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Measurements of Density and of Thermal Expansion Coefficient of Sodium Tetraborate (Borax)-UO_2 and of Sodium Metaborate-UO_2 Solutions

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Measurements of density and of thermal expansion coefficient of sodium tetraborate (borax)-UO_2 and of sodium metaborate-UO_2 solutions

by

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Abstract

Measurements have been performed of the density and volumetric thermal expansion coefficient of liquid sodium tetraborate (borax) and of sodium metaborate both pure and with two different amounts of UO_2 dissolved in each. These data are required for the design of core-catchers based on sodium borates. The measurements have been performed with the buoyancy method in the temperature range from 850°C to 1325°C. The data for the pure borax and for the sodium metaborate agree reasonably well with the data from the literature, giving confidence that the measurements are correct and the new data for the salts with UO_2 are reliable.

Messungen der Dichte und der thermischen Ausdehnungskoeffizienten von Natriumtetraborat (Borax)-UO_2 und von Natriummetaborat-UO_2 Lösungen.

Zusammenfassung

Es wurden Messungen der Dichte und der kubischen Ausdehnungskoeffizienten von reinem Natriumtetraborat (Borax) und Natriummetaborat sowie deren Mischungen mit zwei verschiedenen Mengen von UO_2 durchgeführt. Diese Werte sind für die Auslegung eines Kernschmelzenauffängers (Core-Catcher) erforderlich. Die Messungen wurden mit der Auftriebsmethode im Temperaturbereich von 850°C bis 1325°C vorgenommen. Die erhaltenen Werte der reinen Stoffe stimmen gut mit den Literaturwerten überein und daraus ist zu schließen, daß die Werte der Mischungen auch zuverlässig sind.

1. Introduction

Sodium borates appear to be quite suitable as sacrificial materials for a core-catcher of a nuclear reactor. UO_2, PuO_2 and the fission product oxides, contained in the core debris resulting from a hypothetical accident, will be dissolved by the sodium borates of the core-catcher, placed on the base of the cavity containing the core, provided they remain in contact for a sufficiently long time at sufficiently high temperatures. The core catcher is made up of a matrix of higher melting point material, formed by thin boxes containing the sodium borates. In this way the supporting structure in the catcher consists of a material which fails at higher temperatures, and sufficiently high temperatures are available for the borate to dissolve the oxides.

The studies and investigations in the Karlsruhe Nuclear Research Center forsee the use of sodium tetraborate (borax, $Na_2O \cdot 2B_2O_3$ = $Na_2B_4O_7$) and/or of sodium metaborate ($Na_2O \cdot B_2O_3$ = $2NaBO_2$) /1-4/. Borax has the advantage of a higher boiling point and it is less chemically aggressive; sodium metaborate dissolves the oxides more readily.

The calculations of the temperatures and heat fluxes at the walls of the sodium borate melt containing in solution UO_2, PuO_2 and the fission product oxides after an hypothetical accident involving the whole core of a 1000 MWe fast reactor have been performed either assuming the physical properties of the pure sodium borate or the effect of the large quantities of dissolved UO_2 has been estimated by comparison with other glasses /3/. These assumptions are however too rough and the results of the thermal calculations are affected by a considerable degree of uncertainty. In particular information is required on:

- density and volumetric expansion coefficient of liquid borax and sodium metaborate containing defined amounts of dissolved UO_2

- viscosity and thermal conductivity for the same materials.

The results of our laboratory experiments to determine density and volumetric expansion coefficients of liquid borax and sodium metaborate containing defined quantities of dissolved UO_2 are given in the present paper. Measurements of the viscosity of the same materials have been started at the Karlsruhe Nuclear Research Center. The measurements of thermal conductivity will be part of our future programme.

2. Experimental Apparatus and Data Evaluation

The measurements performed during the present experiment were essentially measurements of the density, and thus of its inverse the specific volume, of a liquid at various temperatures. The variation of the specific volume with temperature is of course the volumetric expansion coefficient. Various systems have been suggested to perform these measurements /5/, however the requirement to operate at relatively high temperatures (850-1300°C) has dictated the choice of the measurement system: the so-called buoyancy system. This method allows a continuous measurement of the density and the determination of the temperature is precise and simple. The buoyancy method has often been used to measure the density of molten salts /6/.

Fig.1 shows schematically the experimental apparatus. One pan of a precision balance has been replaced by a sinker of known weight attached to the bar of the balance by means of long wire. In our experiment we used a platinum sinker about 25 mm long and weighing 42.4721 g, attached to a 440 mm long wire also of platinum. During the experiments the sinker and a small portion of the wire are immerged in the molten salt, whose density has to be measured. The molten salt is contained in a platinum crucible, form and dimensions of which are given in Fig.1. The volumetric capacity of the crucible is about 115 cm^3. During the tests the volume occupied by the molten salt and by the sinker was about 80 cm^3. The crucible was contained in an electrically heated furnace. By varying the heating power, it was possible to obtain various temperature levels in the furnace. The temperature was measured by a platinum/platinum-rhodium (18%) thermocouple immerged in the molten salt. The measurements were performed at temperature intervals of 25^{o}C. After each power variation to obtain another temperature level, the measurement was performed when new stationary temperature conditions in the furnace were achieved, as indicated by the thermocouple reading.

For Archimedes' principle the density of the liquid contained in the crucible is given by:

$$\rho_l = \frac{M_l}{\frac{M_{Pt1}}{\rho_{Pt}(T)}} = \rho_{Pt}(T)\ \frac{M_{Pt}-(M_{Pt}-M_l)}{M_{Pt_1}} \qquad (1)$$

where:

M_l = mass of the liquid displaced by the sinker

M_{Pt}= total mass of the platinum sinker (M_{Pts}) and platinum wire (M_{Ptw})

M_{Pt_1}= mass of the sinker and plantinum wire immersed in the liquid

$\rho_{Pt}(T)$= density of platinum as a function of temperature

$M_{Pt}-M_l$= balance reading at equilibrium

Experiments were performed with six different type of molten salts (s. Table I at the end of the paper). For the first tests with pure borax a thinner wire was used. M_{Pt} and M_{Pt1} are known by weighing sinker and wire before the measurements and recording the small portion of the wire which is immerged during each experiment (see Table I). $M_{Pt}-M_1$ is given by the balance reading at equilibrium. The density of platinum as a function of temperature was obtained from reference /7/ and it is given in Table II. Equation (1) allows therefore the determination of the density of the liquid salt.

