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HIGH-TEMPERATURE MEASUREMENTS OF THE RATE OF UPTAKE OF RUBIDIUM OXIDE VAPOR BY SELECTED OXIDES

by

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ABSTRACT

In a program for elucidation of the process of formation of radioactive fallout, we measured the rates at which substrate samples of a clay loam and a calcium ferrite took up vaporized rubidium oxide. The rate measurements were made in air from 1100 to 1450°C and over a rubidium oxide partial-pressure range of about 1×10^{-5} to 3×10^{-4} atm. We found that the initial rates of rubidium oxide uptake by both the clay loam and the calcium ferrite were about the same but the calcium ferrite melts reached saturation with respect to rubidium oxide uptake in a few minutes while the clay loam continued to take up the rubidium oxide at a high rate for times of at least an hour. For both substrates, the rate-controlling step for the uptake process was the diffusion of the rubidium oxide vapor through the air to the surfaces of the substrate samples. The uptake of rubidium oxide vapor by a series of simple, unmelted oxides at 1400°C was also measured. In general, the uptake behavior of the rubidium oxide was as expected in that it reacted least with the basic oxides such as SrO and CaO and reacted most with the acidic oxides such as Nb_2O_5 and SiO_2.

SUMMARY

The Problem

Much effort has been put into developing mathematical models of the radioactive-fallout-formation process for the purpose of predicting the radiation exposure rates and exposures in the fallout fields resulting from nuclear explosions. One of the most important parameters in such models is the rate at which vaporized radioactive elements or compounds are taken up by molten and solid particles at high temperatures. Essentially no measurements have been made of these rates. It is the purpose of this investigation to measure some of these uptake rates for rubidium oxide, and, if possible, to discover the rate-controlling steps in the high-temperature uptake process.

The materials used in the investigation were among those found in radioactive fallout. $^{86}Rb_2O$ was chosen as the source of the radioactive vapor and the substrate materials were a clay loam (typical of fallout material derived from a silicate soil) and a calcium ferrite (similar to the composition of some types of fallout particles from the Pacific Proving Grounds.)

Findings

Most of the measurements of the rate of uptake of the rubidium oxide vapor onto spherical particles of the substrate samples fall into three categories. The first group consists of measurements made at constant temperatures (1400°C and 1200°C) and constant rubidium oxide partial pressure (about 1.5×10^{-5} atm) but with varying sample particle diameters (about 0.15 to 0.40 cm). The results are shown graphically in terms of uptake of rubidium oxide per particle in μg/min. It was found that the initial rates of uptake of the rubidium oxide by both the clay loam and the calcium ferrite were about the same. However, the calcium ferrite melts reached equilibrium with respect to rubidium-oxide uptake in a few minutes while the clay loam continued to take up rubidium oxide at a high rate for times of at least one hour.

The second group of measurements was made with constant particle diameter (0.345 cm) and at constant temperature (1400°C) but with varying rubidium oxide partial pressure (1×10^{-5} to 3×10^{-4} atm). The third group of measurements was made with the same particle size and with constant rubidium oxide partial pressure (1.85×10^{-5} atm) but with varying temperature (1100 to 1450°C). These results are also presented graphically.

For the interpretation of the data, it was postulated that the uptake process consisted of three steps: (1) the diffusion of the rubidium oxide vapor through the air to the surface of the substrate particle, (2) the reaction or condensation of the rubidium oxide vapor at the surface of the particle, and (3) the diffusion of the condensed rubidium oxide from the surface of the particle into the interior.

For the uptake of rubidium oxide vapor by both the clay loam and the calcium ferrite it was found that the rate-controlling step was the diffusion of the rubidium oxide vapor through the air. By use of Maxwell's equation, it was possible to make theoretical calculations of the rates of uptake of the rubidium oxide vapor; these calculations agreed moderately well with the experimentally measured values.

The uptake of rubidium oxide vapor by a series of 14 simple, solid oxides was measured at 1400°C. In general, the uptake behavior of the rubidium oxide was as expected in that it reacted least with the basic oxides such as SrO and CaO and reacted most with the acidic oxides such as Nb_2O_5 and SiO_2.

INTRODUCTION

This is the third in a series of reports describing experimental studies of the rates of uptake of selected vaporized oxides by oxide substrates at high temperatures. The purposes of these studies are to provide data which can be used in radioactive-fallout formation models and to discover the mechanisms which govern the rates of uptake of the vaporized oxides. Volatile radioactive oxides of elements from important fission-product mass chains are used as the vapor sources, and inert, non-volatile oxides of materials that form radioactive fallout particles are used as the substrates.

The first two reports of this series presented the results of measurements of the uptake rates of MoO_3 and TeO_2 vapors by substrates of calcium ferrite and of a clay loam soil occurring in the Berkeley Hills, California.[1,2] The clay loam soil was more or less typical of silicate soils found in extensive areas in the temperate zones. The calcium ferrite has been observed in fallout resulting from nuclear explosions at the Pacific Proving Grounds where large amounts of calcium oxide, derived from the coral sand, and iron oxide, derived from the towers, barges and other structures, have been fused together. This report presents the results of measurements of the uptake rate of vaporized rubidium oxide upon these same two substrate materials. Rubidium oxide was chosen as the radioactive vapor source because rubidium is the precursor of both the biologically important, long-lived constituent of fallout, ^{90}Sr and the reference nuclide, ^{89}Sr, and also because the chemical behavior of the basic rubidium oxide should provide enlightening contrasts with that of the acidic molybdenum and tellurium oxides studied previously.

EXPERIMENTAL METHOD

Description of Apparatus

Because the experimental apparatus and method have been described in detail in the first report of this series, only a brief summary will be given here. The apparatus consisted mainly of a vertical-tube furnace 74 cm long and 2.2 cm I.D. (Fig. 1). The furnace tube was made of dense, gas-tight, high purity alumina (McDanel Refractory Porcelain Co., Beaver Falls, Pa.). Two independent heating circuits were wound on the exterior of the tube. The top, high-temperature, circuit was wound with 17-gauge Pt-20 % Rh wire and the bottom, low-temperature, circuit was wound with 17-gauge Kanthal A-1 wire.

Rubidium titanate, which served as the source for the radioactive rubidium oxide vapor, was contained in a platinum crucible which was positioned in the low-temperature zone of the furnace on top of an assembly of two porous alumina plugs which were mounted on a small gas-tight alumina tube. The substrate samples were pre-fused nearly spherical beads formed on platinum wire loops. The platinum loops holding the samples were suspended in the high-temperature zone of the furnace. Temperature measurements were made with two Pt-10 % Rh thermocouples; one was placed next to the vapor source in the low-temperature zone and the other was placed next to the suspended substrate sample in the high-temperature zone. The radioactive vapor was carried from the low-temperature zone up into the high-temperature zone by a steady flow of dry air which was introduced into the furnace through a hole in the small, gas-tight alumina tube which supported the vapor source. The interior of the alumina furnace tube was protected from the rubidium vapor by a platinum-foil liner. Three perforated platinum-foil diaphragms were placed at intervals between the vapor source and the high-temperature zone in order to protect the vapor source from direct radiation from the high-temperature zone, and to insure mixing of the radioactive vapor with the carrier gas.

Preparation of Materials and Samples

Preparation of a source for the rubidium oxide vapor was somewhat of a problem. In the previous experiments, solid molybdenum and tellurium oxides had been used successfully as vapor sources. In the present experiment solid rubidium oxide was not suitable because of its extreme hygroscopicity with atmospheric moisture and its chemical reactivity with platinum containers. Rubidium compounds such as RbOH and RbCl were unsuitable as they do not decompose upon evaporation. Fused $RbNO_3$ was tested as a possible vapor source by condensation onto platinum foil of

the material evaporating from the melt. This condensate gave a strong positive test for nitrate ion indicating that the salt had not decomposed upon evaporation.

Finally, a rubidium titanate mixture was tested and found to be adequate. The mixture had an initial composition of 34 mole % Rb_2O: 66 mole % TiO_2 and melted at about 880°C. The condensed evaporate from the melt formed a white coating on platinum foil and gave a strongly basic reaction indicating that the evaporating species was either rubidium or rubidium oxide. The titanate mixture was prepared by fusion of appropriate amounts of AR grade radioactive Rb_2CO_3 and TiO_2. The melt was heated overnight under vacuum to drive off all CO_2 and H_2O. During this heating process, Rb_2O was also lost, whereby the composition of the melt changed a few percent and the melting point rose a few degrees.

The radioactive Rb_2CO_3 was prepared by dissolution of the AR grade carbonate in water followed by addition of the radioactive tracer in the form of $^{86}RbCl$ (supplied by Oak Ridge National Laboratory). The solution was stirred, the water evaporated and the radioactive Rb_2CO_3 dried. A negligible amount of chloride was added in this process. As a check on the radiological purity of the ^{86}Rb, its half-life was found to be 18.9 days, which corresponds closely to the published half-life of 18.7 days.

The calcium ferrite used for the substrate samples was prepared by weighing out of the appropriate amounts of AR grade Fe_2O_3 and CaO powders so that the final composition of the mixture would be 80 % Fe_2O_3 and 20 % CaO by weight. The dry powders were mixed thoroughly in a mortar. The powder was fused directly on the platinum wire loops in the flame of a gas-oxygen torch.

The clay loam was prepared by first being sieved to remove the larger pebbles and pieces of organic matter. The material passing the sieve was dried and ground and then melted in a nickel crucible at about 1300-1400°C for about an hour. Upon cooling, the melt formed a black glass which was broken up and ground to a powder in a steel mortar. An analysis of the soil for the non-volatile oxides was made by Metallurgical Laboratories, Inc., San Francisco, California. These oxides comprise 89 % of the original clay loam; the remaining 11 % are volatile oxides (CO_2, H_2O, etc.) and minor constituents. The results of the analysis for the non-volatile oxides follow:

Oxide	Weight (%)
SiO_2	67.5
Al_2O_3	15.9
Fe_2O_3	7.3
CaO	2.7
MgO	2.7
Na_2O	2.3
K_2O	1.6
	100.0

Experimental Procedure

In preparation for a series of experimental runs, the top and bottom sections of the furnace were brought to their proper operating temperatures, the air flow was started, and a standby rubidium titanate source was inserted into the lower section of the furnace. The furnace was allowed to equilibrate with the rubidium oxide vapor under the chosen operating conditions for about 18 hours prior to each experimental run. About 3 hours before the start of each experimental run, another rubidium titanate source, which had just been weighed, was substituted for the standby source in the lower part of the furnace.

