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BNWL-2111
UC-70

Volatility of a Zinc Borosilicate Glass Containing Simulated High-Level Radioactive Waste

by
W. J. Gray

October 1976

Prepared for the Energy Research
and Development Administration
under Contract E(45-1)-1830

 **Battelle**
Pacific Northwest Laboratories

BNWL-2111

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ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Under Contract E(45-1)-1830

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$5.00; Microfiche \$2.25

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VOLATILITY OF A ZINC BOROSILICATE GLASS CONTAINING
SIMULATED HIGH-LEVEL RADIOACTIVE WASTE

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October 1976

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ABSTRACT

Volatilities of a zinc borosilicate glass containing 25 wt.% simulated high-level radioactive waste calcine and of the calcine itself were determined in the range 800-1200°C. The fission products Rb, Mo, Ru, Te, and Cs were detected in the vapor from both the glass and the calcine. In general, the vaporization rates were lower from the glass with the exception of Rb and Cs at 1200°C, where the rates were about the same from the glass as from the calcine. Furthermore, slopes of Arrhenius plots for Rb and Cs were higher for the glass indicating that more of these elements would be lost from the glass above 1200°C than from the calcine. Vaporization of all volatile elements from the glass seems to be dominated by a single mechanism; thus, vapor composition over the glass is essentially temperature independent. Several mechanisms apply to vaporization of the various elements from the calcine. Gross weight-loss from the glass and calcine appears to be surface and diffusion controlled, respectively.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.	i
INTRODUCTION.	1
EXPERIMENTAL.	2
RESULTS	4
Gross Volatility	4
Specific Element Volatility.	5
Heats of Vaporization.	6
DISCUSSION.	7
Qualification of Results and Experimental Procedures	7
Heats of Vaporization.	9
Vapor Pressure Estimates	11
Comparisons With Other Work.	12
Future Work.	13
CONCLUSIONS	13
REFERENCES.	R-1

VOLATILITY OF A ZINC BOROSILICATE GLASS CONTAINING SIMULATED HIGH-LEVEL RADIOACTIVE WASTE

INTRODUCTION

High-level radioactive wastes, which are produced from reprocessed commercial reactor fuel, will be isolated from man's environment by solidifying them and, most likely, incorporating them into some type of glass or ceramic; then they will be further isolated from the biosphere by placing them in stable geologic formations. The potential hazard to man of a given waste form will partially depend on the possibilities for it to be released during shipment or from the repository, dispersed, and transported into his environment. Three basic physical properties of the solid waste form help determine the extent to which this can occur: volatility, leachability, and frangibility. Furthermore, changes in physical and chemical properties can occur during an initial accidental release which can affect the subsequent transport of radioactive materials to and through the environment. For example, material vaporized from the solid is likely to condense, either in the atmosphere or on cold surfaces, as micron or submicron-sized particles. Such particles would have considerably different leach characteristics than the parent solid. In some cases, they could also be easily airborne although the extent to which this might occur will depend on their chemical form (e.g., if the particles are predominantly alkali metal oxides, they will react with moisture in the atmosphere and tend to adhere to any surface). Knowledge of the above three properties is therefore required for proper risk analysis.

While it is the purpose of waste management to make sure the waste is never subjected to conditions where it could be released to the environment, there is always the concern that something unforeseen may occur. Thus, for example, basic volatility data are required for the evaluation of consequences in the unlikely event of either a shipping or storage accident involving high temperatures, such as a fire or loss of coolant, and the simultaneous loss of integrity of the waste canister. Other unlikely scenarios dictate the need for leachability and frangibility data.

In addition to accident situations, volatility is also of importance from the standpoint of processing and its effect on off-gas treatment requirements. Other studies much more applicable to this aspect of waste management are being conducted and some results have been published elsewhere.^(1,2)

This report presents results from the first phase of a volatility study on a zinc borosilicate glass containing 25 wt.% of a simulated high-level waste calcine. The particular formulation studied is the first zinc borosilicate glass to be characterized in detail. In addition, data for the pure calcined waste are presented. Data cover the temperature range 800-1200°C, the upper limit of which was based on maximum hydrocarbon fire temperatures of about 1050°C.⁽³⁾ More recent information⁽⁴⁾ indicates that temperatures of about 1300°C can be achieved in such a fire. Future efforts will be directed toward higher temperatures and on obtaining more quantitative data on loss of radioactive fission products from the glass and perhaps also from the calcine. Glass formulation development is continuing; thus, future volatility studies will also be extended to other glasses.

EXPERIMENTAL

The philosophy of the experimental approach to this study was to measure volatility under conditions either as realistic as possible or under conditions more pessimistic than might be expected to occur. A situation wherein air, perhaps containing some moisture, flows across the sample surface in such a manner as to sweep away the vapor as quickly as it leaves the surface seemed most appropriate. That is, efforts were made to conduct the measurement in region IV of the generalized transpiration curve shown in Figure 1. Vaporization rates thus obtained would be more rapid than expected under some accident conditions but should closely approximate the worst case. In retrospect, as is discussed later, worst case conditions probably were not quite achieved.

Compositions of the fission product oxides (calcine) and of the zinc borosilicate glass used in this study are shown in Table I. The calcine was clean in the sense that it was mostly fission products with only small

Table I. Composition of Zinc Borosilicate Glass and Calcine

	<u>CONSTITUENT</u>	<u>NOMINAL CONCENTRATION WT%</u>
Glass Frit (75%) 27.50	SiO ₂	27.71
	ZnO	21.64
	B ₂ O ₃	11.30
	Na ₂ O	4.12
	K ₂ O	4.12
	CaO	1.50
	MgO	1.50
	SrO	1.50
	BaO	1.50
	Calcine (25%) (Typical Clean High-Level Commercial Waste) 27.50 1.34	Y + RE ₂ O ₃
MoO ₃		4.29*
ZrO ₂		3.28
RuO ₂		1.97
Cs ₂ O		1.91
BaO		1.04
Fe ₂ O ₃		1.00
PdO		0.98
SrO		0.70
TeO ₂		0.48
P ₂ O ₅		0.44
Rh ₂ O ₃		0.32
Cr ₂ O ₃		0.23
Rb ₂ O		0.23
NiO		0.09
Ag ₂ O		0.06
CdO		0.06
Actinide Oxides		1.50**

*Includes 0.86% MoO₃ as standin for Tc.

**Representative concentration present in actual waste, not included in present study.

amounts of corrosion products from the reprocessing equipment and little if any processing elements such as sodium. The glass was molten at all temperatures used in this study but the calcine remained a powder of ~ 10 μm diameter particles although it did sinter slightly.

The apparatus used in this study is shown schematically in Figure 2. It allows continuous recording of weight loss from the sample while a portion of the volatiles are simultaneously collected on the water-cooled cold-finger and can be removed at intervals for chemical analysis. Although air, either dry ($< 3.5 \times 10^{-3}$ mg water per liter of air) or moist, flows downward through the tube, some of the vapors condense in the upper portion. It was simply assumed, therefore, that the material condensed on the cold-finger was representative of the whole. Weight-loss rates were found to be independent of air-flow rate over the range used (1-3 SCFM) indicating that the weight-loss rates were indeed maximized and could not be increased by more rapid air-flow rates. Thus, it appeared that the measurements were indeed made in region IV of Figure 1 but again, as discussed later, this apparently was not quite true.

All weight-loss data were taken by first bringing the furnace to the desired temperature and then introducing the sample. At the end of the run, the sample was removed from the hot furnace and weighed as a double check on the total weight loss. Moisture was added to the air stream by bubbling the air through a constant-temperature water bath. Rather than assume the air to be saturated, its moisture content was calibrated as a function of flow rate and bath temperature by simply recondensing the water and comparing the quantity to the saturation value.

The calcine contained 4.7 wt.% water and nitrates which could be eliminated quickly by heating to 500°C or above. Thus, when the sample was placed directly into the hot furnace, most of the water and nitrates were lost during the five minutes or so required to position the sample thereby resulting in a large uncertainty in the starting position of the recording balance. The weight lost during this brief period was obtained by the difference between the total recorded weight loss and the weight loss obtained by before and after weighings of the sample. For the glass samples, the before and after weighings agreed well with the recorded weight losses.

