NOLTR 69-191

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

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27 JANUARY 1970

NOL
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NOLTR 69-191

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High-Temperature Measurements of the Rate of Uptake of Rubidium Chloride Vapor by Selected Oxides

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ABSTRACT: In a program for the 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 chloride. The rate measurements were made in air from 1100° to 1450°C and over a rubidium chloride partial pressure range of about 1×10^{-6} to 5×10^{-4} atm. The clay loam took up rubidium chloride vapor at a rate determined by the rate of diffusion of the rubidium chloride vapor through the surrounding air. The calcium ferrite took up the rubidium chloride at a slower rate which was governed by the rate of reaction of the rubidium chloride with the calcium ferrite at the substrate surface. The uptake of rubidium chloride vapor by a series of simple, unmelted oxides at 1400°C was also measured. In general, the rubidium chloride reacted most with acidic oxides such as Nb_2O_5 and TiO_2 and least with basic oxides such as SrO and MgO.

PUBLISHED 27 JANUARY 1970

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NOLTR 69-191 27 January 1970

High-Temperature Measurements of the Rate of Uptake of Rubidium Chloride Vapor by Selected Oxides

This is the fourth in a series of reports which presents the measurements of the uptake rates at high temperatures of some radioactive vapors of volatile oxides by molten and solid substrates of various refractory oxides. The results have been used to determine the mechanisms which govern the rates of the uptake reactions. These rates and mechanisms are useful in describing the formation processes of radioactive fallout particles resulting from nuclear explosions.

This work has been sponsored by the Division of Biology and Medicine of the U. S. Atomic Energy Commission under contract number AT(49-7)-1963.

GEORGE G. BALL
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ALBERT LIGHTBODY
By direction

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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 chloride, 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}RbCl 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 chloride 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 1175°C) and constant rubidium oxide partial pressure (about 8×10^{-6} 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 chloride per particle in μg/min. It was found that the uptake of rubidium chloride vapor by the clay loam was proportional to time for intervals up to at least an hour. The uptake of the rubidium chloride by the calcium ferrite was slower and decreased with time reaching an apparent equilibrium value in a few minutes.

For the interpretation of the data, it was postulated that the uptake process consisted of three steps: (1) the diffusion of the rubidium chloride vapor through the air to the surface of the substrate particle, (2) the reaction or condensation of the rubidium

chloride vapor at the surface of the particle, and (3) the diffusion of the condensed rubidium chloride from the surface of the particle into the interior.

For the uptake of rubidium chloride vapor by the clay loam it was found that the rate-controlling step was the diffusion of the rubidium chloride vapor through the air. By the use of Maxwell's equation it was possible to make theoretical calculations of the rates of uptake of the rubidium chloride vapor by the clay loam; these calculations agreed moderately well with the experimentally measured values. The uptake of rubidium chloride by the calcium ferrite was considerably less than by the clay loam and the rate was governed by a slow rate of reaction at the substrate surface.

The uptake of rubidium chloride vapor by a series of 14 simple, solid oxides was measured at 1400°C. In general, the rubidium chloride reacted least with the basic oxides such as SrO and MgO and reacted most with the acidic oxides such as Nb_2O_5 and TiO_2.

INTRODUCTION

This is the fourth in a series of reports describing experimental studies of the rates of uptake of selected radioactive vapors 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 radioactive vapors. Volatile radioactive compounds 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 three reports of this series presented the results of measurements of the uptake rates of the oxide vapors of molybdenum, tellurium, and rubidium by substrates of calcium ferrite and of a clay loam soil occurring in the Berkeley Hills, California.[1,2,3] 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 chloride upon these same two substrate materials. Rubidium chloride was chosen as the radioactive vapor source because rubidium is the precursor of both the biological important, long-lived constituent of fallout, ^{90}Sr, and also because radioactive rubidium chloride vapor undoubtedly exists in the cooling fireball of nuclear explosions which have been detonated over, or in, seawater. It is also of interest to compare the chemical behavior of the rubidium chloride vapor with that of the rubidium oxide in reference to their reactivity at high temperatures with the oxide substrates.

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 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.

Solid rubidium chloride, which served as the source of the radioactive rubidium chloride 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 chloride 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

The source for the radioactive rubidium chloride vapor was prepared by dissolving crystalline rubidium chloride (Bryant Lab., 99% pure) in water and adding an aqueous solution of ^{86}RbCl (New England Nuclear Corp.). The solution was thoroughly stirred and the solid radioactive rubidium chloride recovered by evaporating the solution to dryness. As a check on the radionuclide purity of the ^{86}Rb, the half-lives of the three batches used were found to be 18.3, 18.8, and 19.0 days, which correspond closely to the published half-life of 18.7 days. Also, no unidentified gamma photopeaks were observed in its gamma pulse-height distribution.