During the actual experimental runs, the substrate samples were pre-heated in a gas flame and then inserted into the top of the furnace for varying lengths of time, usually 2 to 15 minutes depending upon the rate of uptake of rubidium oxide. At the end of this interval, the samples were quickly withdrawn and were counted in a 3 x 3 in. thallium-activated-NaI well-crystal detector. After being counted, the samples were re-inserted into the furnace and the procedure repeated. The total accumulated time in the furnace for each sample was usually about 40 minutes.

At the end of each day's runs, the rubidium titanate source was removed from the furnace and replaced by the standby source. Rubidium titanate is slightly hygroscopic so that it was necessary to prevent its taking up atmospheric moisture while being weighed. This was done by placement of the hot rubidium titanate source in a desiccator immediately upon its removal from the furnace. The source was then

transferred to an air-tight metal capsule inside a dry-box so that exposure of the source to the air was minimal. The air-tight metal capsule containing the source was allowed to cool in the dry box and was then removed and weighed. The amount of Rb_2O which had evaporated was determined from the weight loss. The vapor concentration in the furnace was computed from the amount of Rb_2O evaporated and the known volume of air which passed through the apparatus while the rubidium titanate source was in the furnace.

The range of temperatures for the source region was about 800-1000°C with most of the runs at about 840-880°C. The flow rate of air through the apparatus was 70 ml/min (measured at 25°C).

The actual uptake of Rb_2O by the samples was determined by comparison of the radioactive counting rates of the samples with that of a standard. The standard was prepared by dissolution in 2 ml of dilute acid of a known amount of the same radioactive Rb_2CO_3 that was used in the preparation of the rubidium titanate source. As the substrate samples were in the form of solid spheres on wire loops, their counting geometry was different from that of the liquid standard. In correction for this, at the end of the day's runs, the substrate samples were all counted and then dissolved in 2 ml of either HCl or HF and recounted. The ratio of these counts gave the factor necessary to correct all of the counting rates of the solid samples to conform with the geometry of the liquid standard. This correction amounted to about 10-15 %.

Experimental Errors

The precision of the experimentally measured quantities probably exceeds the overall accuracy of the experiment by an order of magnitude. The sample temperatures were known to within about $\pm$ 4° and the weight losses of the rubidium titanate source, the volumes of air passed through the furnace, the diameters of the substrate samples, the durations of the time intervals in which the samples were in the furnace and the counting rates of the samples all could be measured to within about $\pm$ 5 %.

The greatest source of error probably lay in the difference between the calculated and the actual vapor concentrations of the rubidium oxide in the furnace. The rubidium titanate was not too satisfactory as a source for rubidium oxide vapor. As the rubidium oxide vaporized, the composition of the source became richer in titanium oxide and the volatility of the rubidium oxide decreased. This effect was exacerbated when the temperature of the source was below its melting point and the rubidium oxide which was volatilized from the surface zone was not rapidly replenished by diffusion from the interior. This resulted in noticeable decrease in the rubidium oxide vapor concentration during a

day's run. For minimization of this effect, the rubidium titanate source was remelted after each day's runs to restore the concentration of rubidium oxide in the surface zone. Also, as the most important rate to be measured was the initial rate of uptake of rubidium oxide by the substrate samples, the schedule was arranged so that the initial-rate measurements were in the mid-period of the time in which the rubidium titanate source was in the furnace. If we assume a linear decrease of rubidium oxide vapor concentration with time, the actual vapor concentration in the furnace at mid-period should equal the average vapor concentration based on the weight loss of the source.

In spite of these precautions, there were considerable variations in the computed vapor concentration from day to day ($\pm$ 15 %) and the reproducibility of the experimental measurements suffered. Because of these uncertainties, it is estimated that the absolute accuracy of the uptake data is probably no better than a factor of about four, although the reproducibility of the initial rate determinations by several series of runs is probably good to within a factor of about two.

EXPERIMENTAL DATA

Most of the experimental data can be grouped into three parts: (1) the uptake of rubidium oxide as a function of particle size at constant temperature and constant rubidium-oxide partial pressure; (2) the uptake of rubidium oxide as a function of rubidium-oxide partial pressure at constant particle size and temperature; and, (3) the uptake of rubidium oxide as a function of temperature at constant particle size and constant rubidium-oxide partial pressure.

In computing the partial pressure from the vapor concentration of the rubidium oxide in the furnace, we must know the molecular weight of the vapor. There is some uncertainty as to what vapor species are formed by the vaporization of rubidium oxide. Such estimates as are published indicate that, under the experimental conditions used here, the vapor consists predominantly of RbO with a minor amount of Rb[3]. On this basis, the molecular weight of RbO was used to compute the partial pressure in the furnace. As the molecular weights of RbO and Rb differ by only about 17 %, any error introduced by this assumption is small compared with other sources of errors in the experiment. It was further assumed that the RbO, or Rb, vapor converted to Rb_2O upon condensing.

Figures 2 and 3 show the uptake of RbO by various-sized clay loam particles as a function of time at T = 1400 and 1200°C respectively. The

RbO partial pressure was held constant for each series of runs. Figures 4 and 5 show the same information for various-sized calcium ferrite particles. Figure 6 shows the uptake of RbO at 1400° by various-sized particles of a calcium aluminum silicate melt (CaO 23.3, Al_2O_3 14.7, and SiO_2 62.0 wgt. %)

A large number of runs were made to determine the effects of varying separately the RbO partial pressure and the temperatures of the samples. The same sized particles (0.345 ± 0.010 cm in diameter) were used in all these runs. Figure 7 shows the initial rates of uptake of RbO by both clay loam and calcium ferrite particles at a temperature of 1400°C and a RbO partial pressure varying from about 10^{-5} to 3×10^{-4} atm. Figure 8 shows the initial rates of uptake of RbO by clay loam and calcium ferrite particles at a constant RbO partial pressure of 1.85×10^{-5} atm and with the sample temperature varying from 1100 to 1450°C.

In Figures 7 and 8 the initial rates of uptake of the RbO vapor were plotted. This was done because the uptake rates decrease with time at a rate depending upon particle composition and size. The initial rates are independent of the time of exposure of the samples and they can be used (as will be shown later) to help determine the mechanism which governs the rate of uptake.

Every initial rate shown in the graphs of this report was determined graphically as the slope of a tangent to the curve of the plot of amount of uptake vs time at t = 0. As a check on this method, the initial rates could also be determined analytically in the case of the calcium ferrite particles which were exposed in the furnace at temperatures above their melting point (about 1200°C). Figure 4 shows that the calcium ferrite particles reached equilibrium with respect to RbO vapor in a few minutes. By use of the entire uptake curve from t = 0 to the equilibrium point, it is possible to solve for the rate constant, $\underline{k}$, in the general case of the rate equation,

$$\frac{dx}{dt} = k(a-x)^n$$

where $\underline{x}$ is the RbO uptake at time $\underline{t}$, $\underline{a}$ is the equilibrium uptake and $\underline{n}$ is the overall order of the uptake reaction with respect to RbO vapor. When $\underline{k}$ has been determined, $\underline{n}$ can be found; then at $\underline{t} = 0$, $\underline{x} = 0$ and the initial rate is given by

$$\frac{dx}{dt} = ka^n.$$

For RbO uptake on the calcium ferrite, n was generally close to 1.0. Determinations of the initial rate of uptake by the graphical and by the analytical method usually agreed to within about 15 %.

A series of runs was made in which the uptakes of RbO vapor by samples of single, unmelted oxides were measured. This was done to obtain some information about the relative reactivity of RbO vapor with the various oxides. The furnace temperature was 1400° (below the melting points of all the oxides used) and the RbO partial pressure was about 1.5×10^{-5} atm. The samples were prepared by pressing the powdered oxides (AR grade) into thin pellets about 0.62 cm in diameter and about 0.05 to 0.08 cm thick. The pellets were backed with platinum foil so that only one face was exposed to the RbO vapor. The uptake of RbO vapor by these oxides is shown in Fig. 9.

DISCUSSION AND INTERPRETATION OF EXPERIMENTAL DATA

Theoretical Introduction

For purposes of fallout prediction, it is desirable to go beyond the presentation of the experimental data and, if possible, use these data to deduce the mechanisms which govern the uptake of the RbO vapor. If the mechanisms or processes which determine the rate of uptake can be discovered, then it should be possible to extrapolate the experimental data into other regions of temperature and pressure.

There are three basic steps in the uptake of the RbO vapor by the substrate particles and any one of these might be slow enough in comparison with the others to be the rate-determining step. These three steps are: (1) the diffusion of the RbO vapor molecules through the air to the surface of the particle; (2) the reaction and condensation of the RbO vapor molecules at the surface of the particle; and (3) the diffusion of the condensed Rb_2O into the interior of the particle.

If one assumes that the diffusion of the RbO vapor molecules through the air is the rate-determining step, then this process can be described by Maxwell's equation

$$I = \frac{2\pi d\ D_{12} M\ (P_\infty - P_o)}{RT}$$

where $\underline{I}$ is the rate of impingement of the vapor species of molecular weight $\underline{M}$ upon a particle of diameter $\underline{d}$. D_{12} is the inter-diffusion constant of the vapor species in the gaseous medium. P_∞ is the partial pressure of the vapor at a large distance from the particle and P_o is the partial pressure at the surface of the particle. If vapor diffusion is the rate-determining step, Maxwell's equation shows that, with constant temperature and pressure, the rate of uptake of the RbO vapor will be proportional to the diameter of the particle and therefore that the total amount taken up will be proportional to the product of the particle diameter and time.

If the rate-determining step is the reaction or the condensation of RbO at the surface of the particle, then the rate will be proportional to the surface area of the particle or to the diameter squared. The total amount taken up will be proportional to the product of the diameter squared and time.