The sample surface area assumed in all cases was the cross sectional area of the platinum crucible (1.98 cm^2), and sample weights, with one exception, were always 2.00 g. The exception applies to the data shown in Figure 6 where sample weights of 1.05 g were used.

Vapor condensed on the cold-finger was removed, dissolved, and analyzed via atomic absorption and x-ray fluorescence techniques. As a check on the analytical and dissolution techniques, samples of the glass and of the calcine were dissolved and analyzed. The analytical results were in good agreement with the nominal compositions shown in Table I.

In some instances, material on the cold-finger reacted rapidly with moisture in the atmosphere, probably because it contained a large fraction of alkali metals. In these instances, the material was simply washed from the cold-finger into a flask using distilled water rather than attempting to maintain it in a dry atmosphere at all times. This prevented pre-weighing the sample and therefore allowed an analytical determination only of the relative amounts of the elements present (oxygen was not determined).

RESULTS

Gross Volatility

Figures 3 and 4 show weight loss as a function of time at various temperatures for the glass and calcine respectively. Loss of water and nitrates from the calcine (4.7 wt.%) is not included. All the calcine data are approximately proportional to the square root of time whereas only the 1200°C data for the glass obey this relationship. Glass data at lower temperatures are more nearly linear with time.

Figure 5 is an Arrhenius plot of the data shown in Figures 3 and 4. Because of the small weight loss from the glass at 800°C , these points are within experimental error of the lines drawn. The small change in slope shown for the calcine appears to be real. An anomaly occurs in the weight-loss data for the glass near 1150°C . The 1125° and 1175°C points fall on the lines drawn but the 1150°C points, which are quite reproducible, fall below the lines and, in fact, below the 1125°C points. Apparently some low-volatility phase that probably involves cesium (since it is the predominant vapor component) forms over a very narrow temperature range.

Figure 6 shows the effect of moisture on weight loss from the glass in 4 hours. Sample weights of only 1.05 g were used to obtain these data rather than the normal 2.0 g. While the reproducibility of these data are unknown because each point was measured only once, it is clear that the relative effect is smaller at the higher temperatures and may even begin to saturate at 1200°C.

Specific Element Volatility

Figures 7 through 9 show the weight loss of individual elements from the glass and calcine respectively. Elements not shown were detected in very small quantities if at all. The following procedure was used to produce these data. By assuming that the elements found on the cold-finger via atomic absorption and x-ray fluorescence techniques were present as the same oxides listed in Table I, a very good mass balance was achieved for the calcine at both 1200 and 1100°C. The same assumption for the calcine at 1000°C resulted in the analytical data accounting for only about 80% of the material on the cold-finger. Vapor from the calcine at 800°C reacted with moisture in the atmosphere too rapidly to obtain an accurate weighing. It seems likely, therefore, that the vapor collected at 1000°C also absorbed some moisture which would account for more mass being collected on the cold-finger than was found via chemical analysis. For the glass, the vapor collected at all temperatures reacted with moisture in the air too rapidly to permit accurate weighings. Therefore, because of the good mass balance for the calcine at 1200 and 1100°C, and for lack of something better, the assumption was made that the material collected on the cold-finger at all temperatures for both the glass and calcine was present as the same oxides listed in Table I. It was further assumed that the composition of the material on the cold-finger was the same as that lost from the sample in each case. Therefore, the relative amounts of the different elements found on the cold-finger were normalized, on the basis of their oxides, to the total weight loss from the sample in each case to produce the data in Figures 7 through 9.

Data shown in Figures 7 and 9 are the averages of duplicate runs in each case, whereas the data in Figure 8 are from only one run. Analytical results for the duplicate runs were in quite good agreement being, in general,

within about $\pm 10\%$ of the average. Better agreement than this was usually found where the amount of a given element was relatively large, but generally poorer agreement obtained when only a small amount of a given element was present. Thus, data at the higher temperatures and for the major vapor components are more reliable. In the case of the glass samples where only relative rather than absolute composition was determined, an error in the determination of one element was reflected in all the elements and the detection limit for boron was, unfortunately, quite high. Nevertheless, the data in Figures 7 and 8 were made self-consistent within limits of about $\pm 10\%$ of the values shown by allowing the amount of boron present to float in those cases where it was not detected. In those cases, this resulted in assigning values to the quantity of boron equal to its detection limit in some cases and less than its detection limit in others, not an unreasonable requirement.

Heats of Vaporization

Heats of vaporization listed in Table II were determined from the slopes of the lines in Figures 7 through 9. Figure 7 shows that the values of ΔH_V for the individual elements are about the same as the mean value for the glass, 56.1 kcal/mole. The major exception is Te where $\Delta H_V = 46.0$ kcal/mole. The quantity of Ru is small and therefore subject to larger uncertainty so that it cannot be stated that its heat of vaporization is significantly different than for the other elements even though the lines drawn are substantially different.

Adding moisture to the air stream slightly lowers the mean heat of vaporization of the glass to 51.3 kcal/mole. Figure 8 indicates a larger deviation from the mean for the individual elements than is shown by Figure 7. However, the data in Figure 8 are from only one sample at each of two temperatures and are therefore less reliable than the data in Figure 7.

Table II. Heats of Vaporization

Element	ΔH_v (kcal/mole)
Glass	
in dry air (mean)	56.1
in air with 7.1 wt% H ₂ O (mean)	51.3
Calcine	
in dry air (mean)	
low temp.	22.0
high temp.	28.9
Rb	15.7
Mo	28.0
Ru	
low temp.	31.2
high temp.	54.7
Te	62.9
Cs	14.7

DISCUSSION

Qualification of Results and Experimental Procedure

The real question here is how can the data in Figures 7-9, which are for 4 hours, be applied to real situations and to times other than 4 hours. The answer depends on the rate controlling mechanism, i.e., diffusion or surface limited. If it is the former, then both material thickness and time will be important. If the latter, then neither will matter. Diffusion appears to be rate controlling for the calcine and at 1200°C for the glass because these weight-loss data are approximately proportional to the square root of time. Therefore, a limited investigation was made to determine whether some reasonable thickness could be considered to be infinitely thick so that further increases in thickness would have no effect.

Weight-loss rates were determined for samples of various thickness. However, if there is stagnant air above the sample surface so that the vapor is not swept quickly away, the vaporization rate is reduced because the carrier gas (air) becomes partially saturated with vapor. Thus, one is working in region III of the generalized transpiration curve shown in Figure 1 rather than region IV, and the worst-case conditions sought were not achieved. The amount of stagnant air varies with the amount of sample in the crucible and, therefore, weight-loss rates vary with this parameter as well as with sample thickness. These two variables, sample thickness and amount of stagnant air space, were not easily separated with the existing experimental set-up. Nevertheless, it appeared that weight-loss rates were at least approximately independent of sample thickness at all temperatures for samples thicker than about 1 cm and with essentially no stagnant air space. Furthermore, these weight-loss rates were about double those observed for samples (~3.2 mm glass samples and ~6 mm calcine samples, both with some stagnant air space) upon which the reported data are based.

Whereas the calcine weight-loss data at all temperatures vary approximately with \sqrt{t} , only the 1200°C data for the glass obey this relationship. This implies diffusion control at 1200°C and surface control at lower temperatures. Yet, the data shown in Figure 7 indicate that a single

mechanism dominates the vaporization of all elements from the glass over the range 1000 to 1200°C. Perhaps the \sqrt{t} dependence at 1200°C is simply fortuitous since a comparison of the 1200°C data in Figure 7 with the concentration of the various elements in Table I shows that essentially all of the Cs has been lost in 4 hours and that fairly large fractions of Te and Rb are also lost. (Note that since sample weights were 2.00 g and the cross-sectional area of the crucible was 1.98 cm², the data in Figures 7-9 can be divided by ~ 10 to obtain percentage weight loss.) Thus, at 1200°C, some of the vaporizing species are being depleted fairly rapidly not just from the near-surface region but from the entire sample, which may explain the decrease in weight-loss rate with time.