The calcium ferrite used for the substrate samples was prepared by weighing out the appropriate amounts of AR grade Fe_2O_3 and CaO

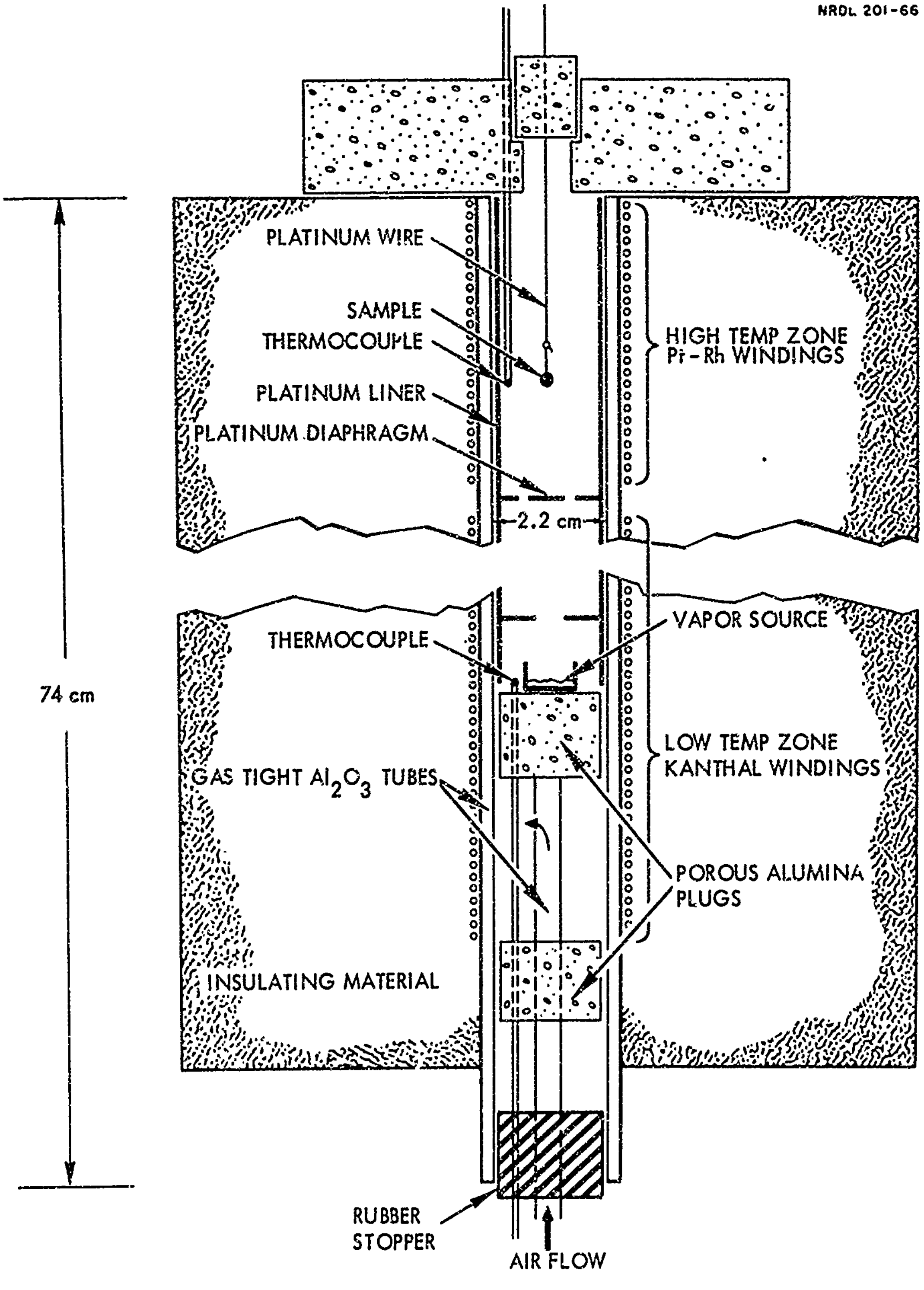

FIG. 1 TWO-TEMPERATURE FURACE.

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 chloride source was inserted into the lower section of the furnace. The furnace was allowed to equilibrate with the rubidium chloride 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 chloride 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 preheated in a gas flame and then inserted into the top of the furnace for varying lengths of time, usually 2 to 10 minutes depending upon the rate of uptake of rubidium chloride. At the end of this interval, the samples were quickly withdrawn and were counted in a 3 x 3 in. NaI(Tl) 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 25 minutes.