After the experiments were performed, it was observed that the solidified melt of borax containing 15.8% UO_2 presented two well separated regions: one yellow and one green (see Fig.2). It was therefore feared that a separation in two regions with different UO_2 concentrations had taken place. Similar, if less pronounced separation of regions were observed with the metaborate-UO_2 samples (Fig.3 and 4). The samples were therefore subjected to a X-ray fluorescence analysis with an EXAM-MAX system for the determination of the uranium distribution in the samples. It was found that the uranium is uniformly distributed within the accuracy of the instrument (10%). The different colour and the phase separation is likely due to the presence in the UO_2 of two slightly different oxidation degrees. It is indeed known that a borax bead containing uranium oxide is orange-yellow in the oxidation flame and green in a reduction flame /8/.

3. Experimental Results

3.1 Density

Tables III to VIII give the experimental results for the six series of experiments: one with pure borax, one with pure metaborate and the others with two different amounts of dissolved UO_2 in each. The Tables show the balance reading and the value of ρ_1 calculated with equation (1), the other parameters being obtained for each series from Tables I and II.

Figures 5 and 6 show the same data in the plot density ρ_1 versus temperature T, for borax and sodium metaborate respectively. The agreement of the borax density with a value at 1000°C from the literature /9/ is relatively good, (difference = 1.7%). Figures 7 and 8 show the variation of density with the amount of dissolved UO_2 at constant temperatures.

3.2 Volumetric Thermal Expansion Coefficient

Once the density is known, the specific volume of the molten salt v_1 can be obtained by the equation:

$$v_1 = \frac{1}{\rho_1} \qquad (2)$$

and the coefficient β of volumetric thermal expansion is defined by equation (3):

$$v_1 = v_o(1+\beta T) \qquad (3)$$

where T is the temperature in $^{\circ}$C and v_o the specific volume of the molten salt, if it were still liquid, at 0°C.

From Figures 5 and 6 it can be seen that up to 1200°C the variation of ρ_1 with temperature is approximately linear. The same can be said of v_1, and thus the value of β is a constant up to 1200°C for each molten salt investigated. Table IX and Fig.9 show these constant values of β, valid up to T=1200°C, obtained with equation (3). For pure borax one has $\beta=3.83\times10^{-4}\ {}^{\circ}C^{-1}$. This value can be compared with the value obtained by Volarovich by direct measurement of the volume change with temperature: in the temperature range from 859°C to 1305°C β is equal to $2.6\times10^{-4}\,{}^{\circ}C^{-1}$ /10/ as quoted in the reference /11/. The definition of β used in this relatively old paper is however different from ours. Volarovich uses the definition of β:

$$\beta_v = \frac{v(T=1305^{\circ}C)-v(T=859^{\circ}C)}{v(T=859^{\circ}C)\,(1305-859)} = 2.6\times10^{-4}\,{}^{\circ}C^{-1} \qquad (4)$$

A value of $\beta_V = 2.6\times10^{-4}\ {}^{o}C^{-1}$ corresponds to a value of $\beta = 3.35 \times 10^{-4}\ {}^{o}C$ with our definition. Thus the difference between our value of β and that of Volarovich is only 12.5%.

Fig.10 shows the specific volume of pure sodium metaborate as a function of temperature. The Russian data obtained with a direct measurement of the volume increase with temperature /11/ lie about 2.3% higher than our data. The coefficient of thermal expansion β is, with our definition, equal to $4.73\times10^{-4}\ {}^{o}C^{-1}$ (with the Russian data definition $\beta_V=3.2\times10^{-4}\ {}^{o}C^{-1}$) against $4.49\times10^{-4}\ {}^{o}C^{-1}$, the difference being 5.3%.

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Table I: Test conditions

Test series number	Type of sodium borate	Quantity of sodium borate (g)	Quantitiy of dissolved UO_2 (g)	Weight percentage of dissolved UO_2	M_{Pts} (g)	M_{Pt_w} (g)	M_{Pt_1} (g)
1		150	-	0%		1.9913	42.5264
2	borax	149.84	12.77	7.9%			42.5419
3		151.06	28.39	15.8%	42.4721	2.5609	42.6467
4		150	-	0%			42.5419
5	sodium	148.569	15.323	9.3%			42.5419
6	metaborate	147.538	30.601	17.2%			42.6467

Table II: Platinum density /7/

T (^{o}C)	$\rho_{Pt}(T)$ (g/cm^3)
850	20.905
875	20.89
900	20.87
925	20.86
950	20.84
975	20.83
1000	20.81
1025	20.79
1050	20.78
1075	20.76
1100	20.75
1125	20.73
1150	20.72
1175	20.70
1200	20.68
1225	20.67
1250	20.65
1275	20.64
1300	20.62
1325	20.61

Table III: Density of pure sodium tetraborate (borax)

T (^{o}C)	$M_{Pt}-M_{l}$ (g)	ρ_{l} (g/cm^3)
850	40.2203	2.086
875	40.2581	2.066
900	40.2735	2.056
925	40.3013	2.042
950	40.3250	2.028
975	40.3446	2.017
1000	40.3643	2.006
1025	40.3944	1.989
1050	40.4122	1.980
1075	40.4423	1.963
1100	40.4643	1.951
1125	40.4822	1.941
1150	40.5105	1.926
1175	40.5368	1.911
1200	40.5643	1.896
1225	40.5834	1.886
1250	40.6205	1.866
1275	40.6533	1.849

Table IV: Density of borax with 7.9% UO_2

T (^{o}C)	$M_{Pt}-M_l$ (g)	ρ_l (g/cm^3)
875	40.5460	2.203
900	40.5700	2.189
925	40.5920	2.178
950	40.6215	2.161
975	40.6390	2.151
1000	40.6615	2.138
1025	40.6760	2.129
1050	40.6970	2.118
1075	40.7260	2.102
1100	40.7440	2.092
1125	40.7625	2.081
1150	40.7810	2.071
1175	40.8010	2.059
1200	40.8235	2.046
1225	40.8440	2.035
1250	40.8590	2.026