If the diffusion of the condensed Rb_2O into the particle is slow compared to the other two steps, and if condensation is reversible, then the outer surface layer of the particle reaches a steady concentration of Rb_2O and further condensation is governed by the rate at which the Rb_2O diffuses away from the surface zone into the particle. As a model for this process one can envisage a spherical particle of the substrate material surrounded by a solution containing the Rb_2O at a constant concentration. A graphical solution of the mathematical relations for this type of diffusion is given by Crank.[4] At early times in the diffusion process,

$$\frac{M_t}{M_\infty} \sim \left[\frac{Dt}{d^2} \right]^{1/2}$$

where $\frac{M_t}{M_\infty}$ is the ratio of the amount of material diffusing into a particle of diameter $\underline{d}$ at time $\underline{t}$ to the total amount which diffuses into the particle at infinite time.

D is the diffusion constant of the diffusing material in the particle

M_∞ is proportional to the volume of the particle, or to d^3, so that, at constant temperature,

$$M_t \sim d^2 \, t^{1/2}$$

Therefore, if diffusion of Rb_2O into the particle is rate-determining, the total amount of Rb_2O taken up will be proportional to the diameter squared of the particle multiplied by the square root of the time. The rate of uptake of Rb_2O will be proportional to the diameter squared divided by the square root of the time.

These relationships are summarized in Table I. It should be emphasized that these relationships are true only for a relatively small initial time interval during which the composition of the particles has not changed appreciably.

TABLE I

Rate-Controlling Process	Rate of Uptake of RbO is Proportional to:	Amount of Uptake of RbO is Proportional to:
Diffusion of RbO Vapor Through Air	d	dt
Reaction or Condensation Rate at Surface of the Particle	d^2	d^2t
Diffusion of Rb_2O into Particle	$\frac{d^2}{\sqrt{t}}$	$d^2\sqrt{t}$

Determination of the Rate-Determining Step in the RbO Uptake Process

Consider first the uptake of RbO by various sized clay loam particles at 1400°C (Fig. 2). The plots are approximately linear, indicating that the RbO uptake is proportional to the time of exposure of the particles (the tendency for the plots to deviate from linearity can be partly explained by a decrease in the RbO partial pressure during the course of the runs as the surface zone of the rubidium-titanate source becomes partially depleted in Rb_2O). The fact that the amount of RbO uptake is proportional to time indicates that the rate-controlling step may be either diffusion of the RbO vapor through the air to the surfaces of the particles or the rate of reaction of the RbO at the surfaces of the particles (see Table I).

For distinguishing between these two mechanisms, plots have been made of the initial rates of RbO uptake vs particle diameter and diameter squared and also the total amounts of RbO uptake at 5 and 20 minutes vs particle diameter and diameter squared (Fig. 10). In both cases the

graphs show that the rates of uptake and the amounts of uptake are both proportional to the diameters of the particles rather than to the diameters squared, thereby indicating that diffusion of the RbO vapor through the air is the rate-determining step.

The same analysis can be applied to the uptake of RbO vapor by the clay loam particles at 1200°. At this temperature the clay loam is solid and it might be expected that diffusion of the condensed Rb_2O into the particles would be slow enough to be the rate-determining step. However, Fig. 3 shows that the amount of RbO uptake by each particle is approximately proportional to time. Also, the plots of the initial rates of uptake and the total amounts of uptake at 5 and 20 minutes vs particle diameter are linear (Fig. 11) which again shows that the rate-determining mechanism is the diffusion of the RbO vapor molecules through the air.

Fig. 4 shows the uptake of RbO vapor vs time for a series of calcium ferrite particles. From the curvature of the plots it might be suspected that the uptake was proportional to the square root of the time and that the rate of the uptake process is governed by the diffusion of the condensed Rb_2O into the particles. However, it has been pointed out that the criteria of Table I are valid only when the uptake of RbO is relatively small compared with the final uptake at equilibrium. Figure 4 shows that most of the calcium ferrite particles reach equilibrium in a few minutes. For application of the criteria of Table I, the initial rate of RbO uptake has been plotted against diameter and diameter squared (top half of Fig. 12). The graph clearly shows that the initial rate is proportional to the diameter rather than the diameter squared which indicates that the diffusion of the RbO vapor through the air is the rate-determining step. (Data from the largest calcium ferrite particle, 0.395 cm dia., have not been plotted in Fig. 12 as they fall about 50 % too high on both graphs indicating an anomaly with this sample.)

Plotted on the lower graph of Fig. 12 is the amount of RbO uptake at 2 minutes vs particle diameter and diameter squared. At 2 minutes the smallest particles have taken up an appreciable fraction of their final equilibrium uptake, but nevertheless, it is apparent that the amount of RbO taken up is proportional to the particle diameters rather than the diameters squared, which again indicates that the diffusion of the RbO vapor through the air is the rate-determining step.

Figure 5 shows the uptake of RbO by different sized calcium ferrite particles at 1200°. In this case the shapes of the uptake curves are approximately linear as are those of the RbO uptake by the clay loam particles. This again suggests that the diffusion of the RbO vapor through the air is the rate-determining step. However, plots of the initial rates and the amounts of RbO uptake at 5 and 20 minutes (Fig. 13) do not show a linear relation with particle diameter. In terms of

linearity, there is little to choose from between the plots using diameter or diameter squared. It has also been observed that the rate of RbO uptake by the calcium ferrite particles decreases abruptly as the temperature falls below 1200° (see Fig. 8). Apparently there is a transition temperature just below the melting point of the calcium ferrite where the mechanism of the uptake process changes, and this change is reflected by both the ambiguity of the graphs of Fig. 13 and the marked decrease in RbO uptake at lower temperatures.

The RbO uptake data of the calcium aluminum silicate samples at 1400° (Fig. 6) have also been analyzed in the manner just described. The results (Fig. 14) show that the rate-determining step is the diffusion of the RbO vapor through the air to the surfaces of the particles.

Uptake of RbO as a Function of Pressure

If the rate-determining step is the diffusion of RbO vapor through the air, it should be possible to predict the rate of RbO uptake under varying conditions of pressure and temperature by use of Maxwell's equation. The use of Maxwell's equation requires knowledge of the interdiffusion constant of RbO molecules in air. This interdiffusion constant is not known, but it can be estimated by use of the Stefan-Maxwell equation,

$$D_{12} = \frac{1}{\pi\sigma_{12}^{2}(n_1+n_2)} \left[\frac{2kT}{\pi\mu}\right]^{1/2}$$

where σ_{12} is the mean collision diameter of the two vapor species, in this case RbO and air, μ is the reduced molecular mass $(m_1m_2)/(m_1+m_2)$, and n_1 and n_2 are the numbers of molecules of each species per cm^3.

The collision diameter of the RbO molecule is not known so it must be estimated. For many common gases, the collision diameter is roughly twice the average physical or geometric diameter of the molecule as determined by molecular or atomic radii. By use of the monovalent ionic radii of Rb^+ and O^-, the collision diameter of the gaseous RbO molecule was crudely estimated as about 9×10^{-8} cm. The diameter of the neutral Rb atom is roughly the same as that of RbO, so even if the vapor consisted mostly of Rb molecules the interdiffusion constant would be about the same.

Maxwell's equation was used to calculate the mass of RbO molecules striking and sticking to the surface of a particle the same size as those used in the pressure- and temperature-variation runs. It was assumed that the RbO converted to Rb_2O upon condensation. It was also assumed that the term P_o in Maxwell's equation is zero. This term refers to the RbO partial pressure at the surface of the particle. If all the

RbO molecules that strike the surface remain, the assumption that $P_o = 0$ is probably acceptable. Also, because Maxwell's equation assumes air that is stationary relative to the particle, it was necessary to apply a small correction factor[5] for the flow of carrier gas up the furnace tube. This correction amounted to about + 15 % and was undoubtedly small compared with the error introduced by the uncertainty in the RbO collision diameter.

The calculated rate of RbO uptake over the range of experimental pressure has been plotted as a dashed line in Fig. 7. It is apparent that there is a reasonable correspondence between the experimentally measured rates of RbO uptake by both the clay loam and the calcium ferrite particles with those predicted by use of Maxwell's equation. At lower RbO partial pressures the initial rates of uptake for both the clay loam and the calcium ferrite decrease more rapidly than does the calculated rate as the partial pressure decreases.

It was impossible to completely cover all of the exposed aluminum oxide refractory surfaces in the furnace with platinum foil. The RbO vapor reacts with solid aluminum oxide and it is probable that there was some depletion of the RbO vapor in the furnace due to this reaction. This effect would be especially apparent at the lower RbO partial pressures and could lead to an apparent decrease in the rate of uptake.

Uptake of RbO as a Function of Temperature

Similar calculations were made for the series of runs in which the sample temperature was varied. The calculated rate of uptake is shown as the dashed line in Fig. 8. Here the observed rates of uptake are fairly close to the calculated rate at high temperatures but decrease to about half the calculated rate at temperatures below 1400°. Below the melting point of the calcium ferrite, the total RbO uptake drops abruptly to just a few hundredths of a microgram per particle. This is to be expected, as presumably the rate of diffusion of the condensed Rb_2O into the particle becomes very slow in the solid state and as soon as the surface is saturated, the rate of the uptake process drops to a very low value. What is surprising is that the same process apparently does not occur in the case of the clay loam. Here the rate of RbO uptake remains constant at temperatures well below the hardening point of the glass.

A similarly anomalous situation was observed earlier[1,2] for MoO_3 and TeO_2 vapors condensing on the calcium ferrite particles. In these systems the MoO_3 and TeO_2 vapors reacted strongly with the calcium ferrite (just as the RbO vapor does with the clay loam) and no significant decreases in the rates of uptake were observed at temperatures well below the melting point of the ferrite. The amount of vapor condensed was equivalent to several hundred or thousand monolayers and it is difficult to understand how the condensation process can continue at such a

high rate when the diffusion of the molecules in the solid is so much slower than in the liquid.

It was suggested[1,2] that in the case of the uptake of MoO_3 and TeO_2 by the solid calcium ferrite the condensation proceeded by the counter-diffusion of the reacting species in the solid (in these cases CaO) toward the surfaces of the particles rather than the inward diffusion of the MoO_3 or TeO_2 molecules. As the CaO was in much greater concentration than either the MoO_3 or TeO_2, very little CaO in terms of overall concentration would have had to diffuse in order to react completely with all of the condensing vapor molecules. (When RbO condenses onto calcium ferrite, the RbO is apparently reacting with the Fe_2O_3 rather than the CaO as shown by Fig. 9.)