At the end of each day's runs, the rubidium chloride source was removed from the furnace and replaced by the standby source. The regular rubidium chloride source was reweighed and from its weight loss the amount of rubidium chloride evaporated was determined. The vapor concentration in the furnace was computed from the amount of rubidium chloride evaporated and the known volume of air which passed through the apparatus while the rubidium chloride source was in the furnace.

The rubidium chloride vapor concentrations were converted to partial pressures on the assumption that the vapor species was RbCl. Rubidium chloride vapor consists of a mixture of both monomer and dimer, but experimental measurements by Datz, et al.,[4] indicate that at the pressures and temperatures used in the work reported here, the amount of dimer is negligible.

The range of temperatures for the source region was about 540-740°C with most of the runs at about 670-700°C. The flow rate of air through the apparatus was 70 ml/min (measured at 25°C).

A check was made on the effect of varying the flow rate of the carrier gas. Two experimental runs were made under identical conditions except that in one run the flow rate was 70 ml/min and in the second it was increased three-fold to 210 ml/min. After the change in partial pressure of the rubidium chloride vapor by the increased volume of air was taken into account, there was no significant change in the vapor uptake by substrates of either clay loam or calcium ferrite.

The actual uptake of RbCl 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 water a known amount of the radioactive RbCl source material. 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 ± 4° and the weight losses of the rubidium chloride 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 ± 5%.

The greatest source of error probably lay in the difference between the calculated and the actual vapor concentrations of the rubidium chloride in the furnace. At low partial pressures, absorption or reaction of the RbCl vapor with the walls of the furnace can cause important errors. From experience gained in testing the experimental procedures in this and previous work, it can be estimated that the reproducibility of the runs are good to about ± 20% and the overall accuracy is good to within a factor of about 2.

EXPERIMENTAL DATA

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

Figures 2 and 3 show the uptake of RbCl by various-sized clay loam particles as a function of time at T = 1400 and 1175°C respectively. The RbCl partial pressure was held constant for each series of runs. Figure 4 shows the same information for various-sized calcium ferrite particles at T = 1400°C. Figure 5 shows the uptake of RbCl 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 RbCl partial pressure and the temperatures of the samples. The same sized particles (0.272 ± 0.010 cm in diameter) were used in all these runs. Figure 6 shows the initial rates of uptake of RbCl by both clay loam and calcium ferrite particles at a temperature of 1400°C and a RbCl partial pressure varying from about 10^{-6} to 5×10^{-4} atm. Figure 7 shows the initial rates of uptake of RbCl by clay loam and calcium ferrite particles at a constant RbCl pressure of 2.0×10^{-5} atm and with the sample temperature varying from 1100 to 1450°C.

In Figures 6 and 7 the initial rates of uptake of the RbCl vapor were plotted. This was done because in many cases 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