Table V: Density of borax with 15.8% UO_2

T (^oC)	$M_{Pt}-M_1$ (g)	ρ_1 (g/cm^3)
975	40.3059	2.309
1000	40.3085	2.305
1025	40.3115	2.302
1050	40.3140	2.299
1075	40.3170	2.296
1100	40.3200	2.293
1125	40.3250	2.288
1150	40.3280	2.286
1175	40.3315	2.282
1200	40.3350	2.278
1225	40.3380	2.276

Table VI: Density of pure sodium metaborate

T (^{o}C)	$M_{Pt}-M_{l}$ (g)	ρ_{l} (g/cm^3)
975	41.0330	1.959
1000	41.0565	1.945
1025	41.0795	1.932
1050	41.1035	1.919
1075	41.1235	1.908
1100	41.1445	1.897
1125	41.1670	1.884
1150	41.2061	1.864
1175	41.2255	1.853
1200	41.2515	1.838
1225	41.2820	1.823
1250	41.3225	1.801
1275	41.3525	1.786
1300	41.3900	1.766
1325	41.4410	1.740

Table VII: Density of sodium metaborate with 9.3% UO_2

T (^{o}C)	$M_{Pt}-M_l$ (g)	ρ_l (g/cm^3)
950	40.959	1.996
975	40.979	1.985
1000	41.0160	1.965
1025	41.0410	1.951
1050	41.0630	1.939
1075	41.0830	1.928
1100	41.1020	1.917
1125	41.1270	1.903
1150	41.1520	1.890
1175	41.1820	1.874
1200	41.2100	1.858

Table VIII: Density of sodium metaborate with 17.2% UO_2

T (^{o}C)	$M_{Pt}-M_l$ (g)	ρ_l (g/cm^3)
950	40.4720	2.229
975	40.4840	2.222
1000	40.4970	2.213
1025	40.5100	2.205
1050	40.5230	2.198
1075	40.5360	2.190
1100	40.5510	2.181
1125	40.5660	2.171
1150	40.5810	2.163
1175	40.5950	2.154
1200	40.6080	2.146

Table IX: Thermal expansion coefficient β up to 1200 $^{\circ}C$

Test series number	Type of salt tested	$\beta \times 10^4$ ($^{0}C^{-1}$)
1	pure borax	3.83
2	borax with 7.9% UO_2	2.95
3	borax with 15.8% UO_2	0.62
4	pure sodium metaborate	4.49
5	sodium metaborate with 9.3% UO_2	4.17
6	sodium metaborate with 17.2% UO_2	1.82