One other thing that casts doubt on a diffusion mechanism for the glass at 1200°C is that it bubbles and froths somewhat at this temperature. This should stir the glass and upset any diffusion mechanism. Thus, while it cannot be stated unequivocally, the bulk of the evidence obtained to date indicates that a surface rate-controlling mechanism operates in the range 800-1200°C for the glass and that the same mechanism operates for each of the individual elements.

For the calcine, on the other hand, the \sqrt{t} dependence implies a diffusion mechanism. Diffusion through a bed of particles is somewhat harder to visualize than through glass. Perhaps the bed of calcine particles acts somewhat like an ion exchange column. No evidence was obtained, however, that would indicate how the rate for the different elements varies with time.

Two other things should be noted about the calcine data shown in Figure 9. First, the 800°C analytical data particularly for elements other than Cs are subject to considerable uncertainty because of the very small quantity of material for analysis. Thus, the lines for Mo and Ru were not forced through the actual data points. No Te was detected in the vapor at 800°C, but the detection limit lies somewhat above the dashed line drawn. Second, essentially all of the Te has been lost at 1200°C, so that datum point is artificially low. (Note that the concentrations listed in Table I must be multiplied by 4 when considering pure calcine). Therefore, the dashed line in this region has been drawn as a linear extrapolation of the lower temperature data.

The net result of the discussion so far is that the data shown in Figures 7-9 can probably be applied to all glass and calcine samples independent of thickness with a probable error of no more than a factor of about two. For times other than four hours, the glass data can be extrapolated along the lines drawn in Figure 3 with reasonable confidence. One might use Figure 4 to extrapolate the calcine data to times other than 4 hours but with much less confidence because of the uncertain time dependencies for the different elements. When extrapolating to times longer than 4 hours with relatively thin specimens of either glass or calcine, caution must be exercised, particularly at the higher temperatures, because some of the elements may become depleted throughout the entire specimen thereby leading to results that may be grossly in error.

Finally, the reader must be cautioned not to apply these data to sample surface areas derived for small-sized particles for either the glass or the calcine. The surface area used here in all cases was simply the cross-sectional area of the crucible. Probably the most appropriate area to use for accident analyses would be the area of a hole in a defected canister or, if the material is dispersed from the canister, the area of a smoothed surface that conforms approximately to the shape of the pile. Furthermore, the glass softens above $\sim 540^{\circ}\text{C}$ ⁽⁵⁾ so that even if it were initially fragmented, it would flow together at all temperatures of interest from a vaporization standpoint.

Heats of Vaporization

Heats of vaporization were determined from the data in Figures 7 through 9 by assuming that the weight loss was proportional to vapor pressure at all temperatures. Although the data were not taken in region II of Figure 2 where the ratio of vapor pressure to weight loss is known, it seems reasonable to assume that the proportionality is simply some different constant. If that is true, the position of the lines would be changed but the slopes would still be proportional to the heats of vaporization.

Heats of vaporization for the calcine listed in Table II may be compared with those listed for various possible reactions in Table III; the latter were taken from Ref. 6. The heat of reaction 8 is in good agreement with that found for the vaporization of Te while the heat of reactions 6 and 7 are in reasonable agreement with those found in the different temperature ranges for Ru. When more than one species are present in the vapor, the measured heat of vaporization should equal the weighted average of the reactions involved. RuO_3 and RuO_4 are the dominant species respectively above and below 990°C ⁽⁷⁾, and the average heats of vaporization in the ranges $1000\text{--}1100^\circ\text{C}$ and $1100\text{--}1200^\circ\text{C}$ are 37.1 and 46.7 kcal/mole respectively. Considering the accuracy of the present work, the agreement is probably good enough to suggest that these are the reactions taking place in the calcine.

The heat of vaporization found for Mo lies between that for reactions 4 and 5, and it is closer to that for reaction 4 which is reasonable because $(\text{MoO}_3)_3$ is the major specie in the temperature range studied.⁽⁶⁾ Nevertheless, the agreement is probably fortuitous since it is very unlikely that MoO_3 is present in the calcine. Rather, it is probably combined with Sr, Ba and perhaps also Cs and Rb.

The heats of vaporization found for Cs and Rb are not close to any of those listed for the oxides of these elements. Thus, the oxides are apparently not present as such in the calcine, a finding in agreement with the x-ray data of McCarthy and Davidson.⁽⁸⁾ An exhaustive search of the literature has not been made to determine if the measured heats of vaporization for Cs and Rb can be matched with thermodynamic data for some Cs or Rb compound. However, thermodynamic data⁽⁹⁾ involving the seemingly likely possibilities, Cs_2MoO_4 and $\text{Cs}_2\text{Mo}_2\text{O}_7$, for example, don't match the heats of vaporization found here for Cs.

The heat of vaporization found here for the glass, 56.1 kcal/mole, is somewhat higher than $\Delta H_V^\circ(298) = 41.4$ kcal/mole found for the vaporization of CsBO_2 .⁽¹⁰⁾ Furthermore, the heat of vaporization of KBO_2 should be higher,⁽¹⁰⁾ and potassium is the second most prominent element in the

Table III. Heats of Vaporization for Selected Reactions

<u>Reaction</u>	<u>Temp. Range(°K)</u>	<u>ΔH_v° kcal/mole</u>
1. $1/2\text{Rb}_2\text{O}(\ell) + 1/4\text{O}_2(\text{g}) = \text{RbO}(\text{g})$	1000-1500	32.7
2. $1/2\text{Rb}_2\text{O}(\ell) = 1/2\text{Rb}_2(\text{g}) + 1/4\text{O}_2(\text{g})$	1000-1500	41.3
3. $1/2\text{Rb}_2\text{O}(\ell) = \text{Rb}(\text{g}) + 1/4\text{O}_2(\text{g})$	1000-1500	53.6
4. $\text{MoO}_3(\text{s}) = 1/3(\text{MoO}_3)_3(\text{g})$	500-1000	22.6
5. $\text{MoO}_3(\text{s}) = 1/2(\text{MoO}_3)_2(\text{g})$	500-1000	41.8
6. $\text{RuO}_2(\text{s}) + \text{O}_2(\text{g}) = \text{RuO}_4(\text{g})$	1400	22.5
7. $\text{RuO}_2(\text{s}) + 1/2\text{O}_2(\text{g}) = \text{RuO}_3(\text{g})$	1400	51.2
8. $\text{TeO}_2(\text{s}) = \text{TeO}_2(\text{g})$	500-1000	60.6
9. $\text{TeO}_2(\text{s}) = 1/2\text{Te}_2(\text{g}) + \text{O}_2(\text{g})$	500-1000	112.3
10. $1/2\text{Cs}_2\text{O}(\ell) + 1/4\text{O}_2(\text{g}) = \text{CsO}(\text{g})$	1000-1500	39.8
11. $1/2\text{Cs}_2\text{O}(\ell) = 1/2\text{Cs}_2(\text{g}) + 1/4\text{O}_2(\text{g})$	1000-1500	40.1
12. $1/2\text{Cs}_2\text{O}(\ell) = \text{Cs}(\text{g}) + 1/4\text{O}_2(\text{g})$	1000-1500	51.3

glass vapor. Thus, the agreement is reasonably good. However, this does not explain why heats of vaporization of other elements from the glass are about the same nor why there seems to be a single mechanism that dominates the vaporization of all the elements.

Vapor Pressure Estimates

Objectives of the present study did not include the determination of vapor pressures. However, some indication of vapor pressure would be useful simply to assure that a canister could not be over-pressurized during a temperature excursion. Assuming that the vaporization data were taken under equilibrium transpiration conditions, (region II of Figure 2), vapor pressure can be calculated according to:

$$P = \frac{mRT}{VM}$$

where P = vapor pressure in atmospheres

m = weight loss

R = gas constant

T = temperature (°K)

V = volume of carrier gas (1 ft³/hr used in this study)

M = molecular weight of vaporizing species

If the vaporizing species is assumed to be monatomic Cs, the vapor pressure of the glass and the calcine is $\sim 3.6 \times 10^{-4}$ atm and $\sim 4.3 \times 10^{-4}$ atm respectively at 1200°C. Linear extrapolation of the data shown in Figure 7 indicates the vapor pressure over the glass would reach one atmosphere at $\sim 2200^\circ\text{C}$. Using ΔH_v for Te rather than the average value for the calcine, extrapolating the data in Figure 9 indicates the vapor pressure over the calcine would reach one atmosphere at $\sim 2000^\circ\text{C}$.

