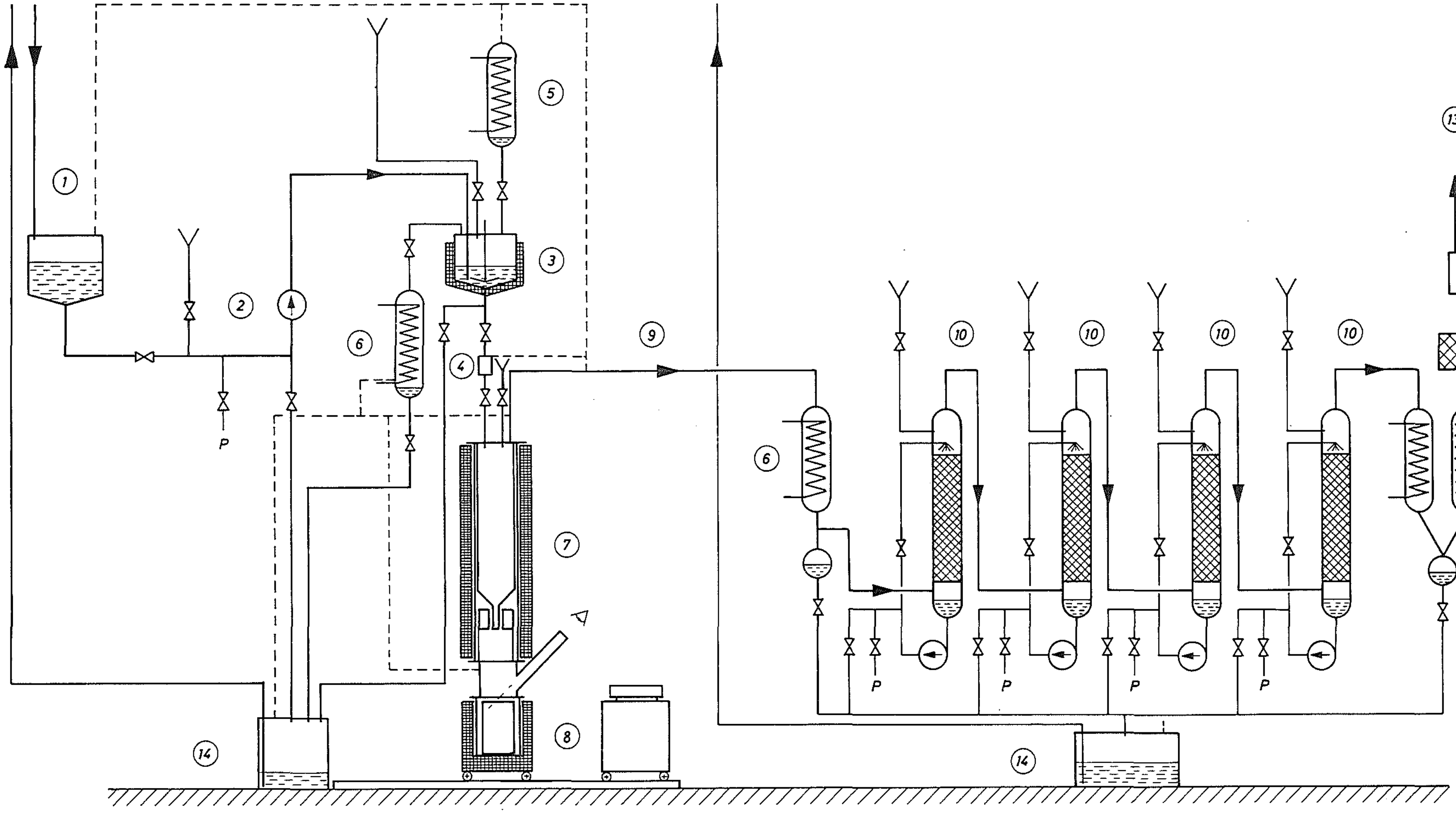


Fig. 6: LABORATORY-SCALE GLASS MELTING PLANT FOR THE SOLIDIFICATION OF HIGH-LEVEL LIQUID WASTES



1	FEED TANK	6	CONDENSER	11	ABSOLUTE FILTER
2	DOSAGE PUMP	7	MELTING FURNACE	12	IONIZATION CHAMBER
3	DENITRATION VESSEL	8	ANNEALING FURNACE WITH MOLD	13	EXHAUST AIR
4	DOSAGE	9	OFFGAS LINE, HEATED	14	SUMP TANK
5	REFLUX COOLER	1o	SCRUBBER COLUMN	P	SAMPLING STATION