Perhaps a similar mechanism is operating in the case of the RbO uptake by the clay loam although in the clay loam the species that the RbO is presumably reacting with are SiO_2 and/or Al_2O_3 groups (see Fig. 9). In alumina-silicate glasses these groups are network formers and usually less mobile than the alkali metal or alkaline earth ions.

Although it is impossible with the data presented in this report to describe the uptake process on the molecular level, nevertheless it seems certain that the rate of the overall process is governed by the rate at which the RbO vapor molecules diffuse through the air to the surfaces of the particles. This is indicated by the analysis of the uptake data in relation to variations in particle size and also by the reasonable agreement between the measured uptake rates predicted by the use of Maxwell's equation over large ranges of temperature and pressure. In systems where the uptake has been governed by slow surface reactions and slow diffusion within the particles (MoO_3 and TeO_2 vapors reacting with clay loam particles) the uptake rates have been 1 to 3 orders of magnitude lower than those predicted on the basis of Maxwell's equation.

Influence of Humidity on the Uptake Process

As a stable rubidium hydroxide vapor molecule is known to exist, two series of runs were made to determine the effects of water vapor on the uptake of RbO. First, two runs were made with dry air as the carrier gas and the uptake of RbO by the clay loam and the calcium ferrite was measured at sample temperatures of 1400 and 1100° (RbO partial pressures = 1.91×10^{-5} and 1.04×10^{-5} atm respectively. Average particle diameter = 0.347 cm). The experimental conditions of the second two runs were identical with those of the first two, except that the carrier gas was saturated with water vapor at 28°.

The presence of water vapor affected both the rate of evaporation of Rb_2O from the rubidium titanate source and the rate of uptake by the

samples. The rate of evaporation of the Rb_2O from the source increased by a factor of three with, presumably, the formation of gaseous rubidium hydroxide. After allowance was made for the enhanced vapor concentration of the rubidium oxide, or hydroxide, it was found that the rate of uptake of the rubidium oxide, or hydroxide, by the clay loam increased by a factor of 1.7 at 1400° and by a factor of 1.4 at 1100°. At 1400° the rate of uptake by the calcium ferrite decreased to 0.60 of its value with dry carrier gas and at 1100° the rate decreased from a few micrograms to essentially zero.

Radioautography of Particles

The distribution of rubidium within four particles was determined by radioautography. Two samples each of clay loam and calcium ferrite were exposed to RbO vapor in the furnace at 1400°. After removal from the furnace, they were embedded in plastic and the plastic was then ground away until sections through the centers of the embedded particles were exposed. Radioautographs of these sections were then made by pressing pieces of Eastman NTB stripping film against them for several days.

Of the two samples of clay loam, one was exposed in the furnace for 10 and the other for 100 minutes. In both samples the radioactive rubidium was concentrated near the surface and had diffused partly into the particles. There was no evidence of convective flows within the highly viscous silicate melts. The only difference between the two samples was that the particle which had been in the furnace 100 minutes picked up considerably more rubidium and showed greater penetration of the rubidium into the particle than did the particle exposed for 10 minutes.

Of the two calcium ferrite particles, one was exposed in the furnace for 4 minutes and the other for 25 minutes. It was estimated that during a 4-minute exposure the particle should pick up about one half of its final equilibrium uptake of RbO, and by 25 minutes it should reach final equilibrium. Radioautographs of the samples showed that in both cases the rubidium was distributed more or less evenly throughout the particles, even though the particle exposed for 4 minutes contained appreciably less rubidium. Apparently, the mixing in the low viscosity calcium ferrite melts is quite rapid due presumably to convection currents within the particles.

Uptake of RbO by Solid Oxide Samples

When RbO is taken up by the various substrate materials, it is not clear which of the components of the melts is reacting with the Rb_2O. In an effort to obtain a qualitative notion of the relative degree of reactivity of Rb_2O with the different components of the substrate samples,

the uptake of RbO vapor by a series of 14 simple, solid oxides at 1400° was measured (Fig. 9). In general, the uptake behavior of the RbO was as expected in that the Rb_2O reacted least with the basic oxides such as SrO and CaO and reacted most with the acidic oxides such as Nb_2O_5 and SiO_2. This behavior is, of course, almost opposite to the uptake behavior[1,2] of the vaporized acidic oxides MoO_3 and TeO_2. These results are only qualitative, as some of the solid oxide samples tended to crumble or shrink in the furnace so that there were irregularities in the surface areas exposed. Also, the rates of Rb_2O reaction will be affected by the rates of diffusion of the Rb_2O into the solid oxides and by the particle size and microscopic surface structure of the oxide pellets.

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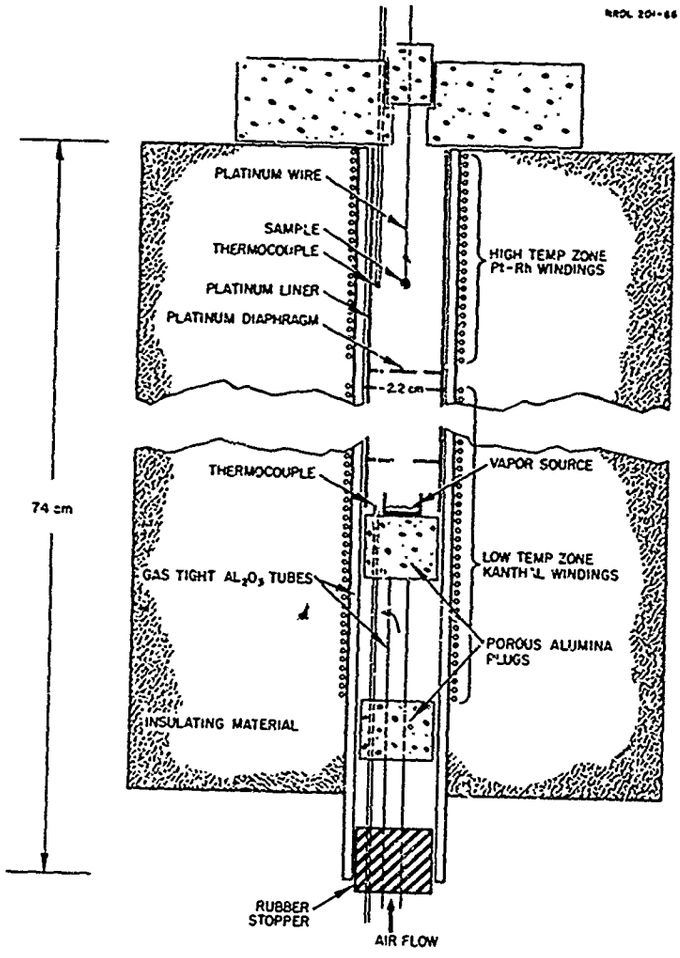

Fig. 1 Two-Temperature Furnace.

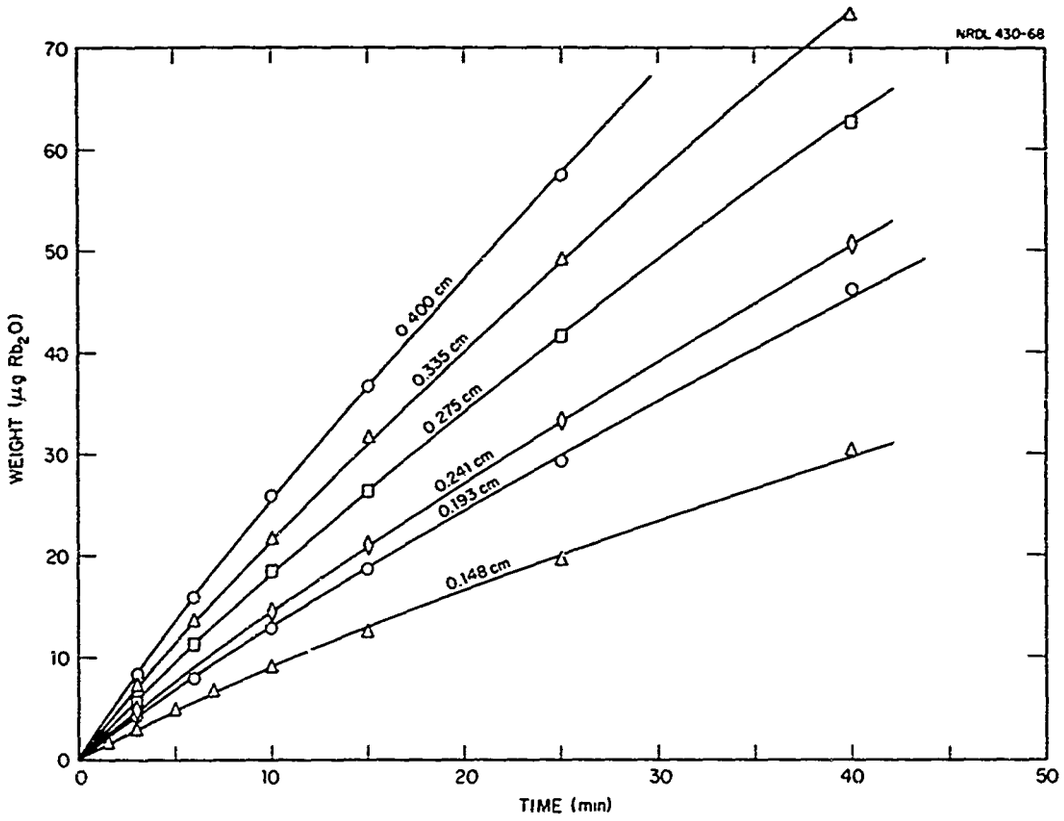

Fig. 2 Uptake of RbO by Clay Loam as a Function of Particle Diameter and Time. T = 1400°C, RbO partial pressure = 1.46×10^{-5} atm.