Examining the assumptions made, it is clear that lower carrier gas flow rates would be required to achieve equilibrium transpiration conditions, probably by a factor of 2 to 5. The weight loss would probably also be lower but by a factor smaller than applies to the flow rate. The vaporizing species are certainly not simply monatomic Cs. For the glass,

however, the major vapor component is Cs and the actual vapor species are probably CsO and Cs. Much smaller quantities of other elements are present; thus, the average molecular weight of the vapor species are not likely to be far different than that of monatomic Cs. The net result for the glass, therefore, is that the calculated vapor pressure is low by a factor of no more than about 5. Using a conservative factor of 10, the vapor pressure extrapolates to one atmosphere at $\sim 1800^{\circ}\text{C}$ rather than the 2200°C obtained above.

Substantial quantities of TeO_2 , RuO_3 , and RuO_4 in addition to CsO and Cs are likely present in the vapor from the calcine. In this case, therefore, the average molecular weight of the vapor species is probably a little higher than for monatomic Cs. For vapor pressure considerations, the weight-loss of Te given by the high-temperature dashed line should probably be used rather than the actual datum point at 1200°C . Thus, the total weight loss should be higher than was assumed above. The factor of 2 to 5 lower carrier gas flow rate also applies to the calcine. Thus, the net result for the calcine is similar to that for the glass. That is, the calculated vapor pressure is probably low by a factor of no more than about 5. Again, using a conservative factor of 10, the calcine vapor pressure extrapolates (using ΔH_V for Te rather than the average value for the calcine) to one atmosphere at $\sim 1700^{\circ}\text{C}$ rather than the 2000° obtained above.

Clearly, there appears to be no reason for concern about canister over-pressurization for either the glass or the calcine.

Comparisons With Other Work

Only very general comparisons between this work and other volatility studies are possible because of differences in glass compositions and experimental details. Data from two studies^(11,12) involving borosilicate glasses together with data from the present work, which involved a zinc

borosilicate glass, are compared in Table IV. In addition, Rostegi, et al.,⁽¹³⁾ have also studied Cs release from a variety of glasses. Their results are in general agreement with both the present study and the work of Walmsley, et al.,⁽¹¹⁾ as opposed to the data of Albrethsen and Schwendiman⁽¹²⁾ which show a considerably lower release rate. Ref. 11 and 12 show the release of both Sr and Ce to be very much smaller than for Cs, in agreement with the present data.

A major difference between the results shown here and those of Walmsley et al.,⁽¹¹⁾ is in the effect of water vapor on vaporization rates. Whereas the results of the present study show a marked effect, their data show none. Perhaps the difference is due to Zn which is a major component of the glass in the present study but was absent from their glass. Barlow,⁽¹⁴⁾ on the other hand, found a marked effect due to water vapor at 1400°C for an alkali-free borosilicate glass.

Future Work

Data reported here constitute just the first phase of this study. Future work will concentrate on both higher and lower temperatures with emphasis on better quantification at the lower temperatures using radioactive isotopes, extension of work to other glass compositions, and on determination of diffusion coefficients of certain fission products in glass. Some effort to ascertain the cause of the anomaly near 1150°C in the present glass may also be made although this seems likely to be mainly of academic interest.

CONCLUSIONS

1. The particular glass formulation studied is effective in reducing the vaporization rate of all fission products at lower temperatures but above ~1200°C, more Rb and Cs are lost from the glass than from the calcine.
2. Addition of moisture to the air significantly increases the vaporization rate for the glass.

Table IV. Cesium and Ruthenium Volatility From Borosilicate and Zinc Borosilicate Glasses

<u>Element</u>	<u>Temp. (°C)</u>	<u>Release Rate* (%/hr)</u>	<u>Source</u>
Cs	1000	1.5	This work
	1000	4.2	Ref. 11
	≥1100	~1	Ref. 12
	1200	33	This work
	1200	10.5	Ref. 11
Ru	1000	7×10^{-2}	This work
	1000	6.7×10^{-5}	Ref. 11
	~1100	Variable	Ref. 12
	1200	1.3	This work
	1200	1.45	Ref. 11

*For this work, release rates are better expressed in terms of mg/cm²-hr. However, for comparison with other work, They have been converted to %/hr.

3. Heats of vaporization of all volatile elements from the glass are about the same and these are only slightly affected by the addition of moisture. Thus, vapor composition over glass is essentially independent of temperature and moisture content of the air at least for times up to four hours.
4. Heats of vaporization of Cs and Rb from calcine are quite low, a fact that is not understood.
5. After due consideration of the various assumptions and possible errors, data shown in Figures 7-9 can probably be applied to all glass and calcine samples independent of thickness with a probable error of no more than a factor of about two. However, sample surface areas used in applying these data must not be based on small particles.
6. Vapor pressure is conservatively estimated to be less than one atmosphere for temperatures lower than $\sim 1800^{\circ}\text{C}$ for the glass and $\sim 1700^{\circ}\text{C}$ for the calcine.