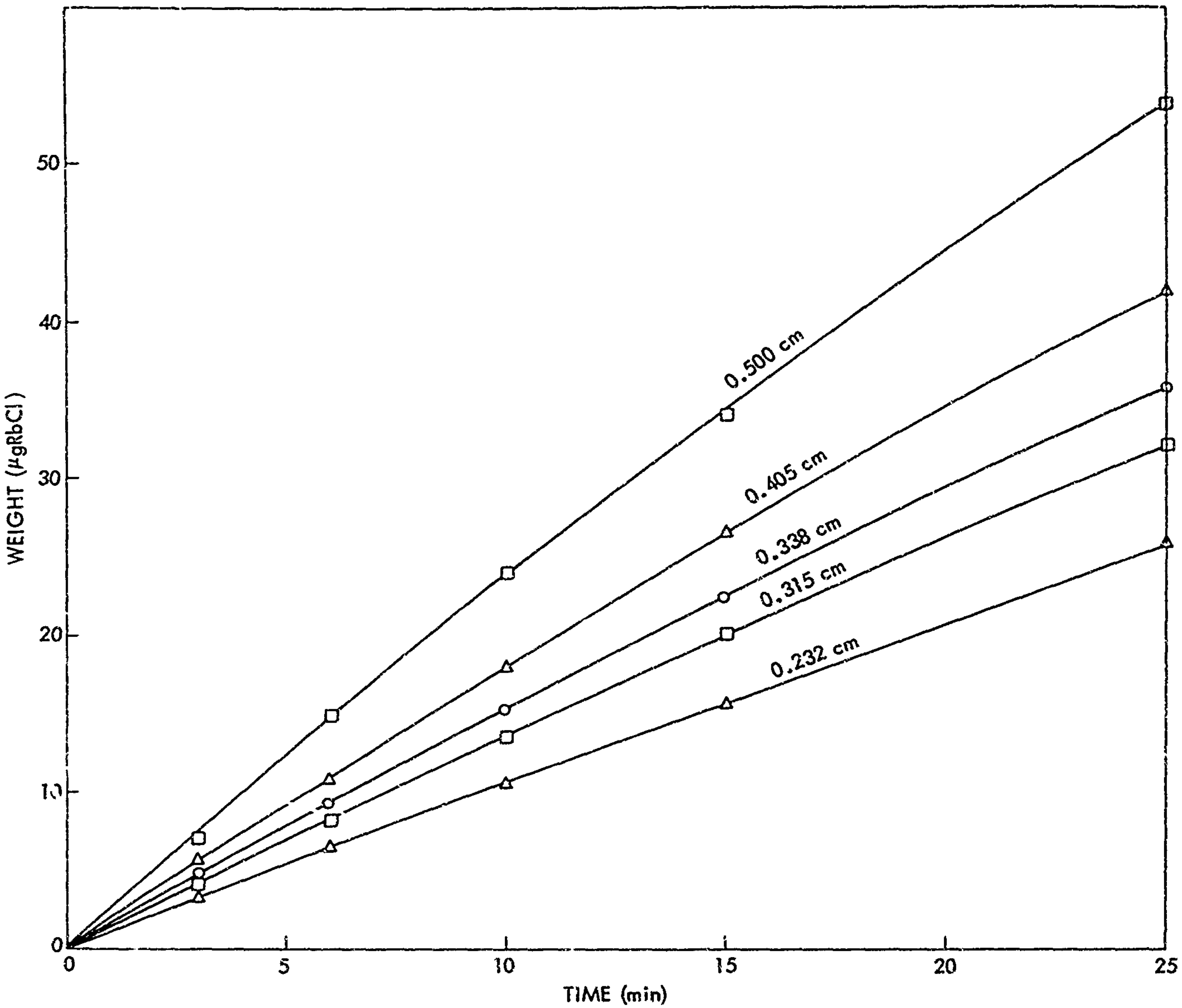

FIG. 2 Uptake of RbCl by Clay Loam as a Function of Particle Diameter and Time. T=1400°C, RbCl partial pressure=8.25 x 10^{-6} atm.