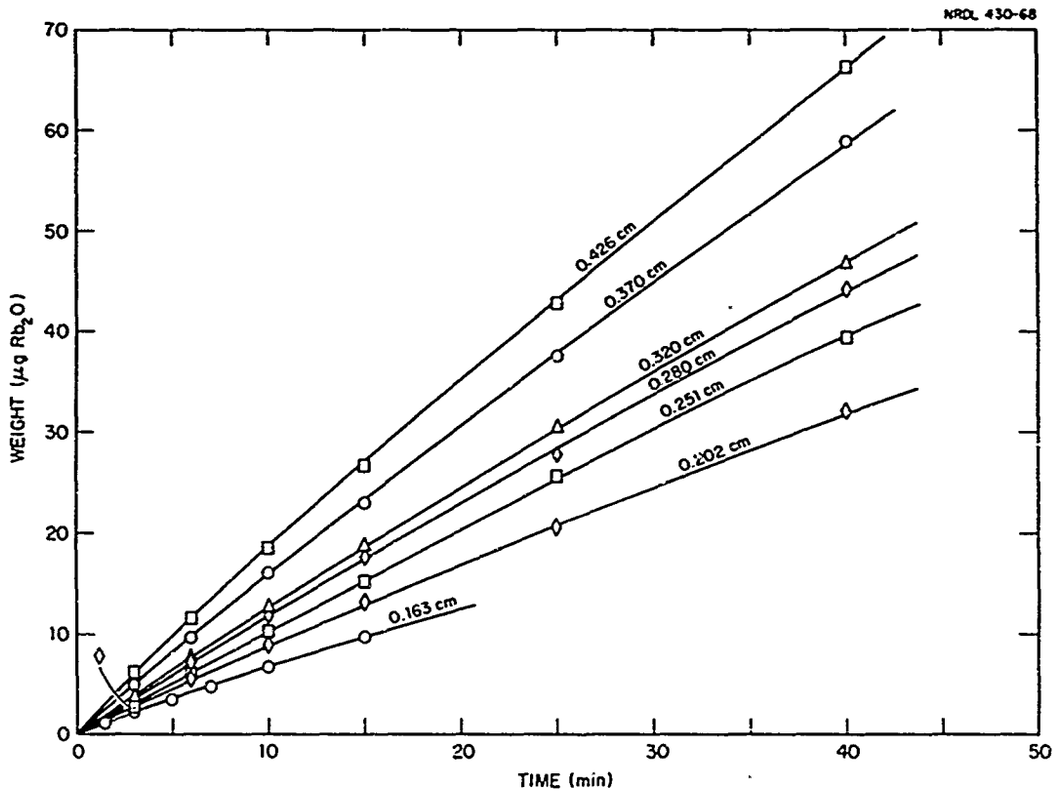

Fig. 3 Uptake of RbO by Clay Loam as a Function of Particle Diameter and Time. T = 1200°C, RbO partial pressure = 1.46×10^{-5} atm.

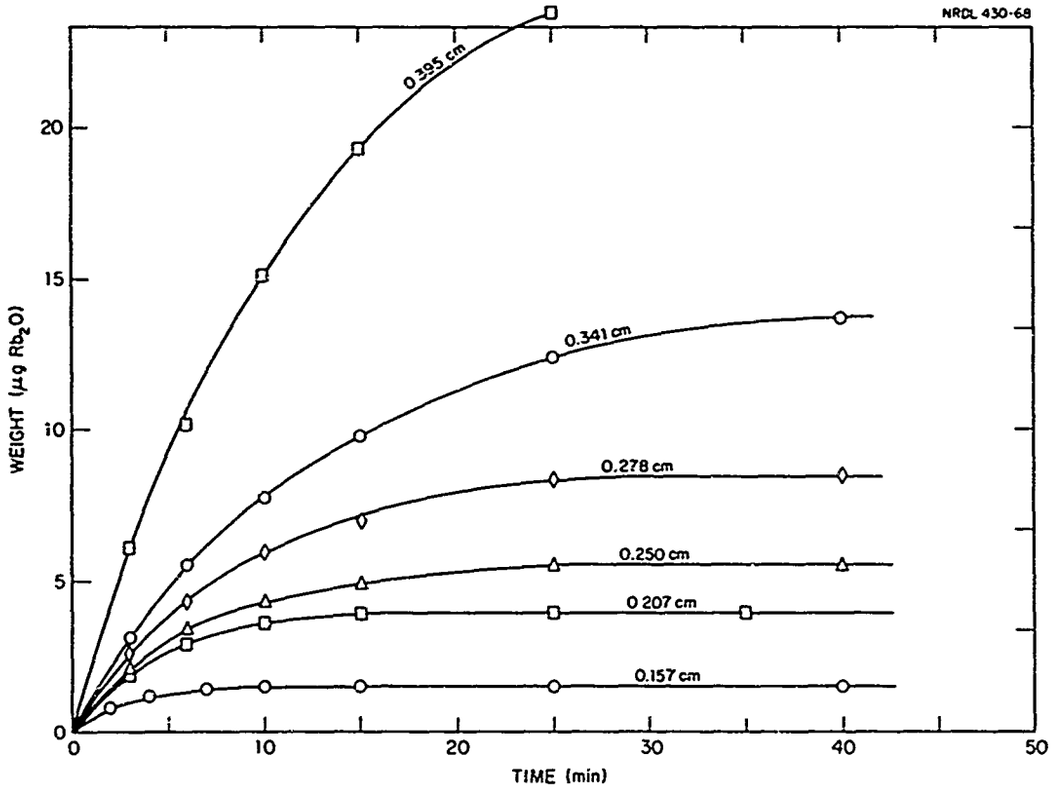

Fig. 4 Uptake of RbO by Calcium Ferrite as a Function of Particle Diameter and Time. T = 1400°C, RbO partial pressure = 1.46×10^{-5} atm.

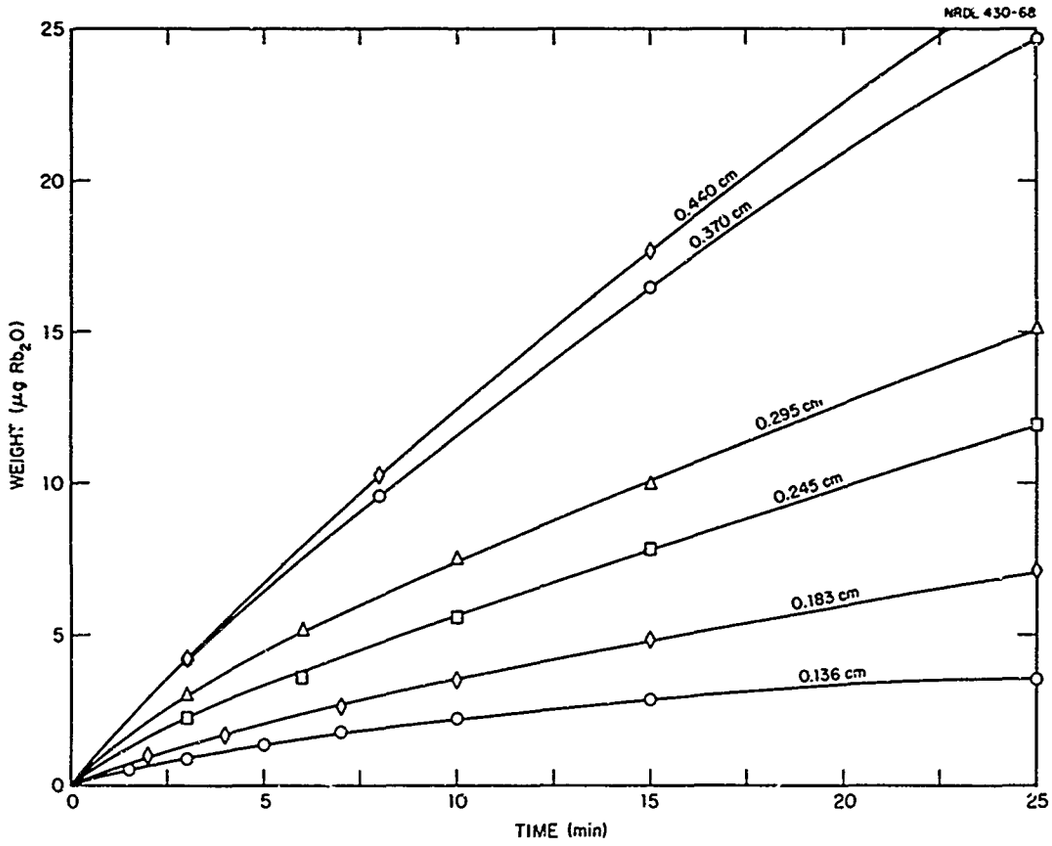

Fig. 5 Uptake of RbO by Calcium Ferrite as a Function of Particle Diameter and Time. T = 1200°C, RbO partial pressure = 1.46×10^{-5} atm.

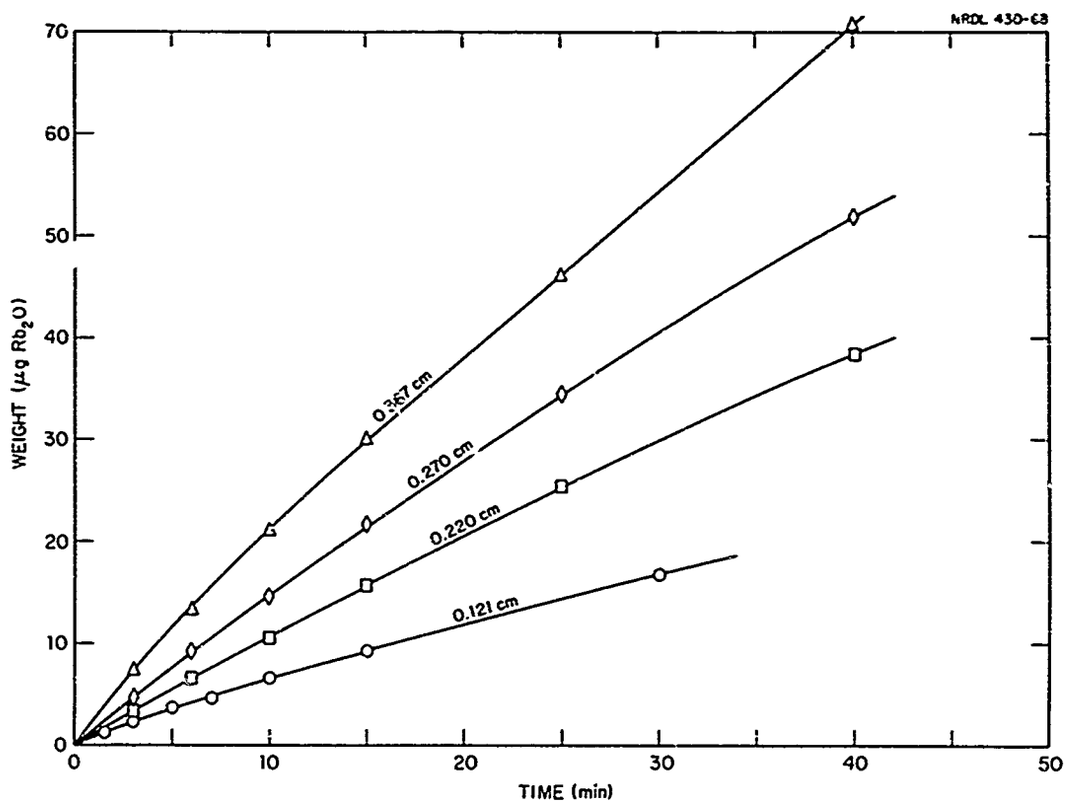

Fig. 6 Uptake of RbO by Calcium Aluminum Silicate as a Function of Particle Diameter and Time. T = 1400°C, RbO partial pressure = 1.46×10^{-5} atm.