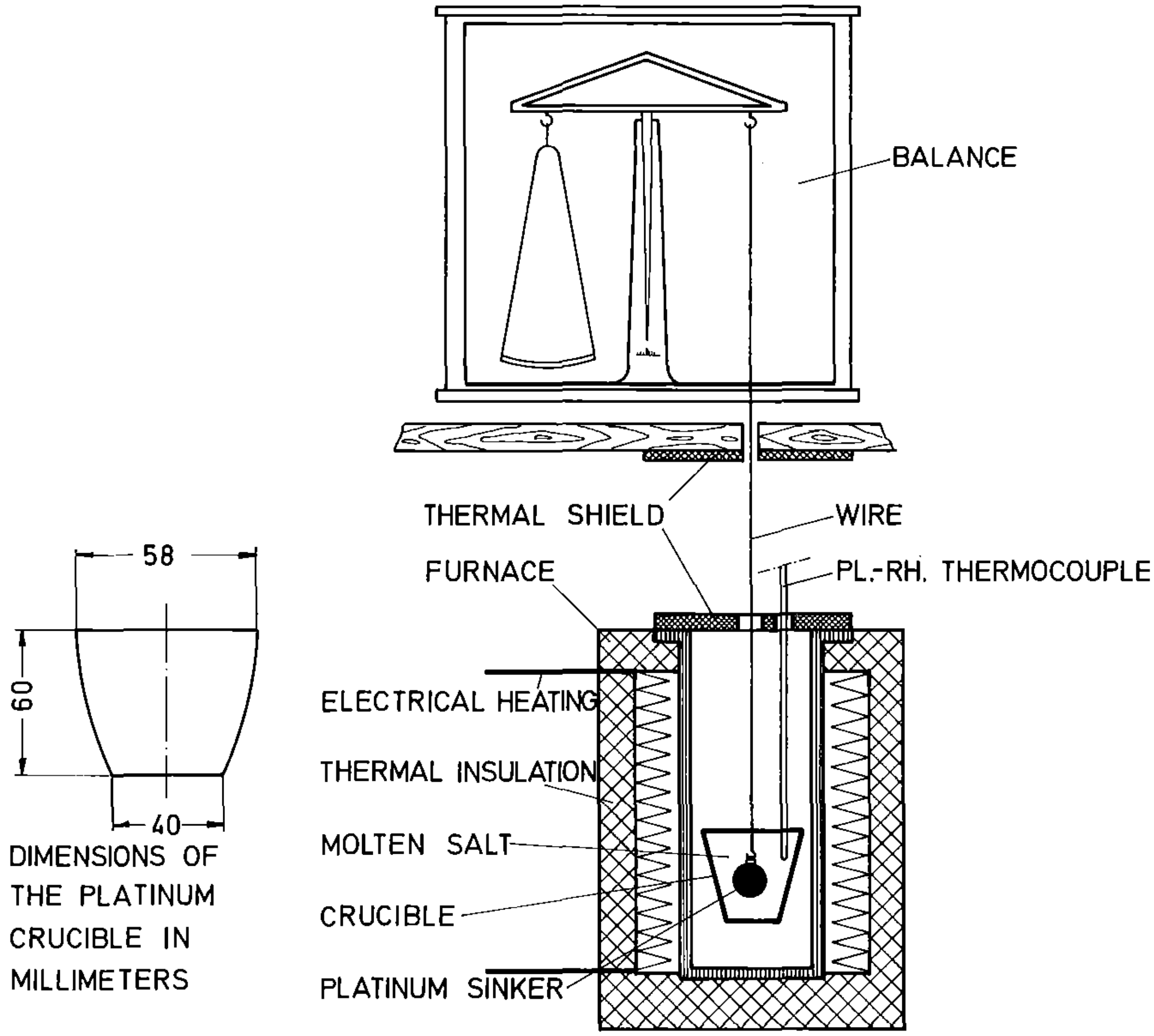


Fig.1: Schematical arrangement of experimental apparatus

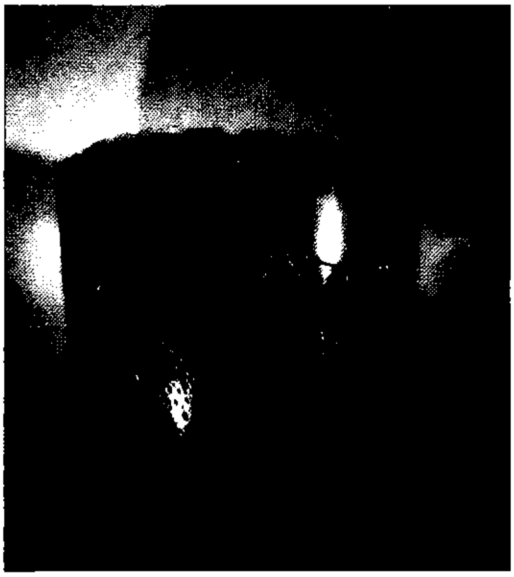


Fig.2: Test sample: borax with 15.8% UO_2

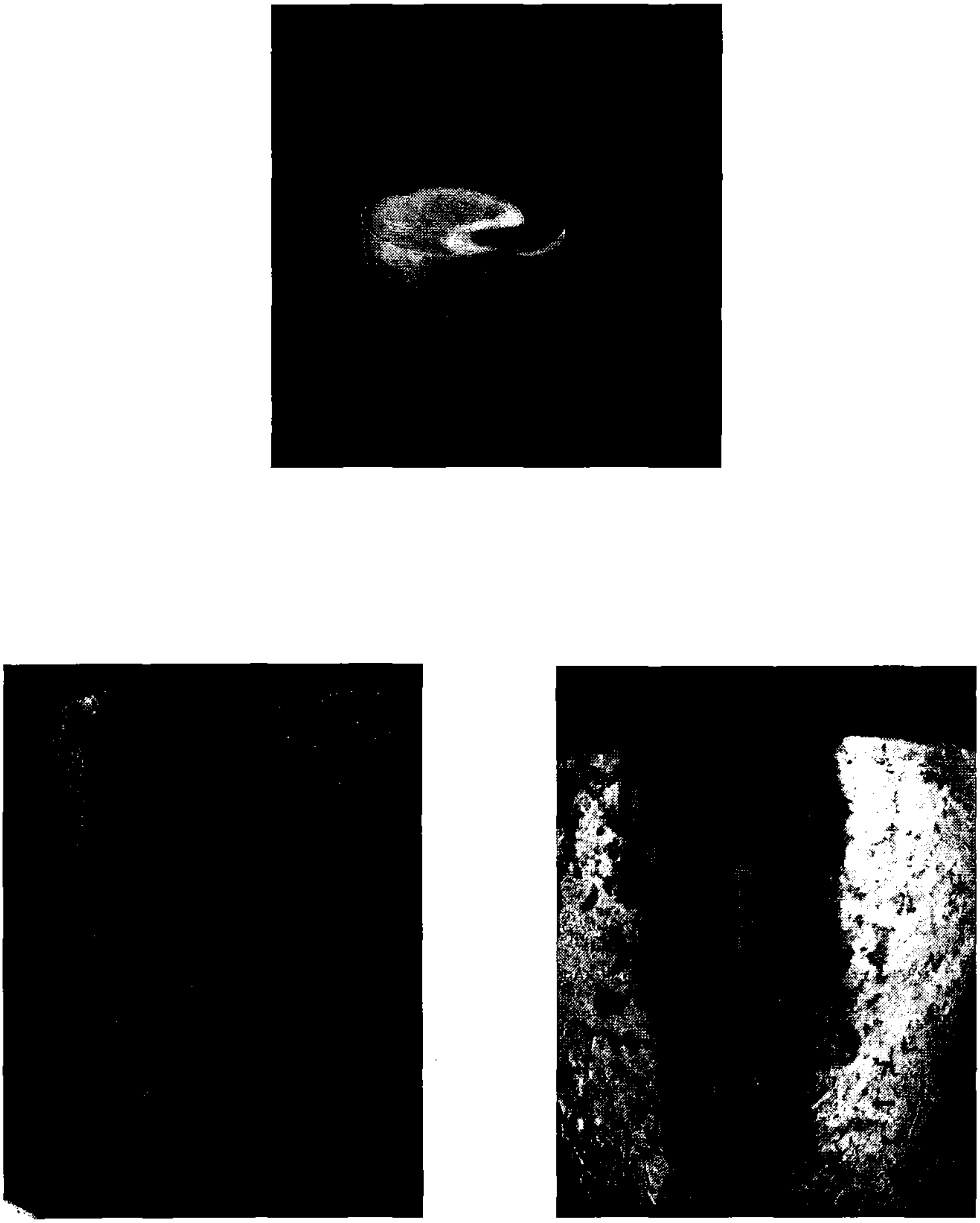
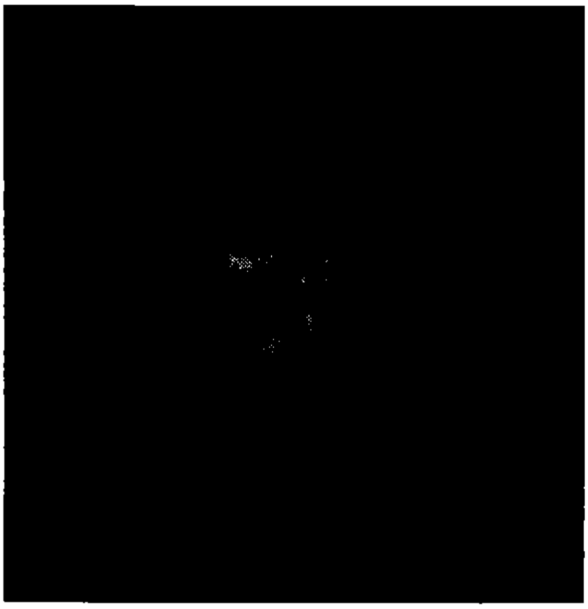