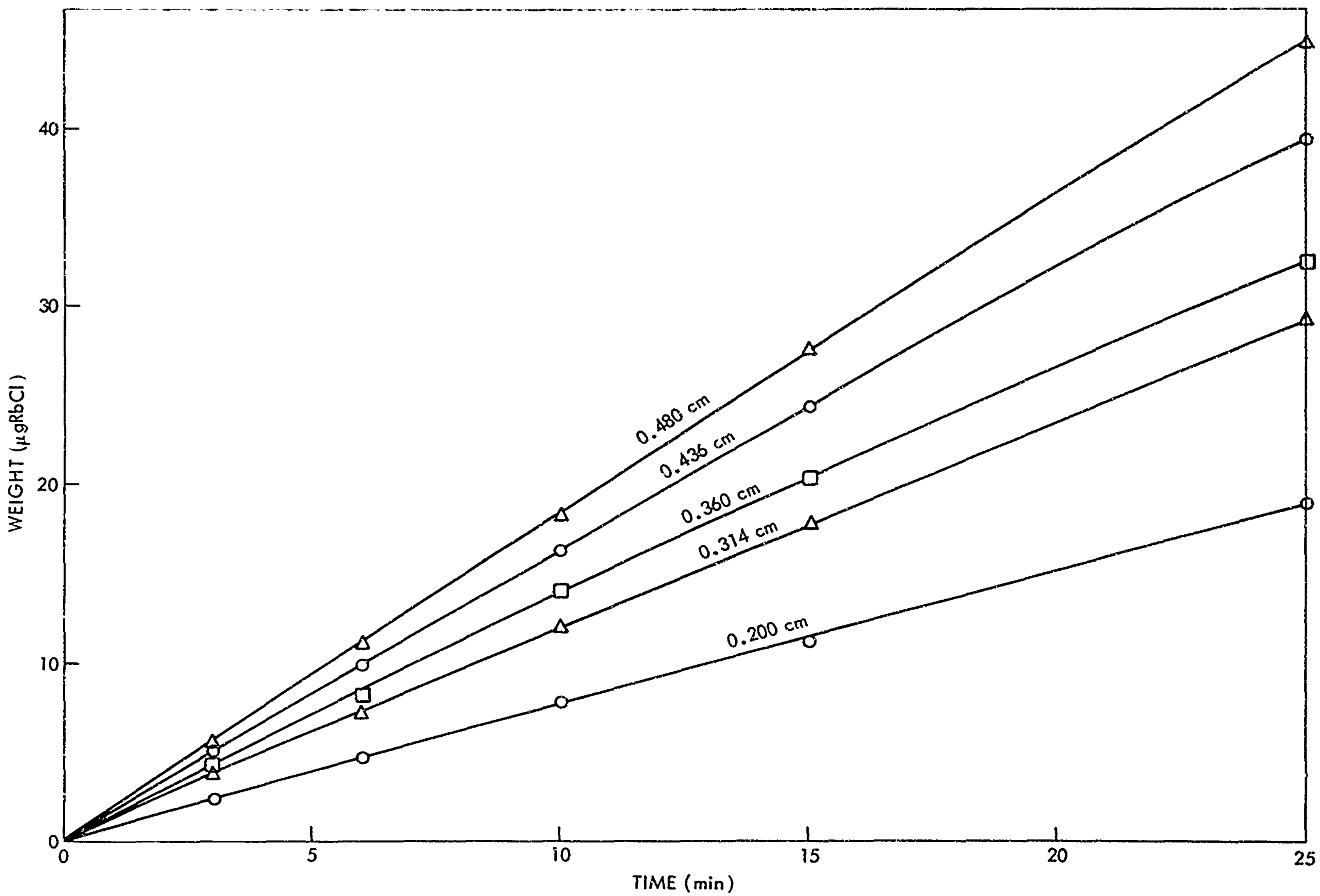

FIG. 3 Uptake of RbCl by Clay Loam as a Function of Particle Diameter and Time. T=1175°C, RbCl partial pressure=7.75 x 10^{-6} atm.

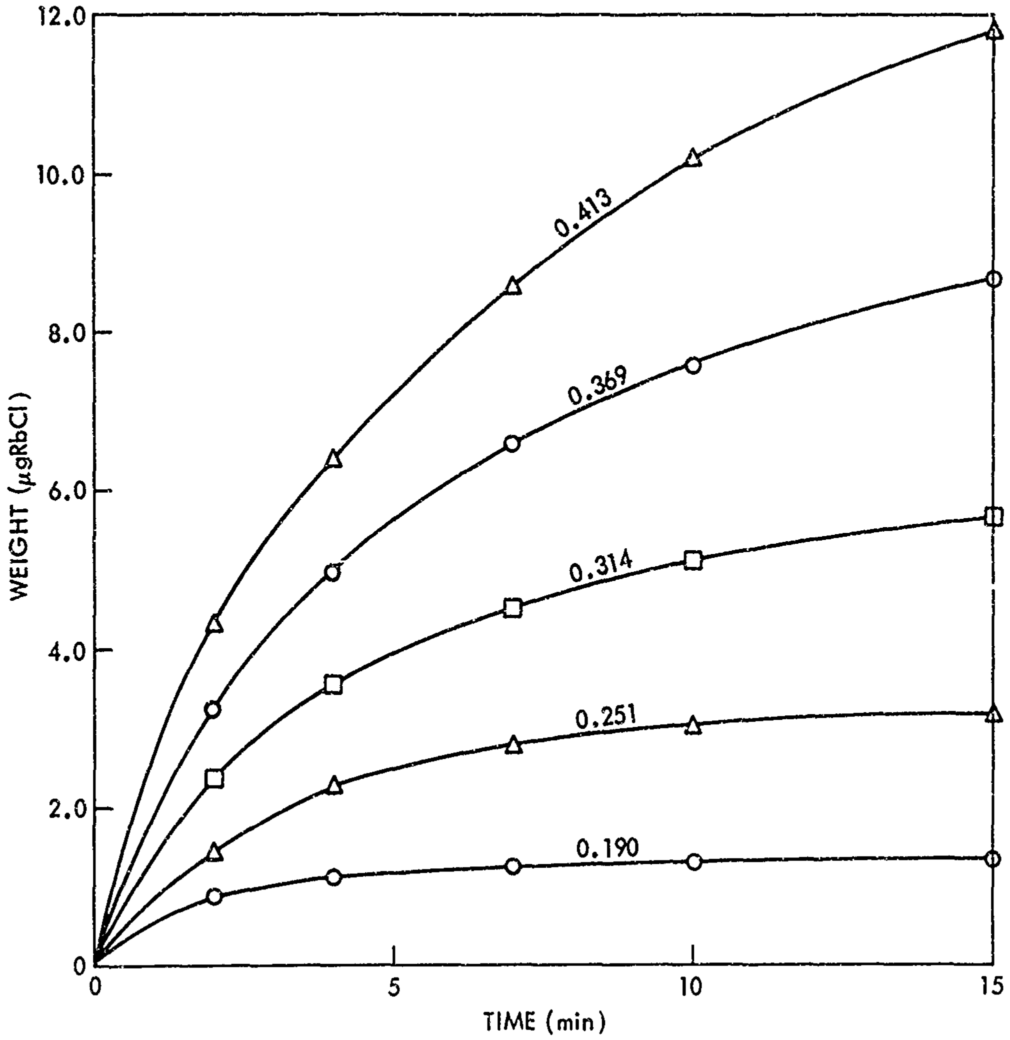

FIG. 4 Uptake of RbCl by Calcium Ferrite as a Function of Particle Diameter and Time. T=1400°C, RbCl partial pressure = 3.80 x 10^{-5} atm.