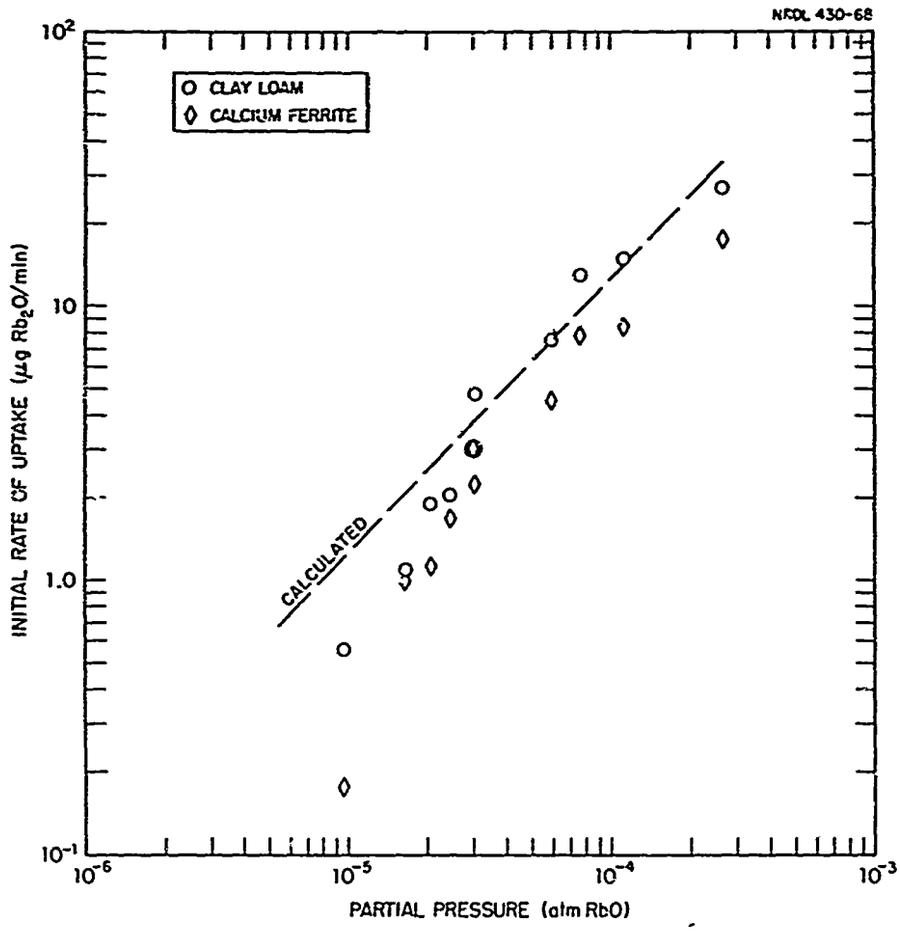

Fig. 7 Initial Rates of Uptake of RbO at 1400°C as a Function of RbO Partial Pressure. The initial rates are shown for both clay loam and calcium ferrite. The dashed line indicates the theoretically calculated uptake rate based on Maxwell's equation. Average particle diameter is 0.345 ± 0.010 cm.

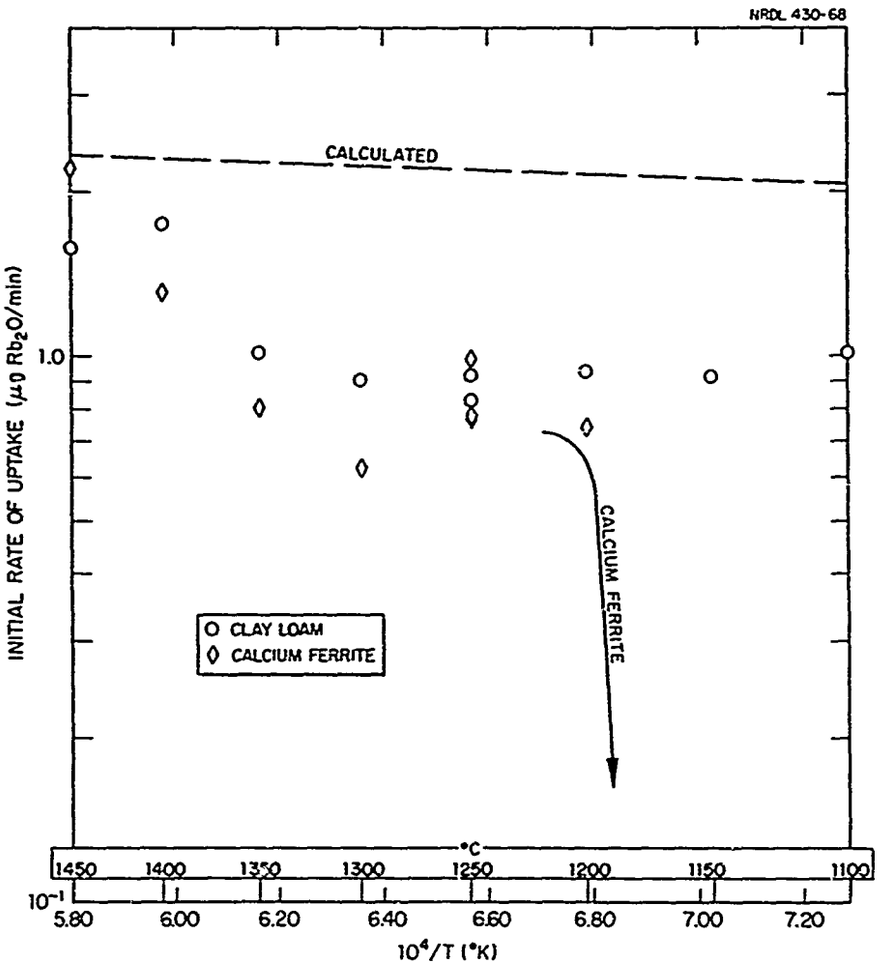

Fig. 8 Initial Rates of Uptake of RbO as a Function of Temperature at a Constant RbO Partial Pressure of 1.85×10^{-5} atm. The initial rates are shown for both the clay loam and the calcium ferrite. The dashed line indicates the theoretically calculated uptake rate based on Maxwell's equation. Average particle diameter is 0.345 ± 0.010 cm.

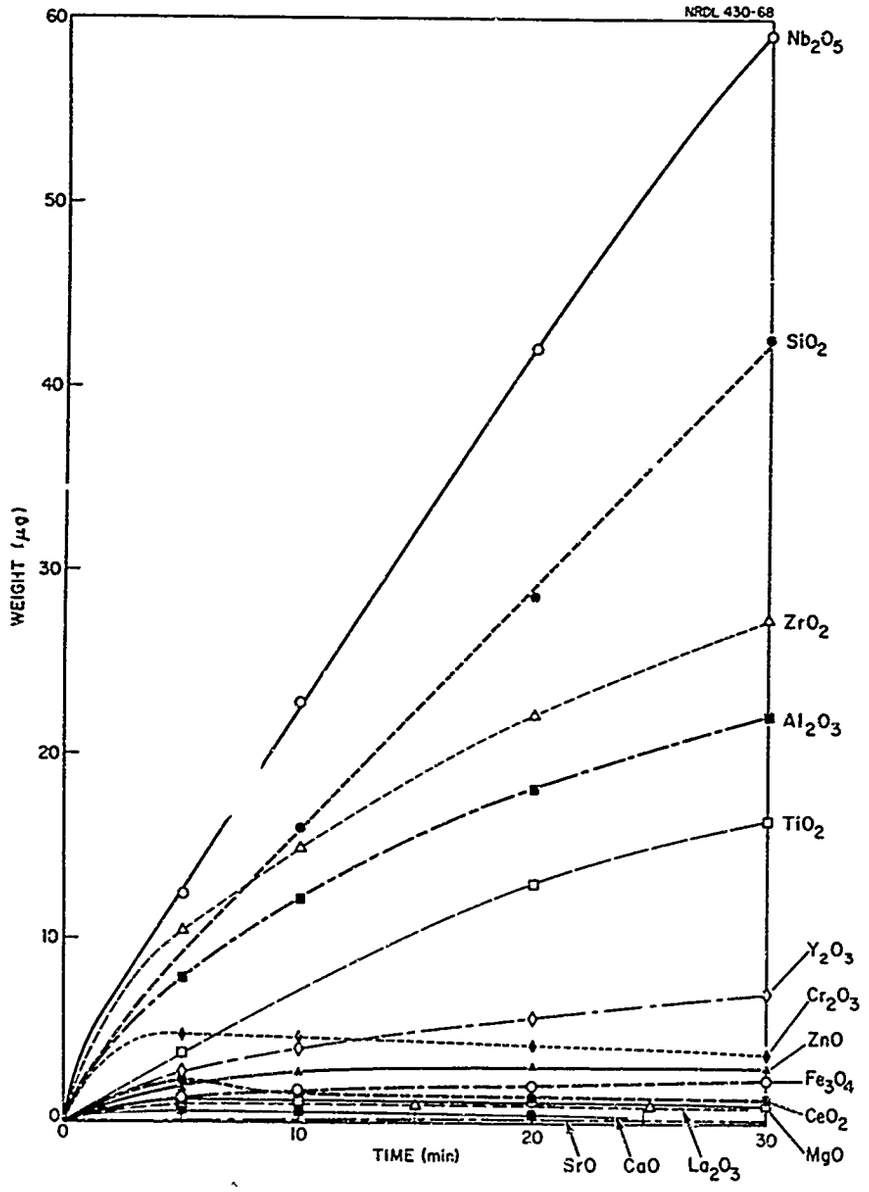

Fig. 9 Uptake of RbO by Solid Oxide Pellets. T = 1400°C, RbO partial pressure = 1.5×10^{-5} atm. The area of each pellet exposed to the RbO vapor was approximately 0.30 cm^2.