Fig.3: Test sample: sodium metaborate with 17.2% UO_2



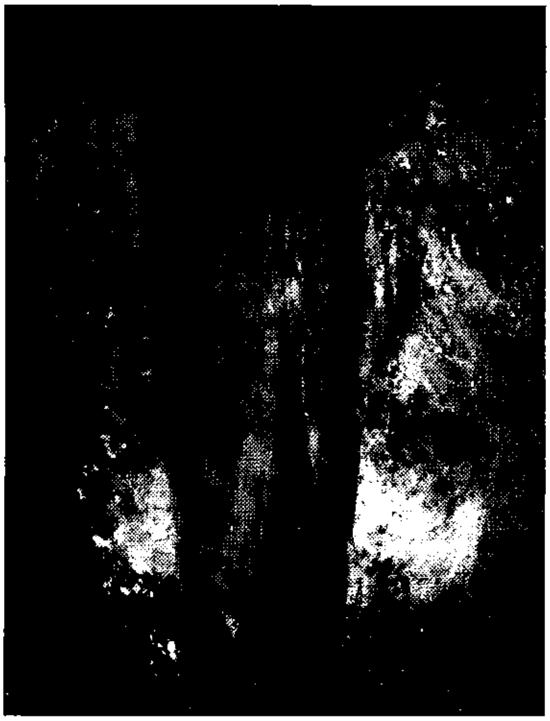


Fig.4 : Test sample: sodium metaborate with 9.3% UO_2

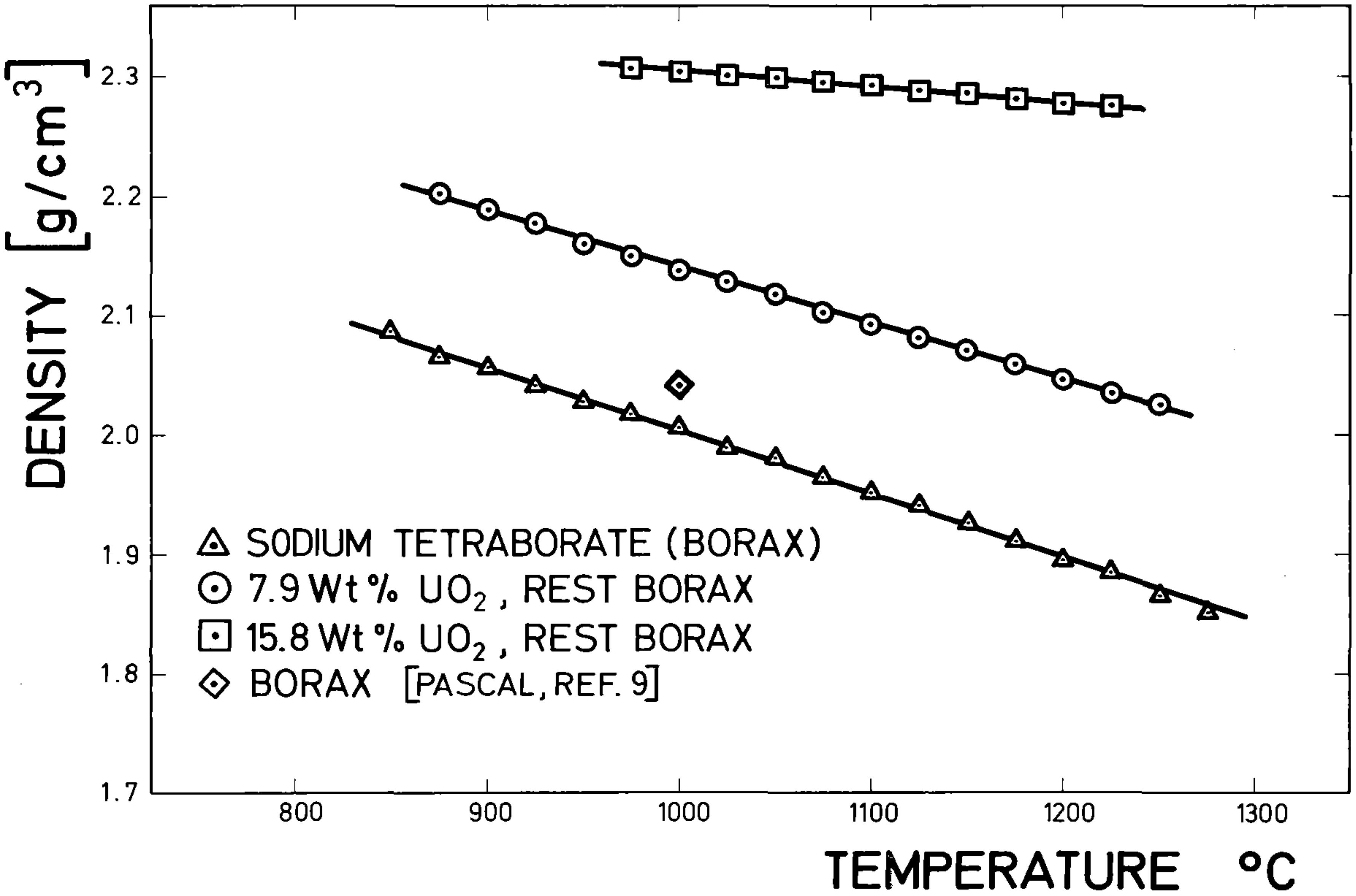


Fig.5: Density of borax, and of borax with UO_2 versus temperature