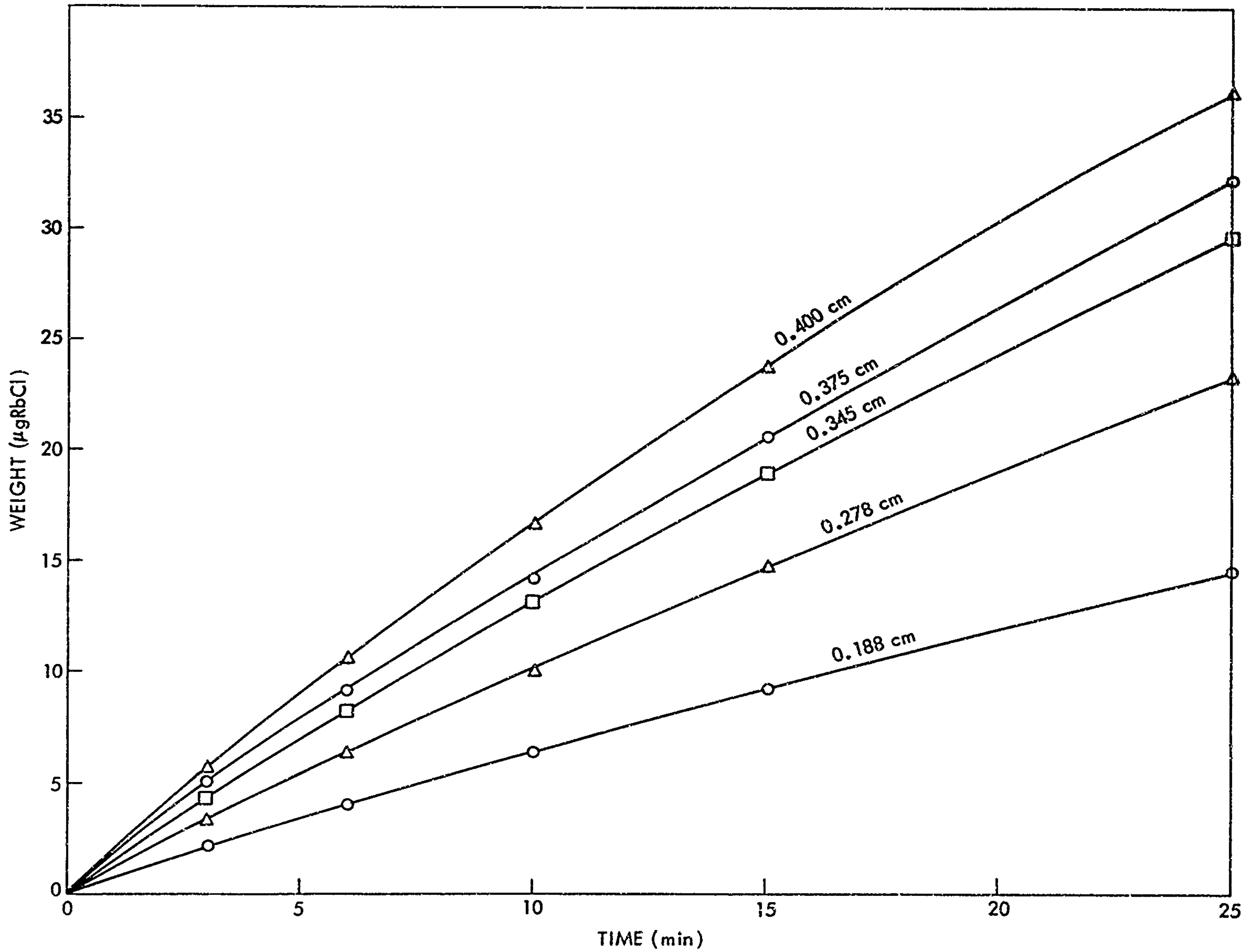

FIG. 5 Uptake of RbCl by Calcium Aluminum Silicate as a Function of Particle Diameter and Time.
T = 1400°C, RbCl partial pressure = 7.70×10^{-6} atm.