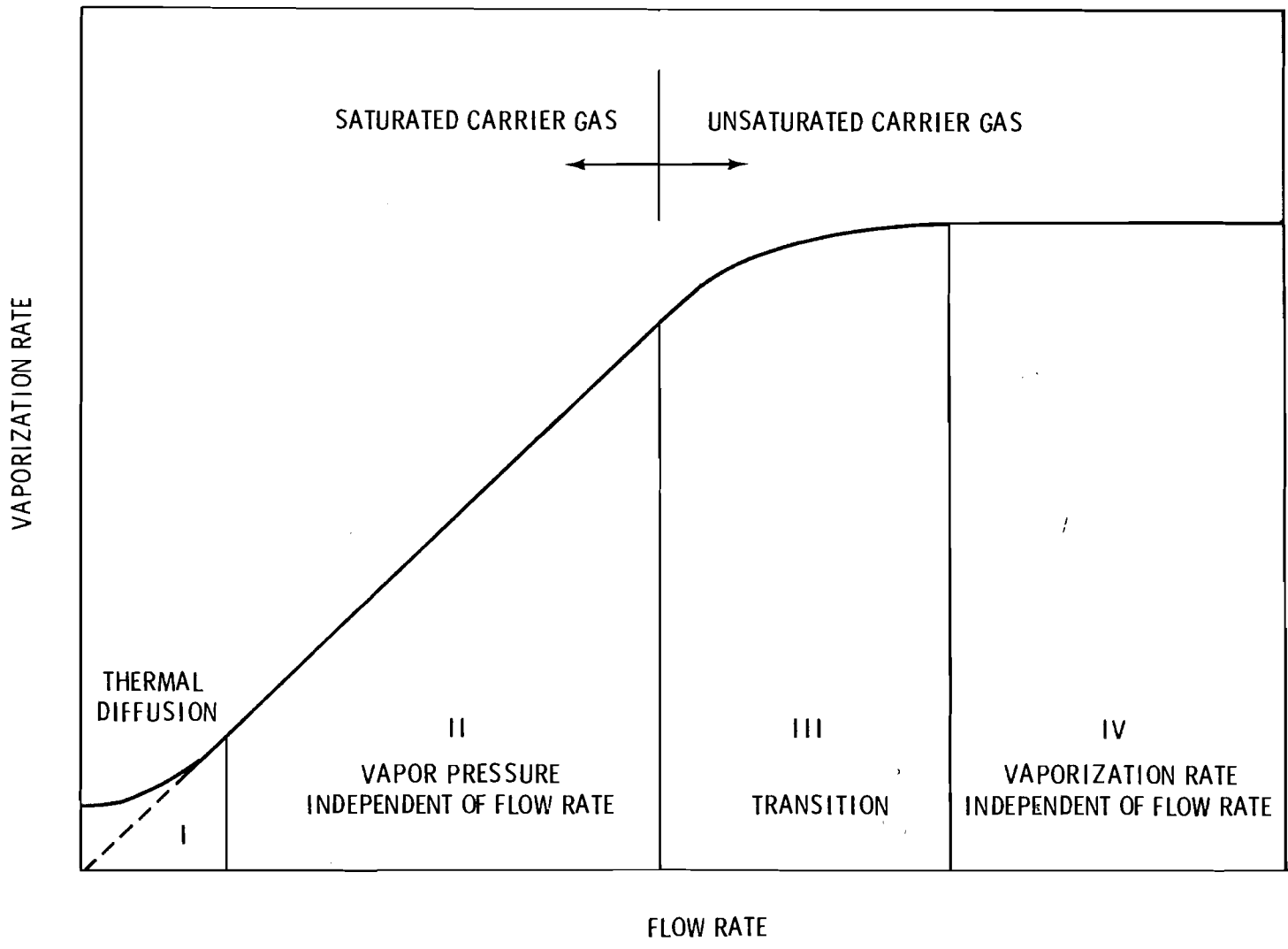


Figure 1. Generalized Transpiration Curve

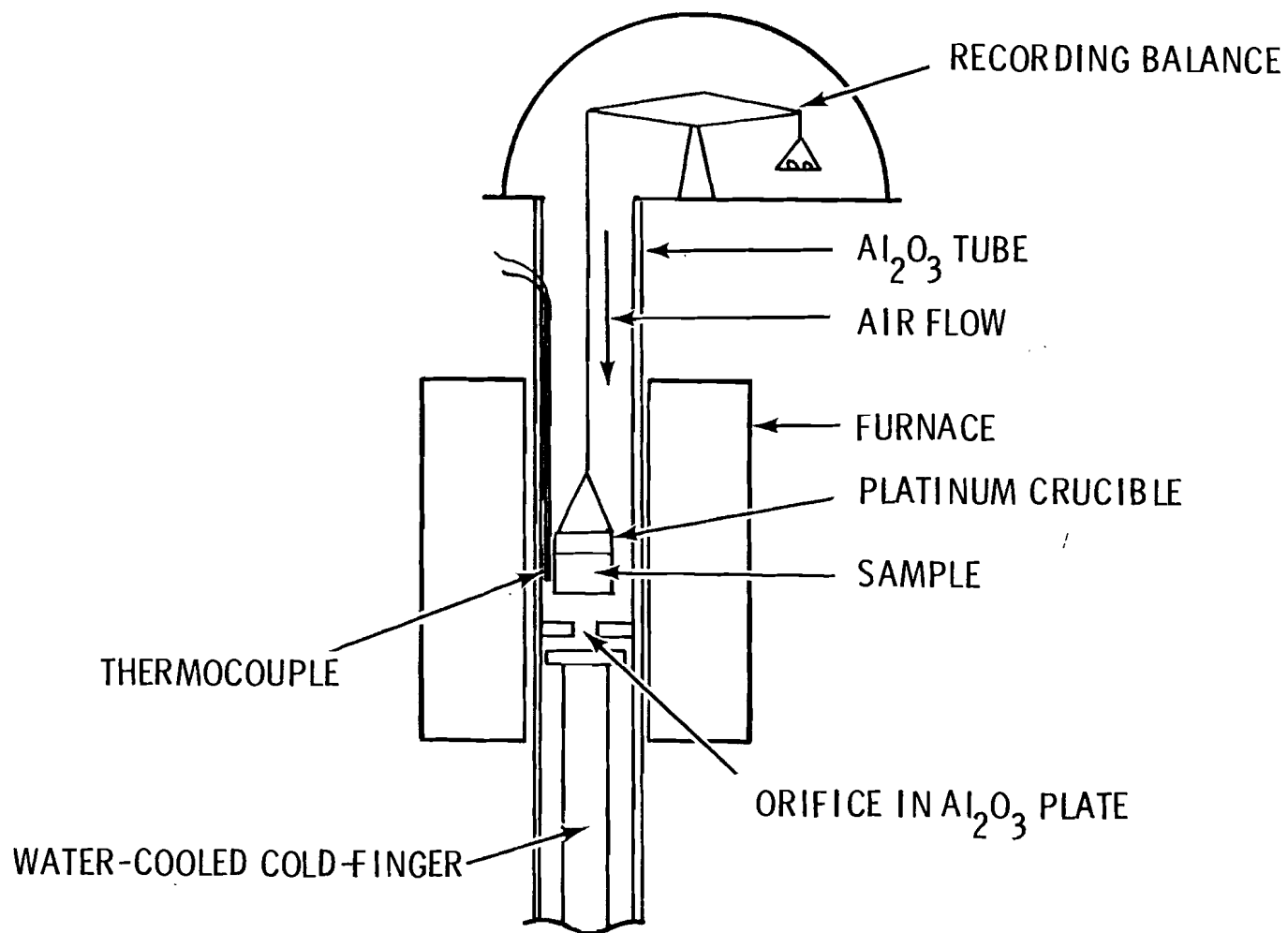


Figure 2. Schematic Diagram of Apparatus

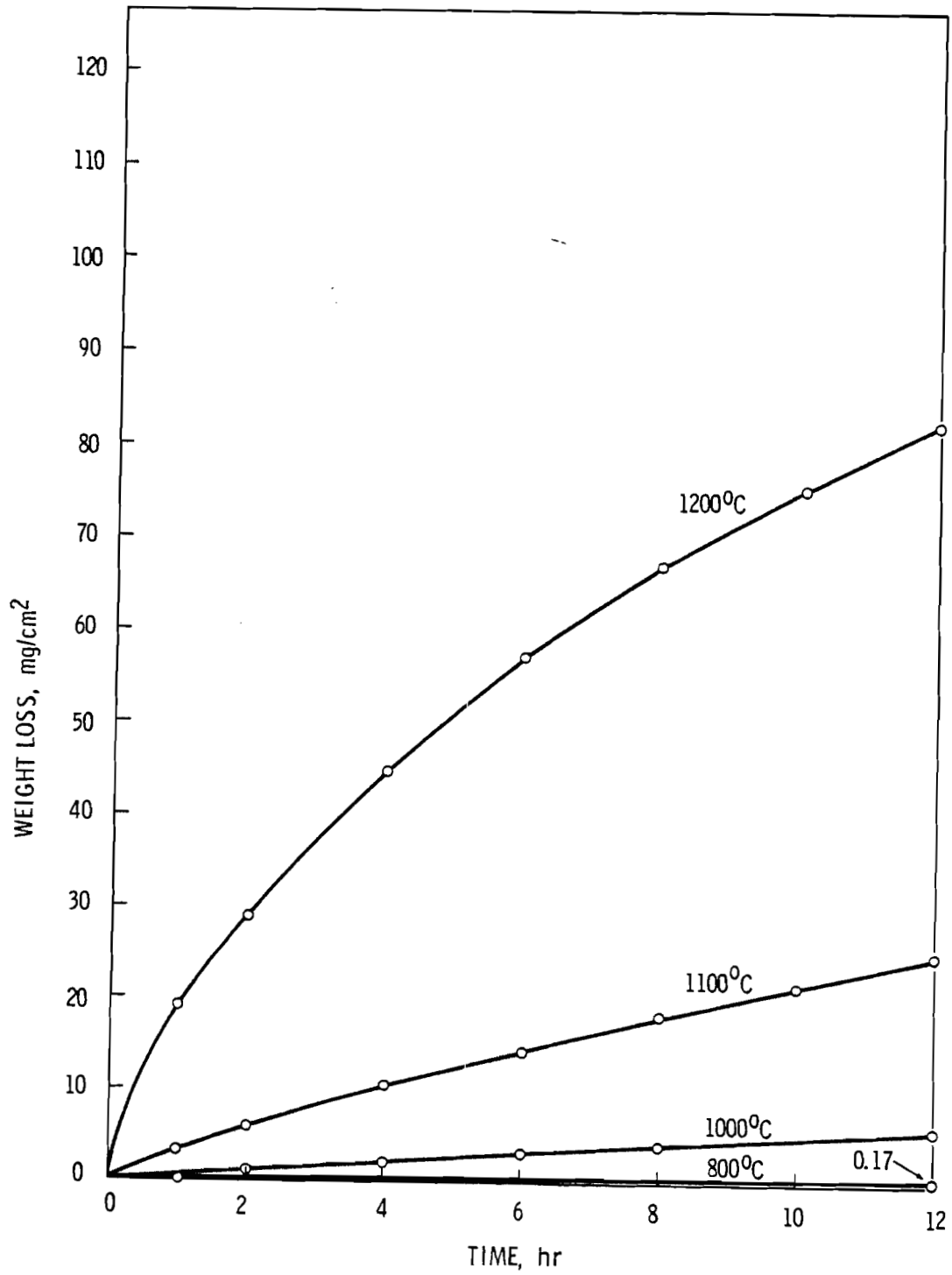