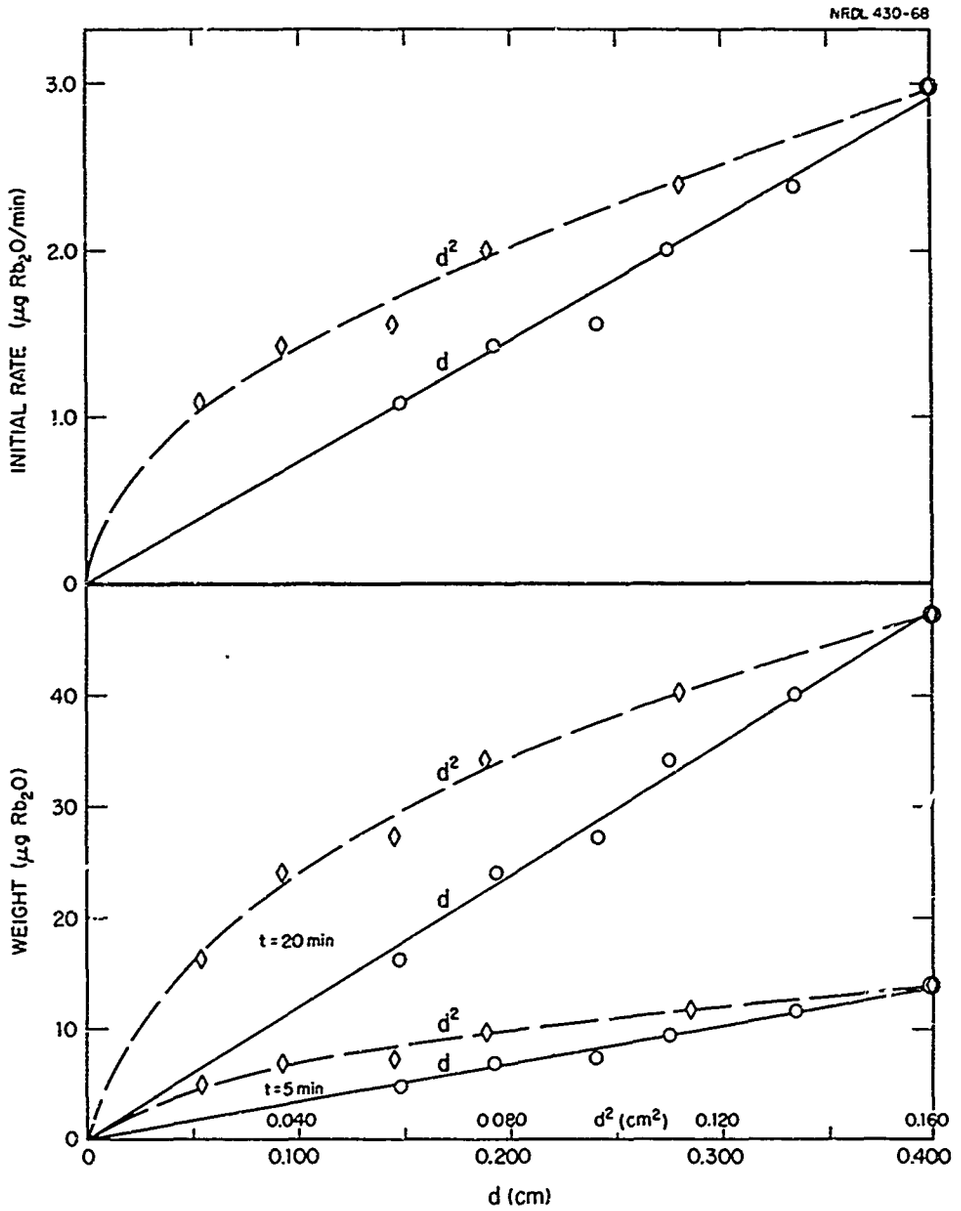

Fig. 10 The Initial Rate of RbO Uptake and the Amount of RbO Uptake at 5 and 20 Minutes by the Clay Loam Particles as a Function of Particle Diameter and Diameter Squared. T = 1400°C, RbO partial pressure: 1.46×10^{-5} atm.

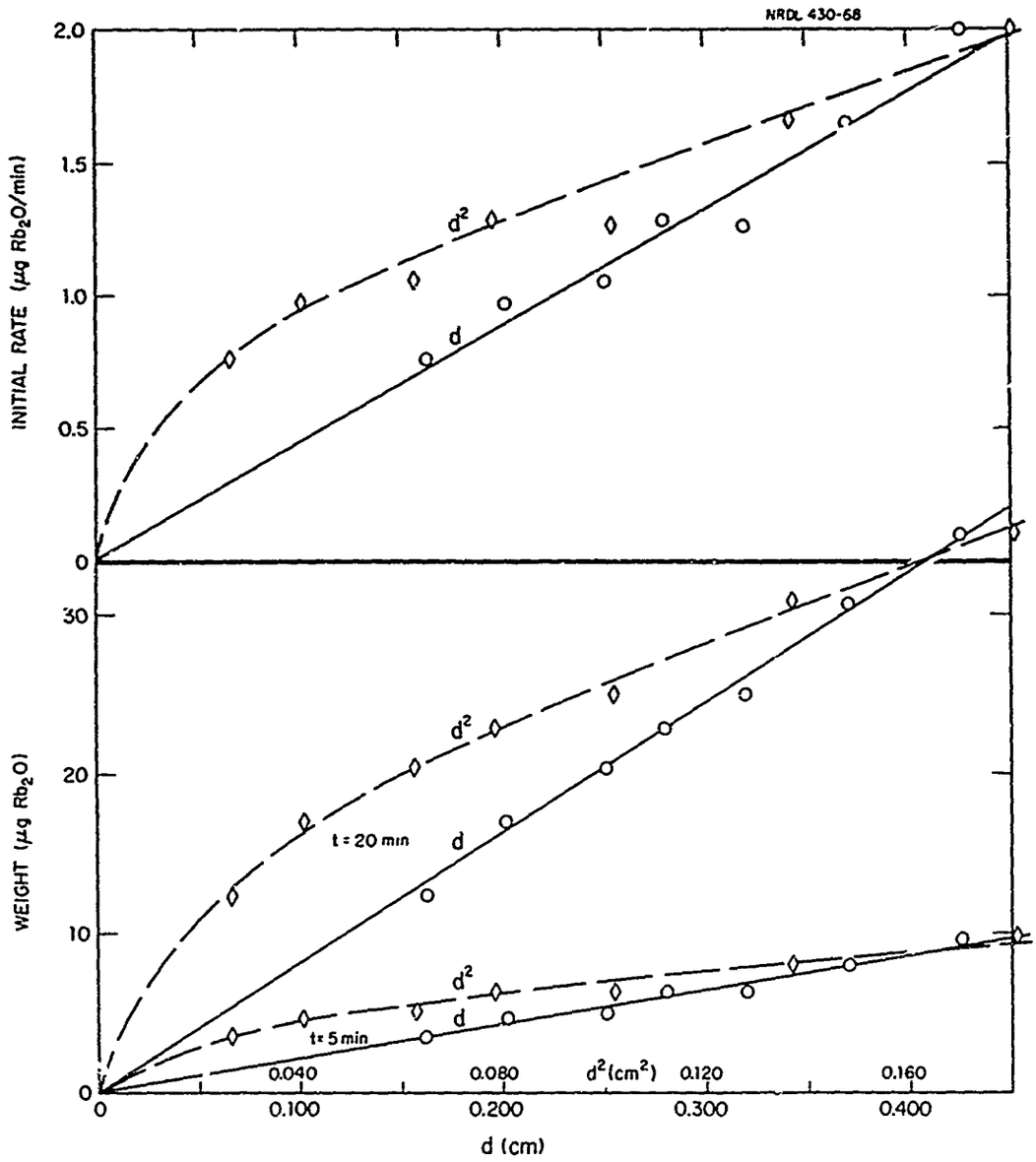

Fig. 11 The Initial Rate of RbO Uptake and the Amount of RbO Uptake at 5 and 20 Minutes by the Clay Loam Particles as a Function of Particle Diameter and Diameter Squared. T = 1200°C, RbO partial pressure = 1.46×10^{-5} atm.