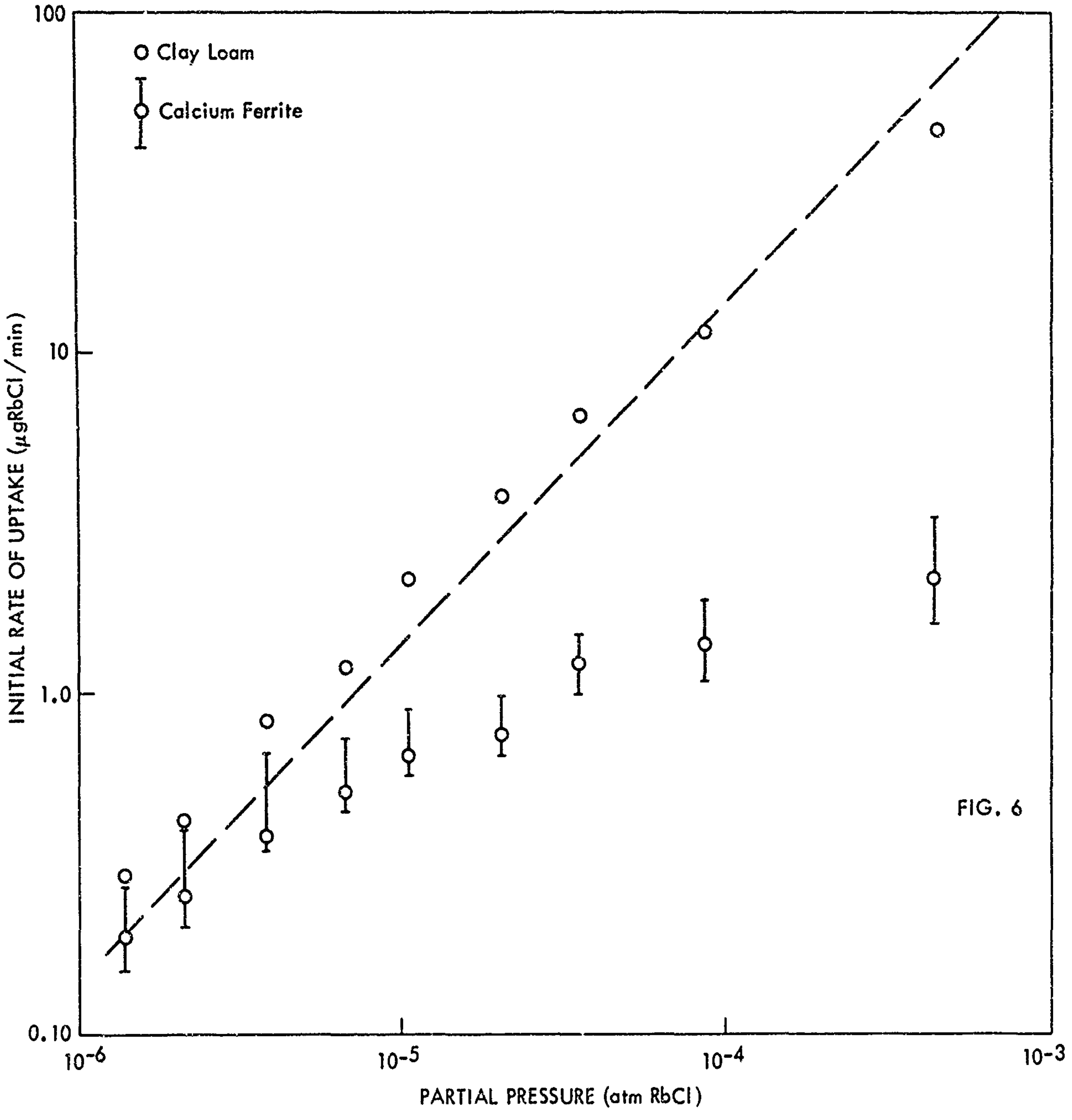

FIG. 6 Initial Rates of Uptake of RbCl at 1400°C as a Function of RbCl Partial Pressure. The initial rates are shown for both clay loam and calcium ferrite. The dashed line indicates the theoretically calculated uptake rate based on Maxwell's equation. Average particle diameter is 0.272 cm.