Figure 3. Weight Loss From Glass in Dry Air

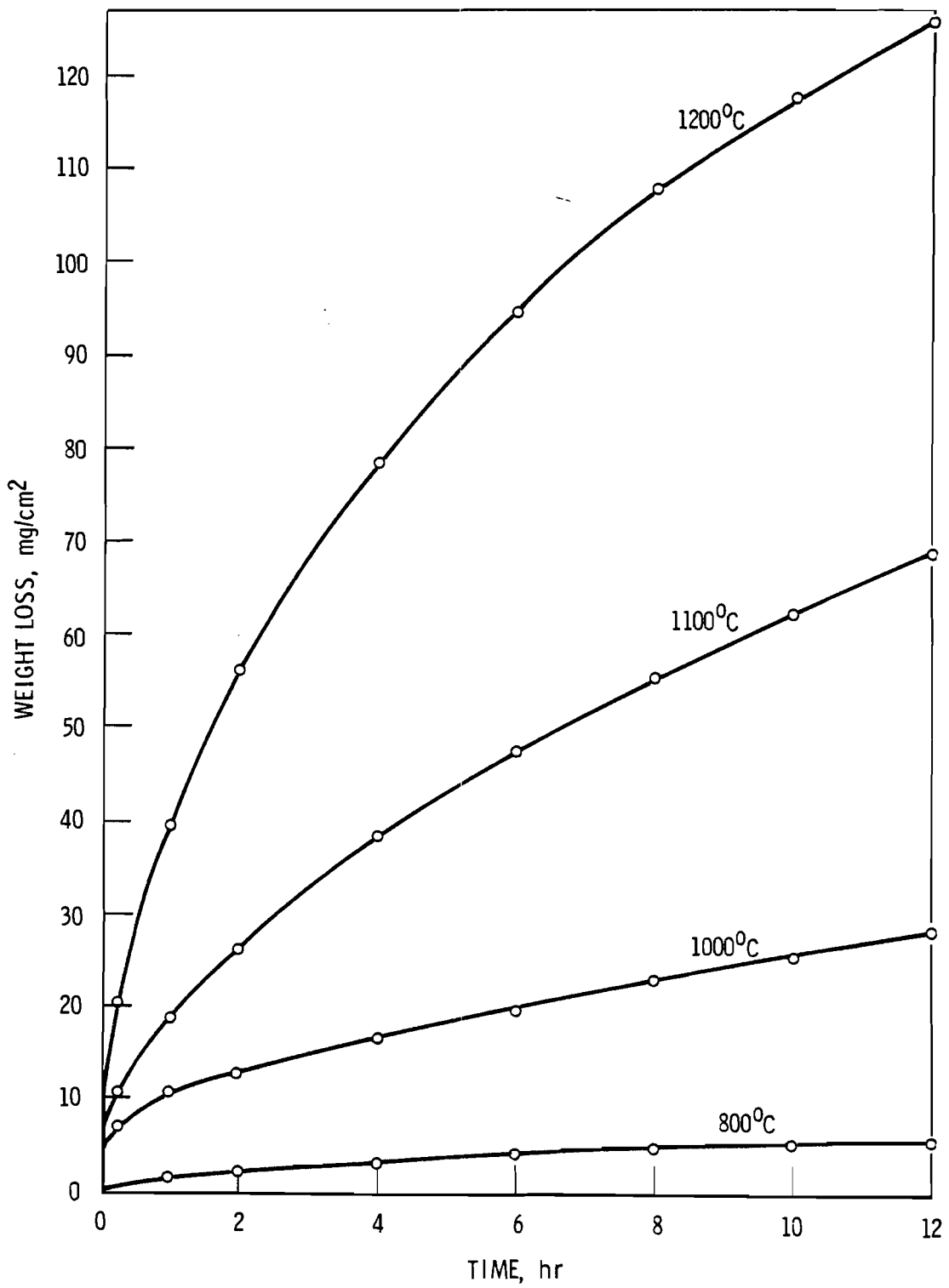


Figure 4. Weight Loss From Calcine In Dry Air

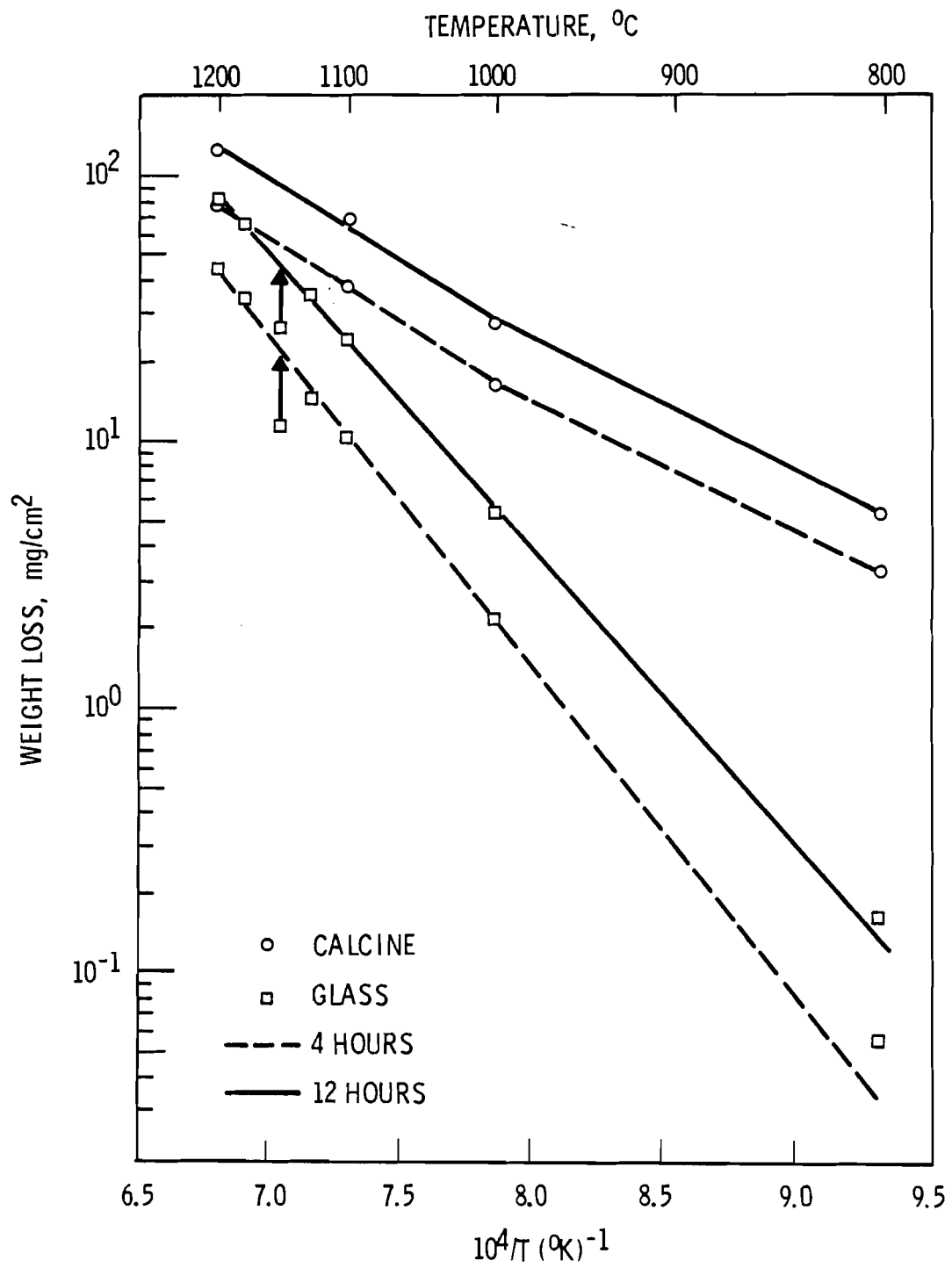


Figure 5. Weight Loss In Dry Air

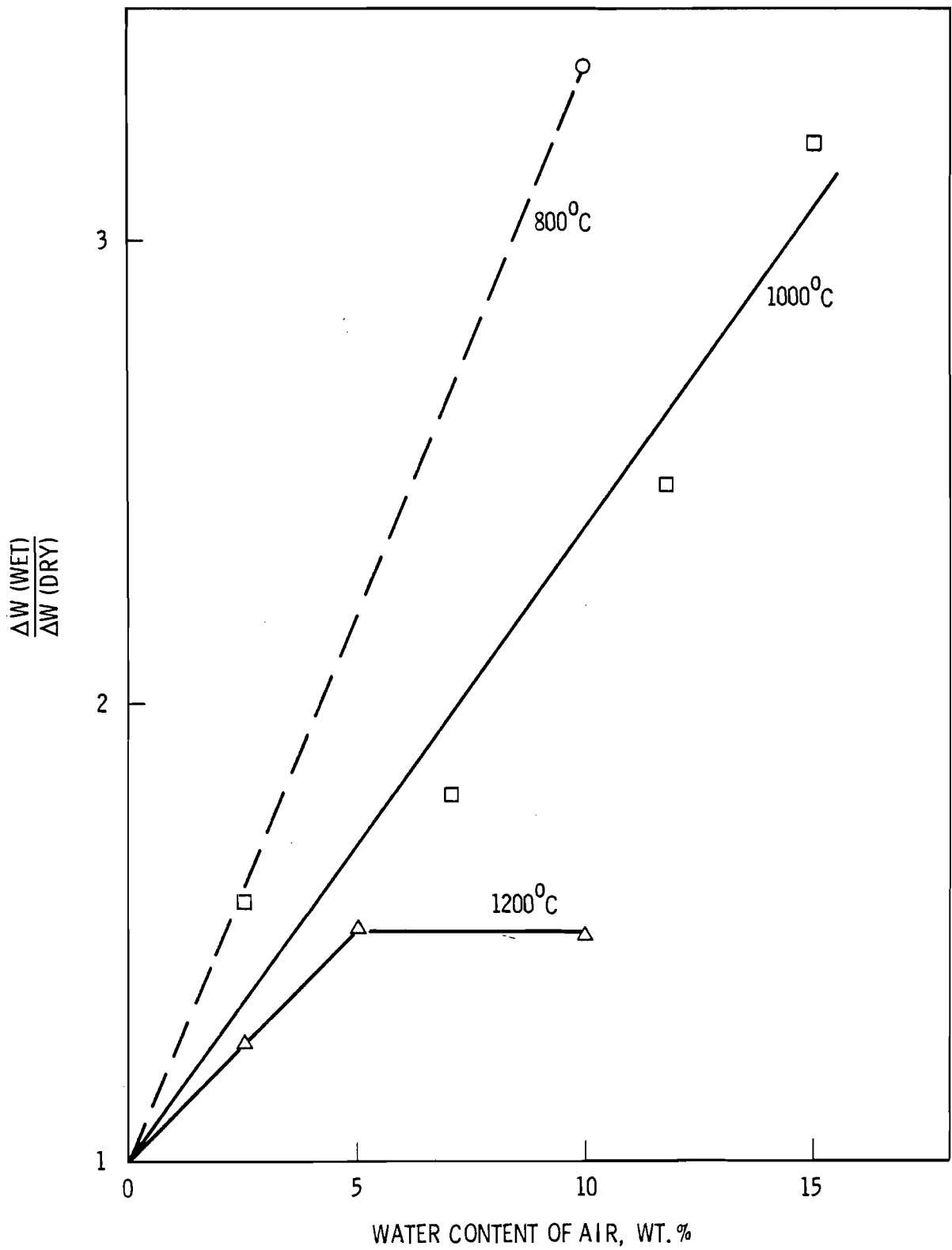