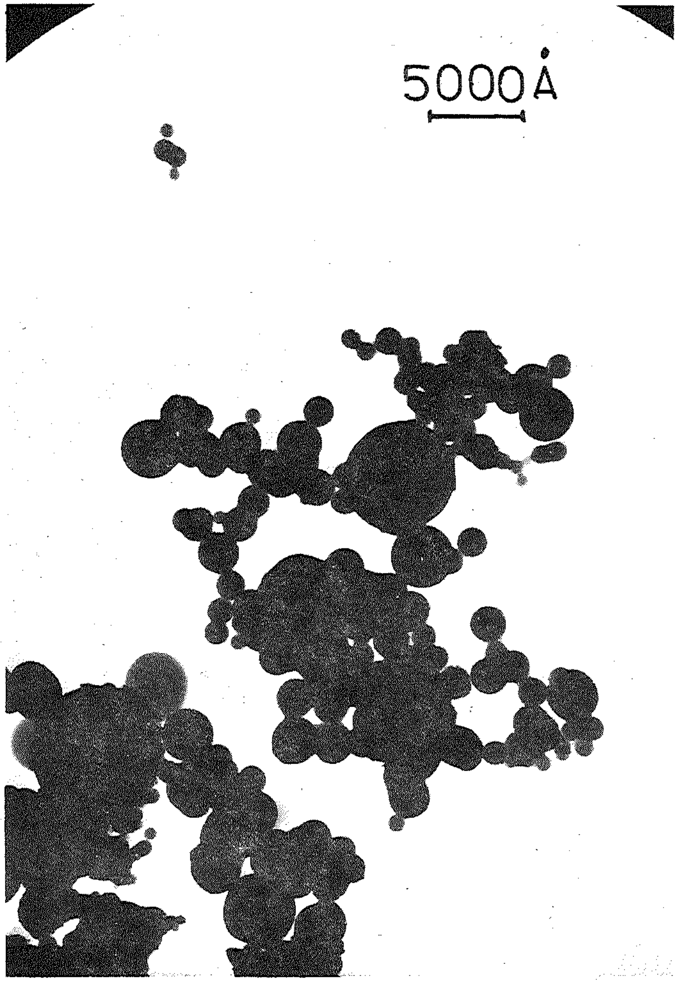


Fig. 7 Electron micrograph of fume particles from a nitrate reaction.

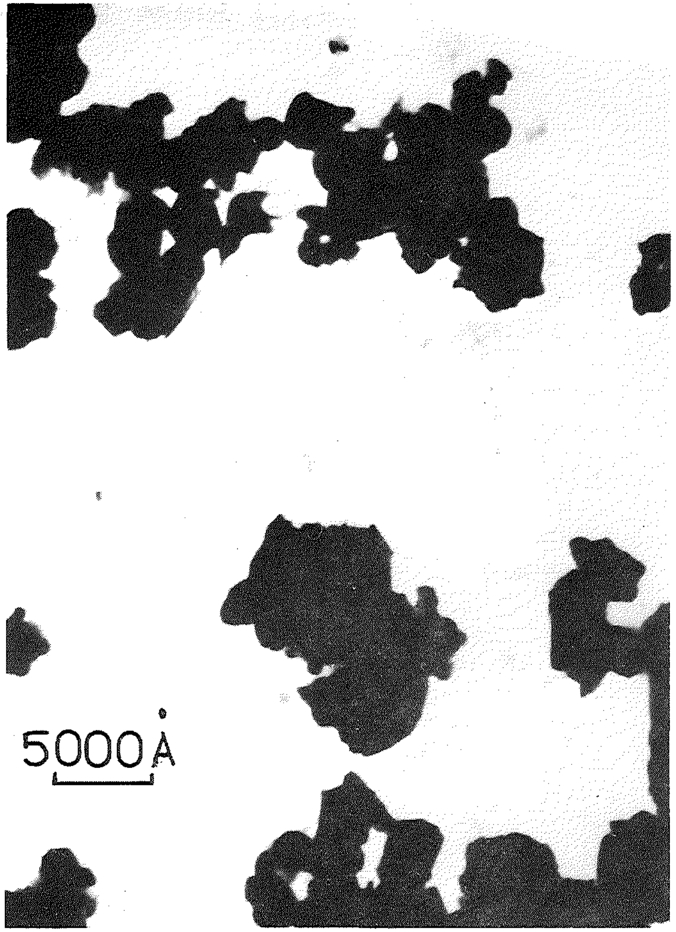


Fig. 8 Electron micrograph of fume particles from a manganese dioxide reaction.