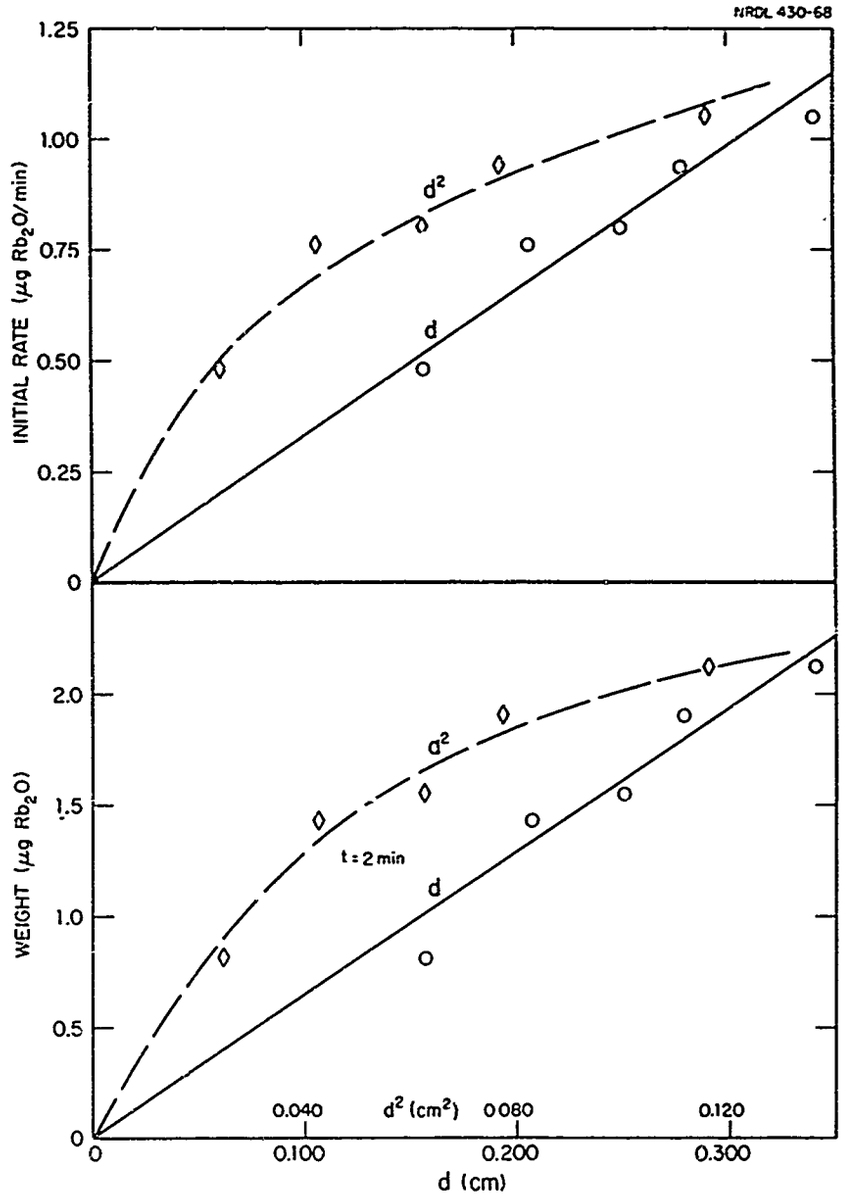

Fig. 12 The Initial Rate of RbO Uptake and the Amount of RbO Uptake at 2 Minutes by the Calcium Ferrite Particles as a Function of Particle Diameter and Diameter Squared. T = 1400°, RbO partial pressure = 1.46×10^{-5} atm.

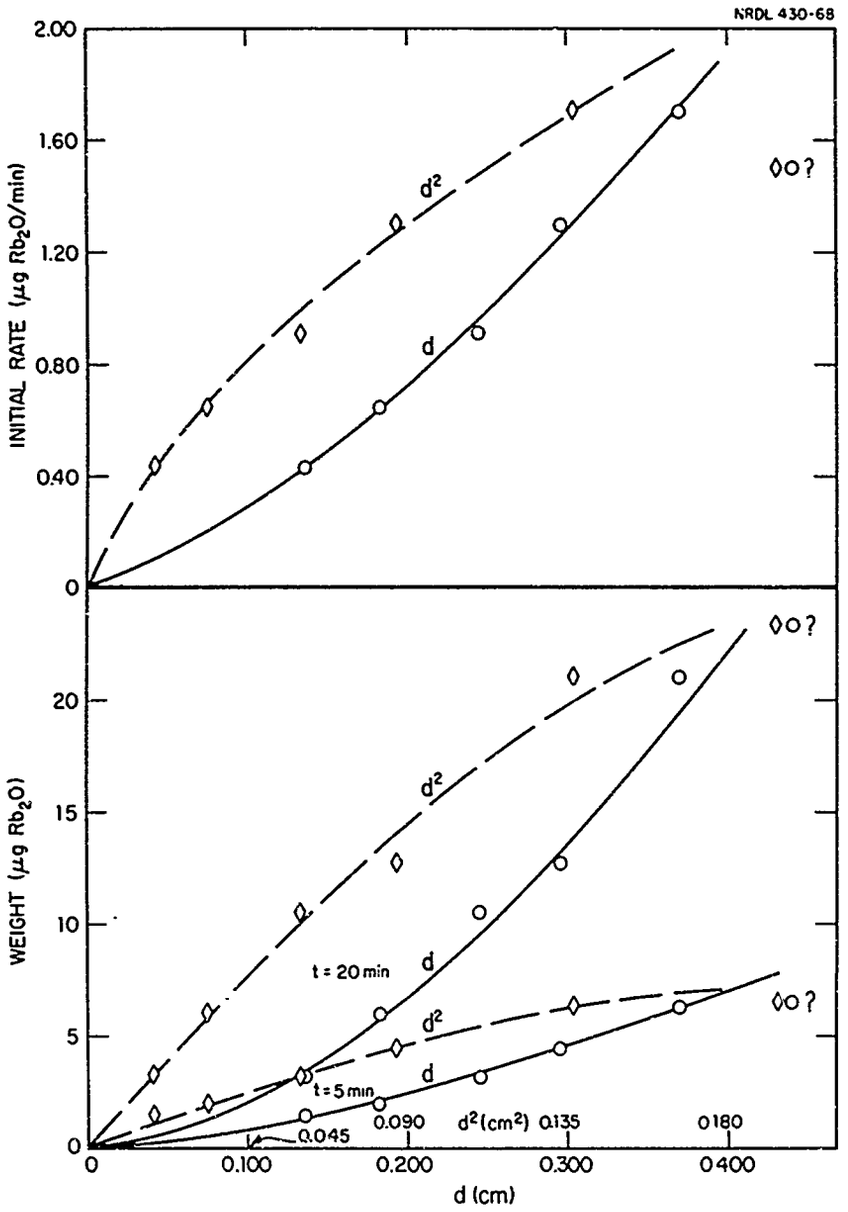

Fig. 13 The Initial Rate of RbO Uptake and the Amount of RbO Uptake at 5 and 20 Minutes by the Calcium Ferrite Particles as a Function of Particle Diameter and Diameter Squared. T = 1200°C, RbO partial pressure = 1.46×10^{-5} atm.

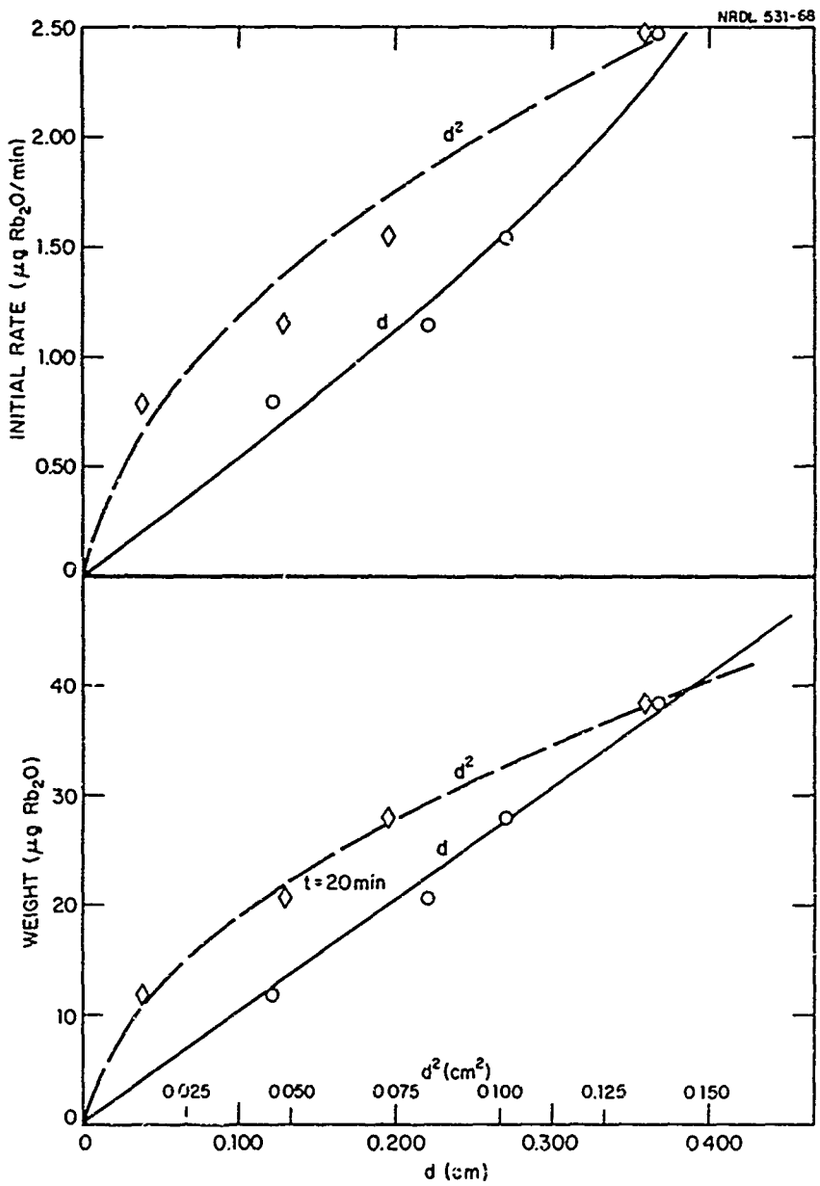

Fig. 14 The Initial Rate of RbO Uptake and the Amount of RbO Uptake at 20 Minutes by the Calcium Aluminum Silicate Particles as a Function of Particle Diameter and Diameter Squared. T = 1400°C, RbO partial pressure = 1.53×10^{-5} atm.

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13. ABSTRACT

In a program for elucidation of the process of formation of radioactive fallout, we measured the rates at which substrate samples of a clay loam and a calcium ferrite took up vaporized rubidium oxide. The rate measurements were made in air from 1100 to 1450°C and over a rubidium oxide partial-pressure range of about 1×10^{-5} to 3×10^{-4} atm. We found that the initial rates of rubidium oxide uptake by both the clay loam and the calcium ferrite were about the same but the calcium ferrit melts reached saturation with respect to rubidium oxide uptake in a few minutes while the clay loam continued to take up the rubidium oxide at a high rate for times of at least an hour. For both substrates, the rate-controlling step for the uptake process was the diffusion of the rubidium oxide vapor through the air to the surfaces of the substrate samples. The uptake of rubidium oxide vapor by a series of simple, unmelted oxides at 1400°C wal also measured. In general, the uptake behavior of the rubidium oxide was as expected in that it reacted least with the basic oxides such as SrO and CaO and reacted most with the acidic oxides such as Nb_2O_5 and SiO_2.

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