Figure 6. Effect of Moisture on Weight Loss From Glass in 4 Hours

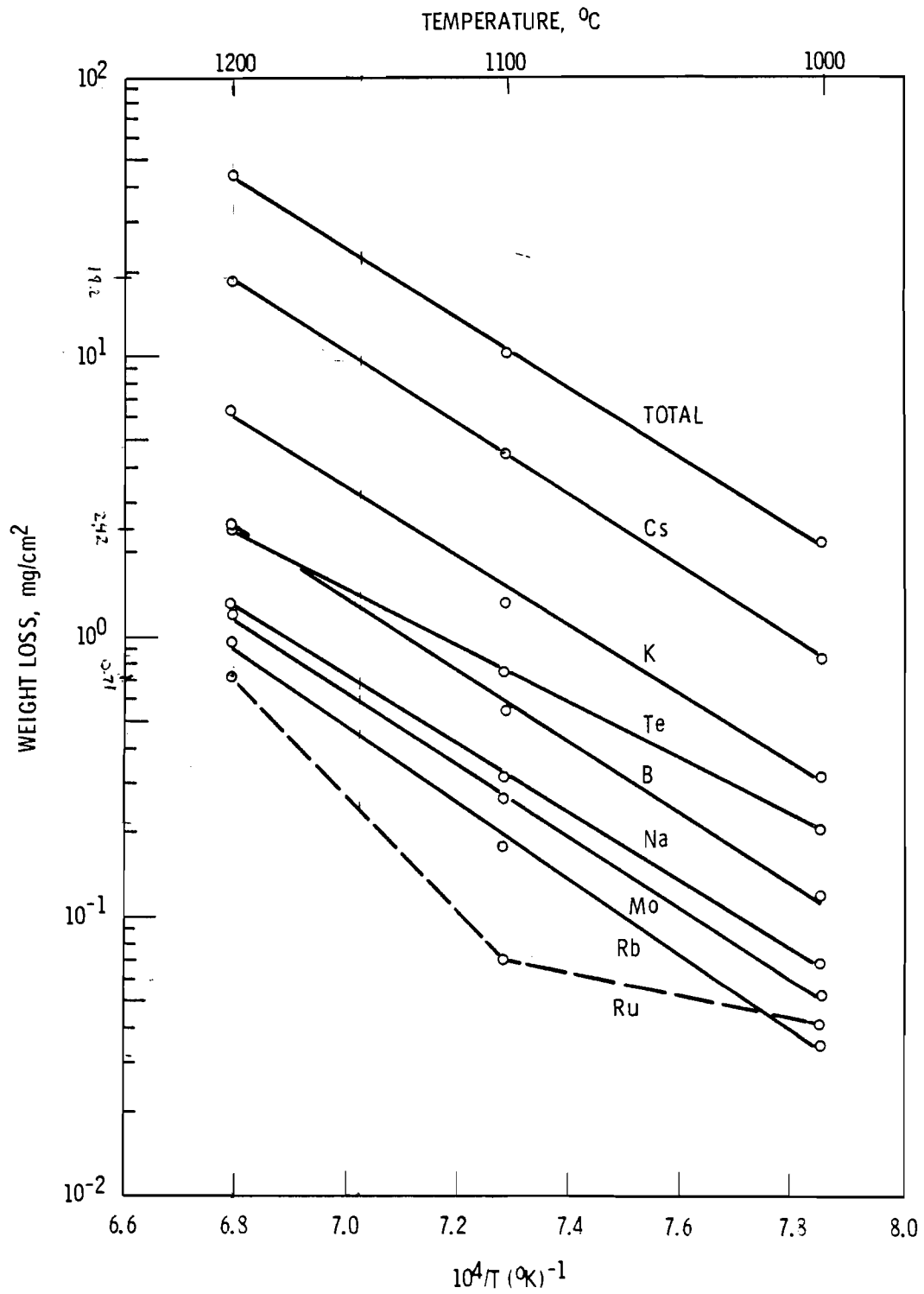


Figure 7. Weight Loss From Glass After 4 Hours in Dry Air

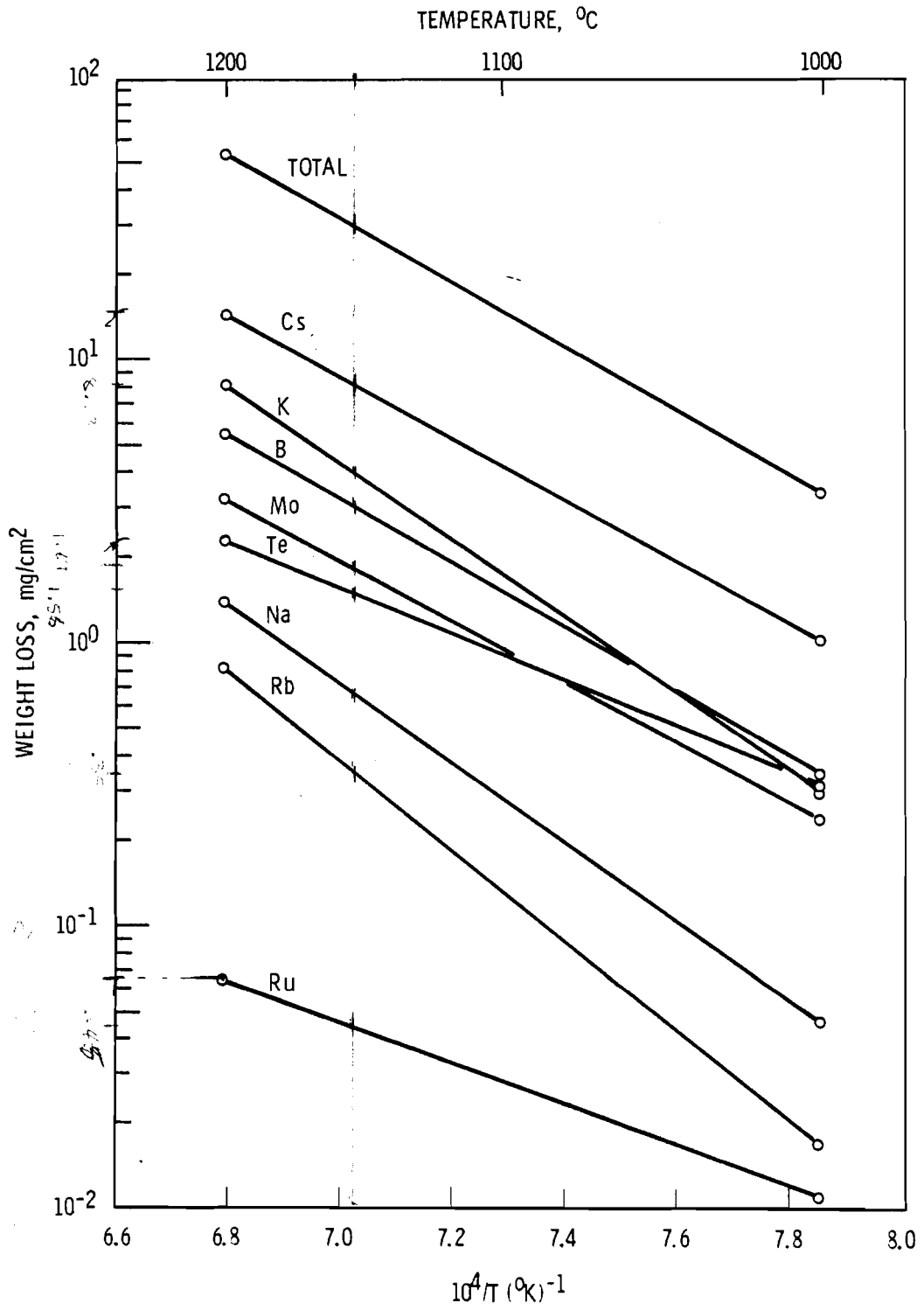