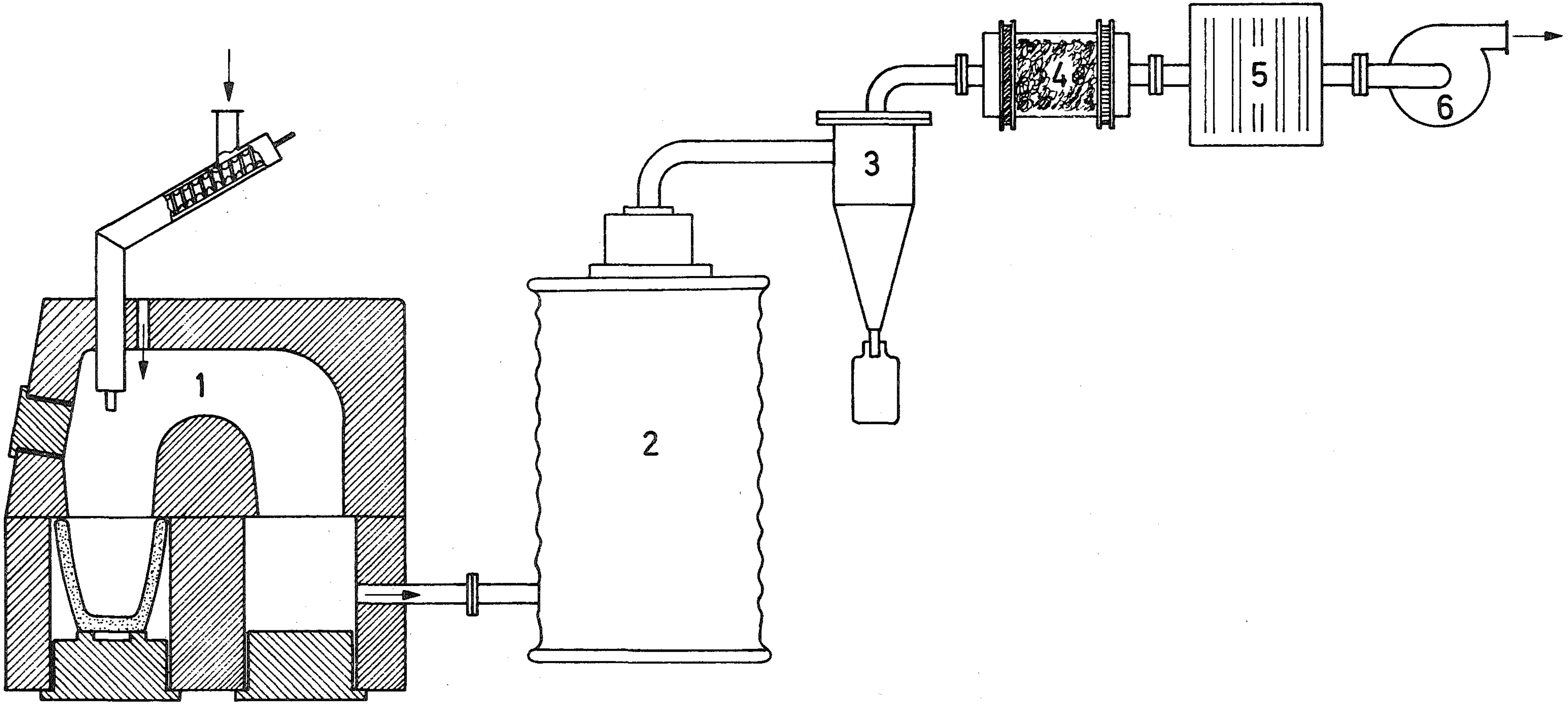


Fig. 9

1 Thermite oven
2 200l-drum
3 Cyclone
4 Glass wool filter
5 HEPA filter
6 Ventilator