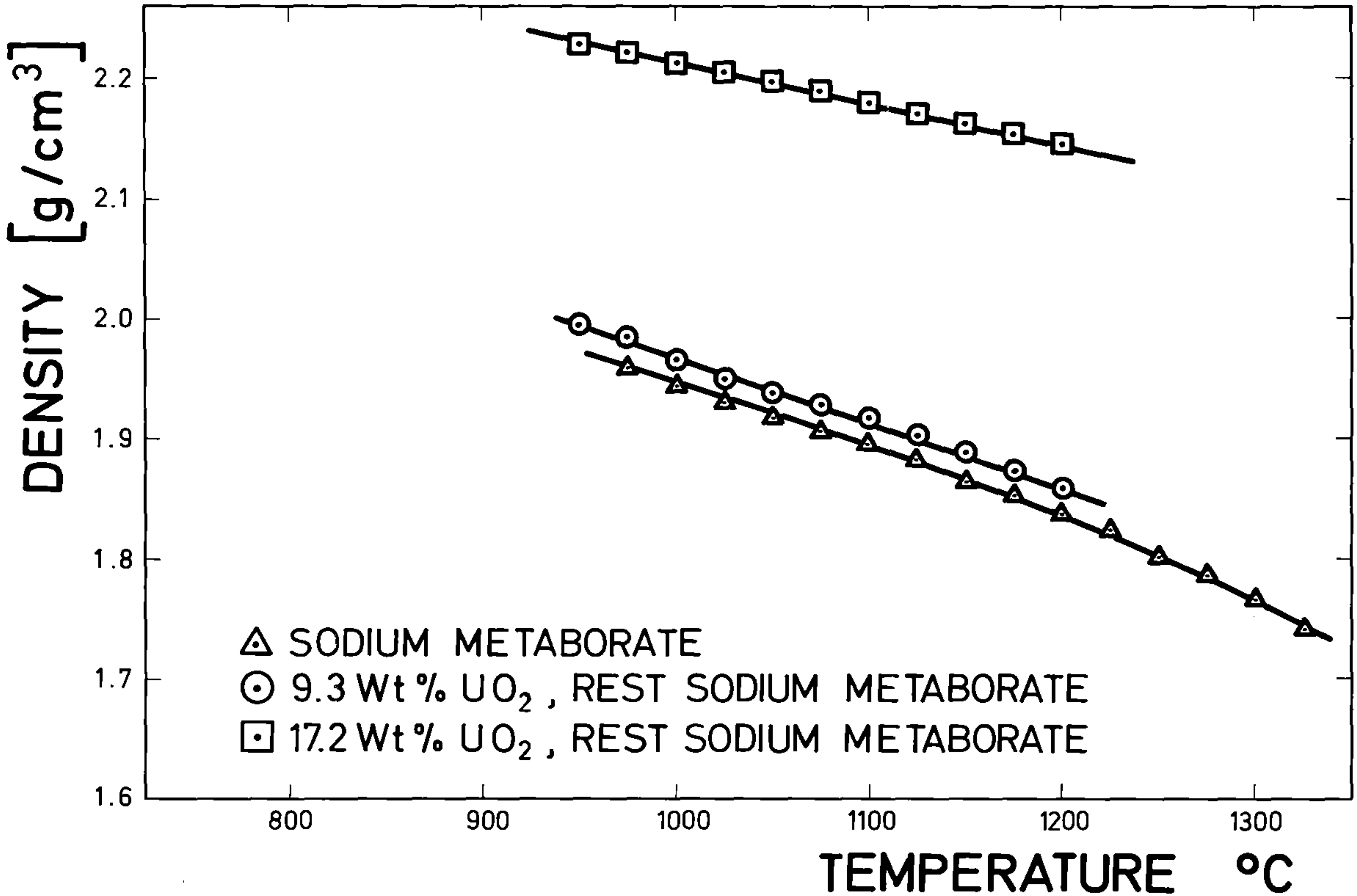


Fig.6: Density of sodium metaborate and of sodium metaborate with UO_2 versus temperature.

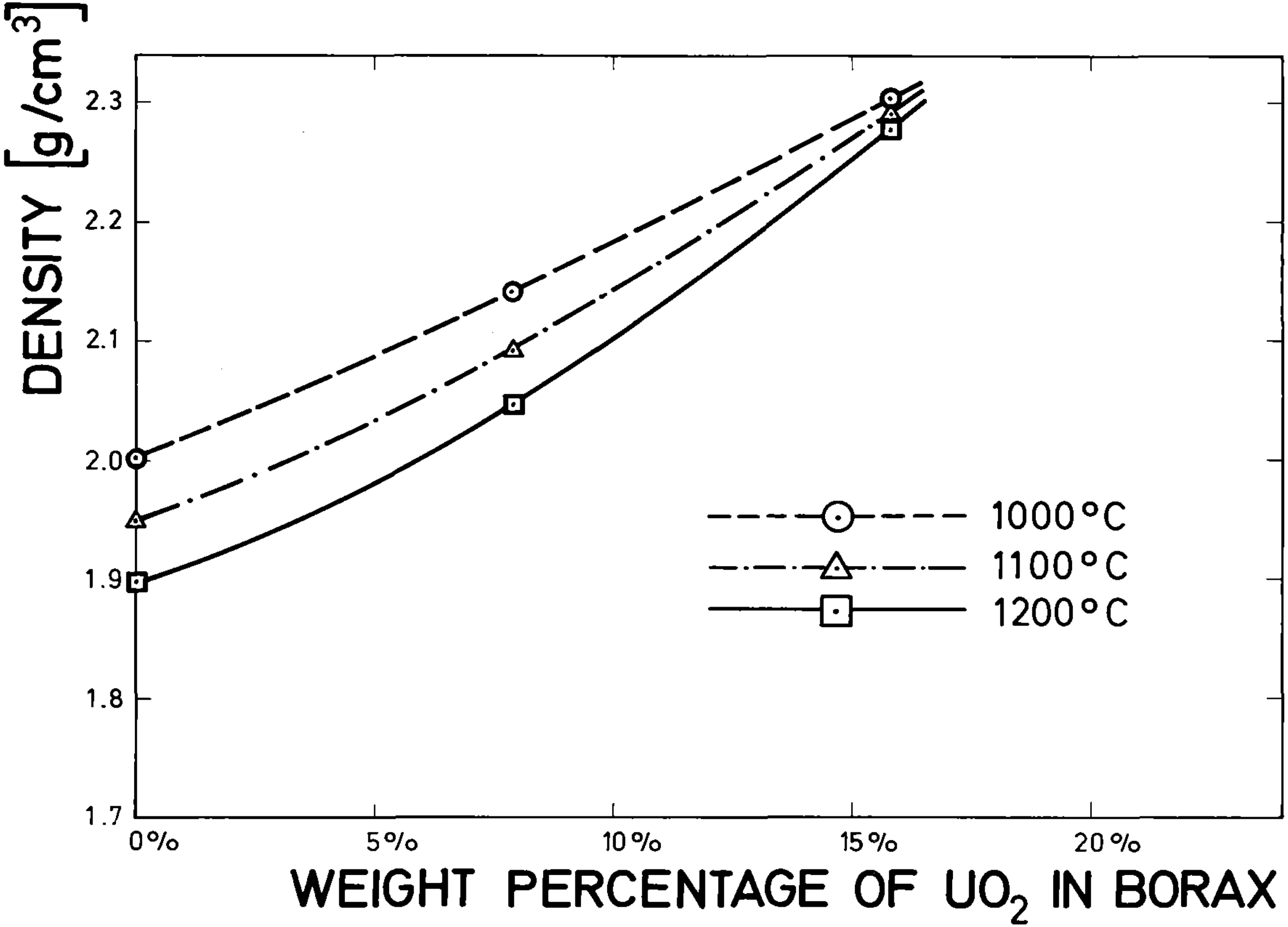


Fig.7: Density of borax-UO_2 as a function of percentage of UO_2 at various temperatures