Figure 8. Weight Loss From Glass After 4 Hours in Air Containing 7.1 Wt.% H₂O

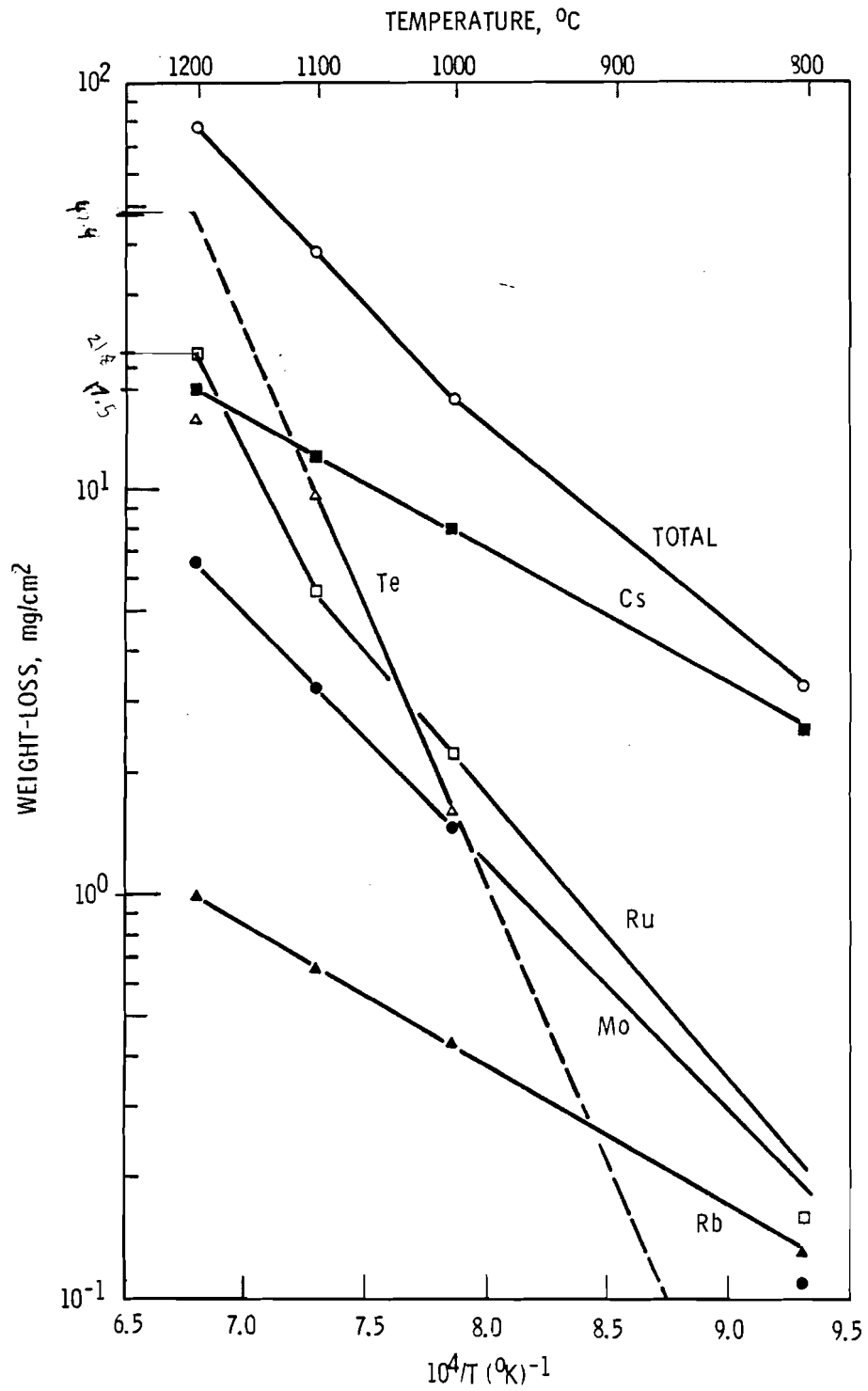


Figure 9. Weight Loss From Calcine After 4 Hours in Dry Air

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