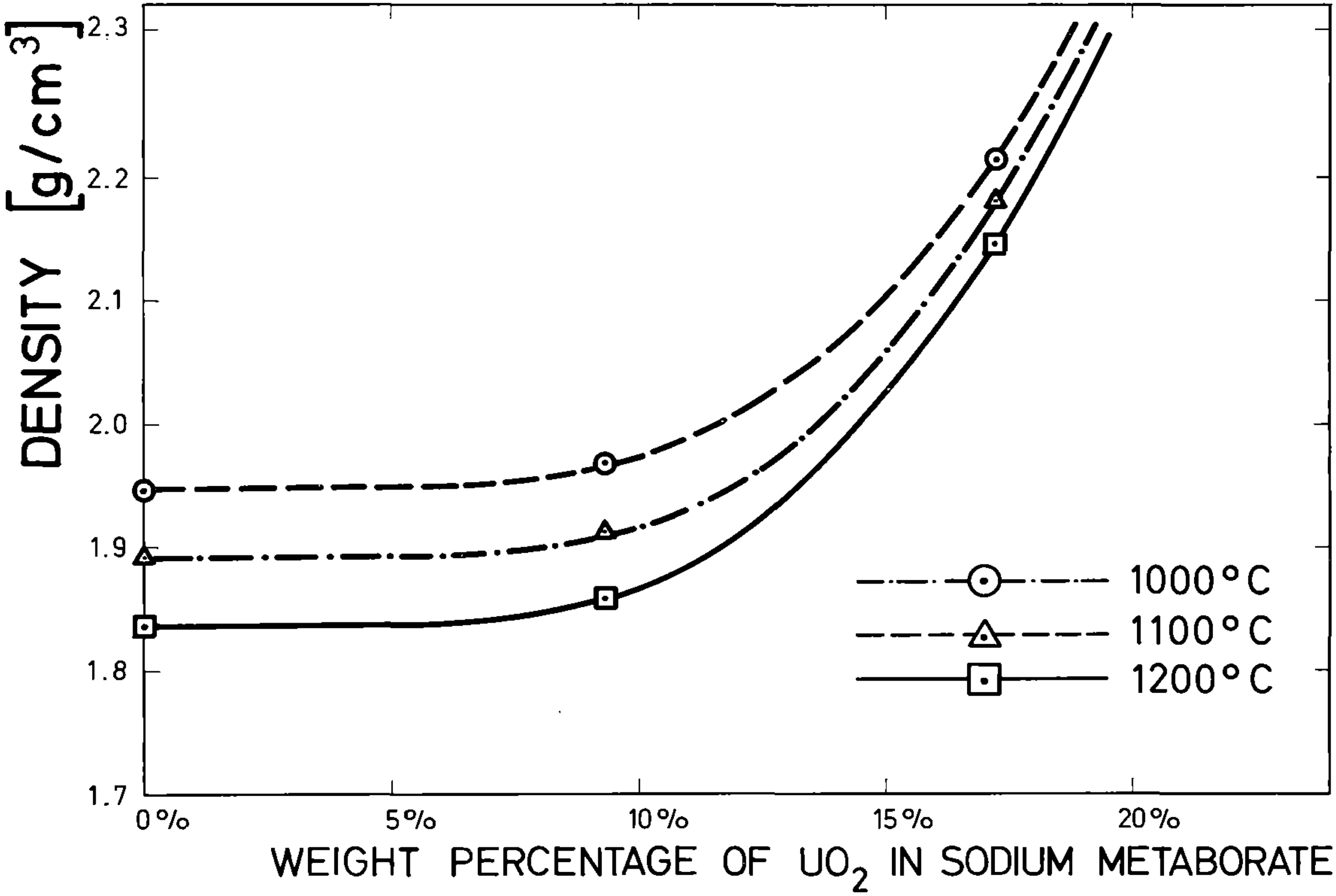


Fig.8: Density of sodium metaborate-UO_2 as a function of percentage of UO_2 at various temperatures

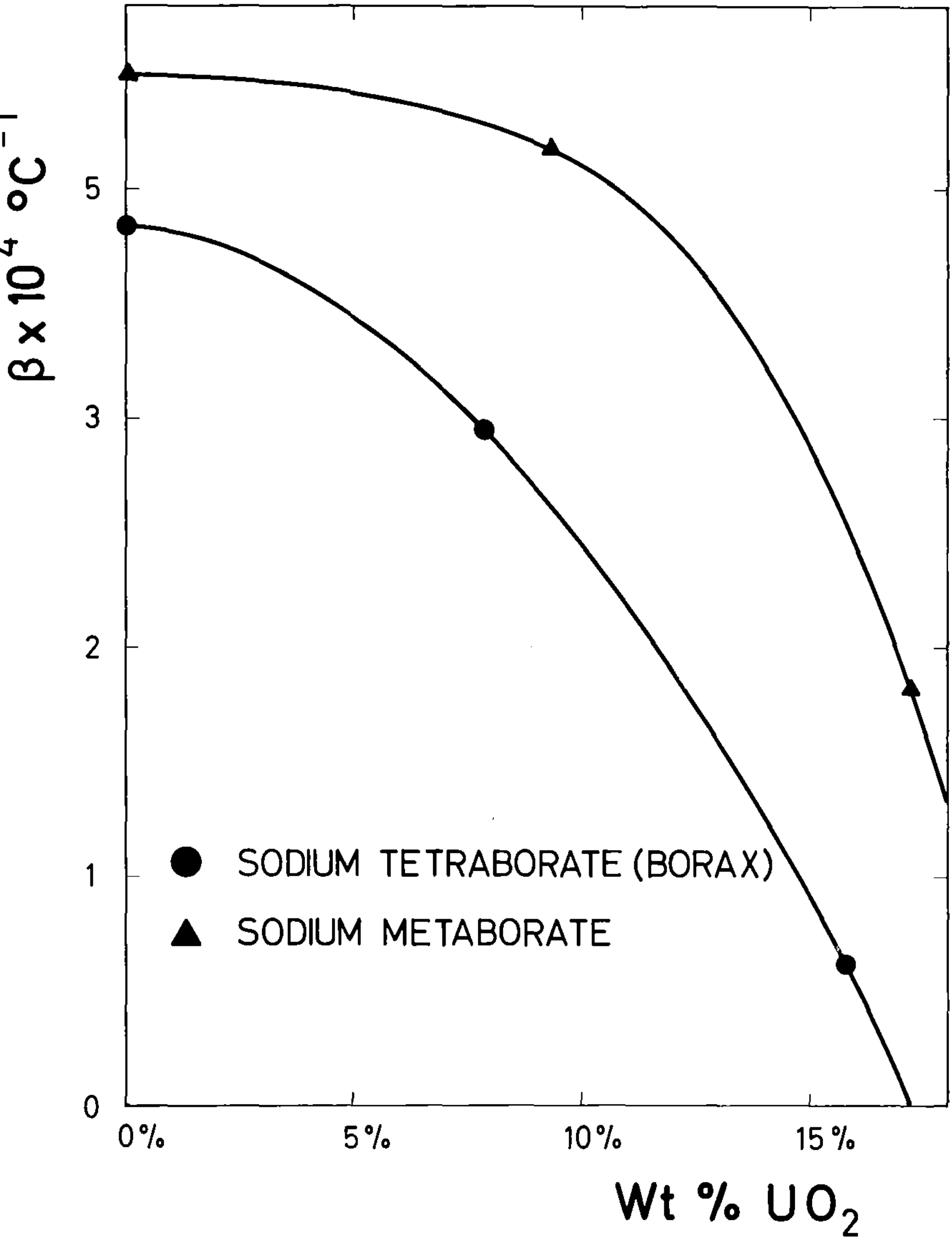


Fig.9: Coefficient of volumetric thermal expansion as a function of UO_2 percentage

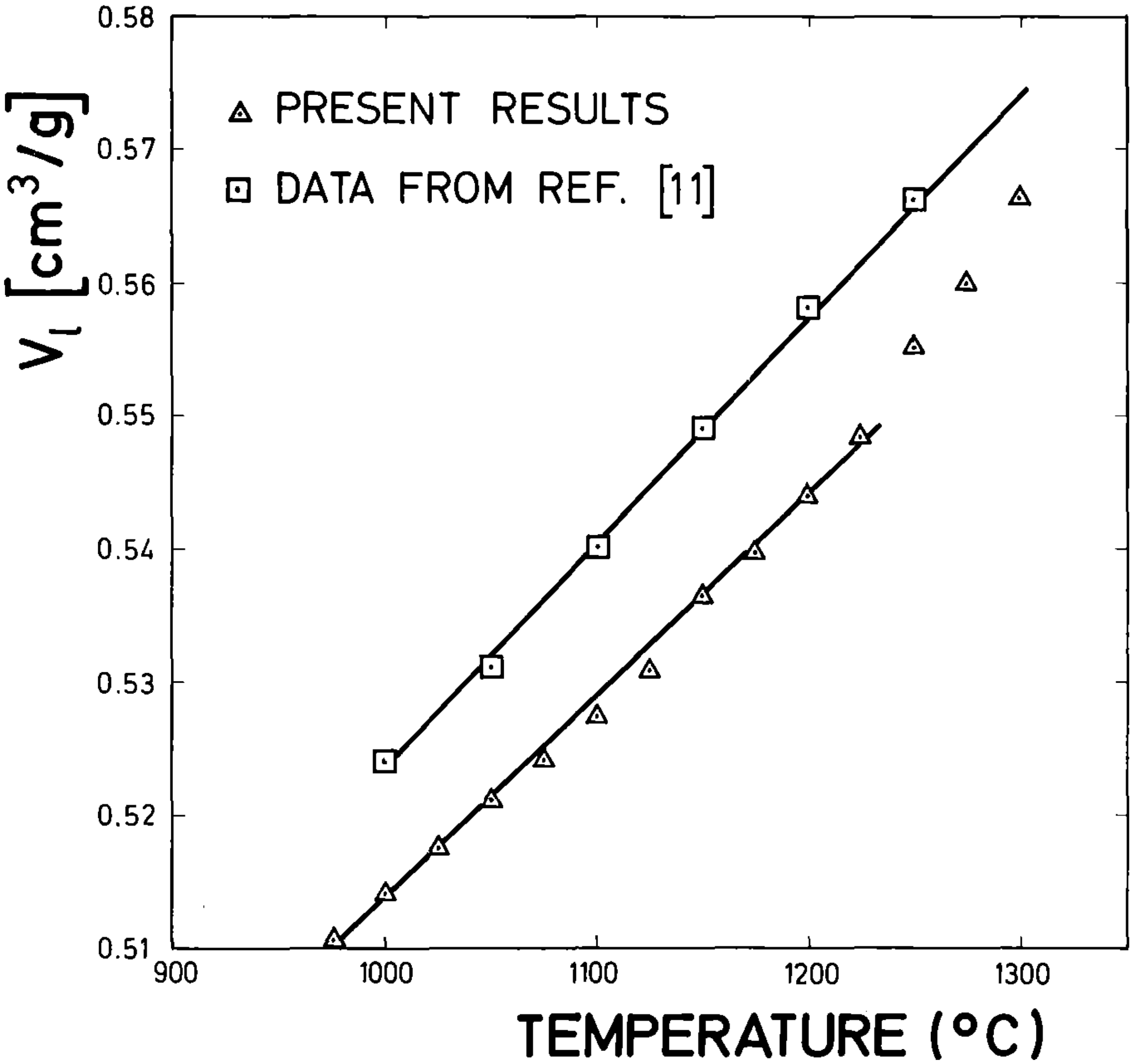


Fig.10: Specific volume of sodium metaborate versus temperature