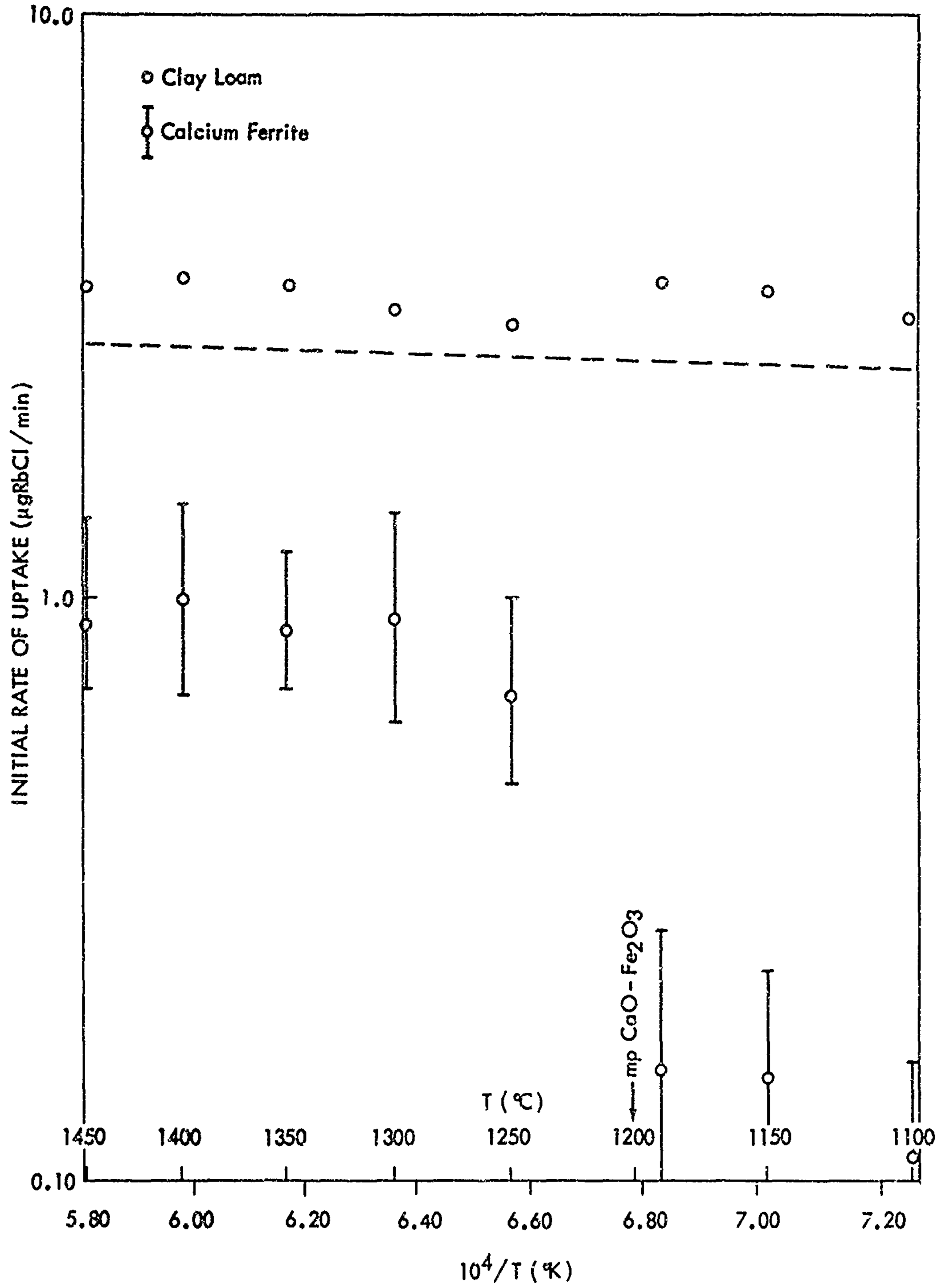

FIG. 7 Initial Rates of Uptake of RbCl as a Function of Temperature at a Constant RbCl Partial Pressure of 2.0×10^{-5} atm. The initial rates are shown for both the clay loam and the calcium ferrite. The dashed line indicates the theoretically calculated uptake rate based on Maxwell's equation. Average particle diameter is 0.272 cm.

determine the mechanism which governs the rate of uptake. The initial rates were determined graphically as the slope of a tangent to the curve of the plot of amount of uptake vs time at t = 0.

A series of runs was made in which the uptakes of RbCl vapor by samples of single, unmelted oxides were measured. This was done to obtain some information about the relative reactivity of RbCl vapor with the various oxides. The furnace temperature was 1400° (below the melting points of all the oxides used) and the RbCl partial pressure was about 2.3×10^{-5} atm. The samples were prepared by pressing the powdered oxides (AR grade) into thin pellets about 0.60 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 RbCl vapor. The uptake of RbCl vapor by these oxides is shown in Figure 8.

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 RbCl 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 RbCl 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 RbCl vapor molecules through the air to the surface of the particle; (2) the reaction and condensation of the RbCl vapor molecules at the surface of the particle; and (3) the diffusion of the condensed RbCl into the interior of the particle.

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

$$I = \frac{2\pi d\ D_{12} M\ (P_\infty - P_0)}{RT}$$

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_0 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

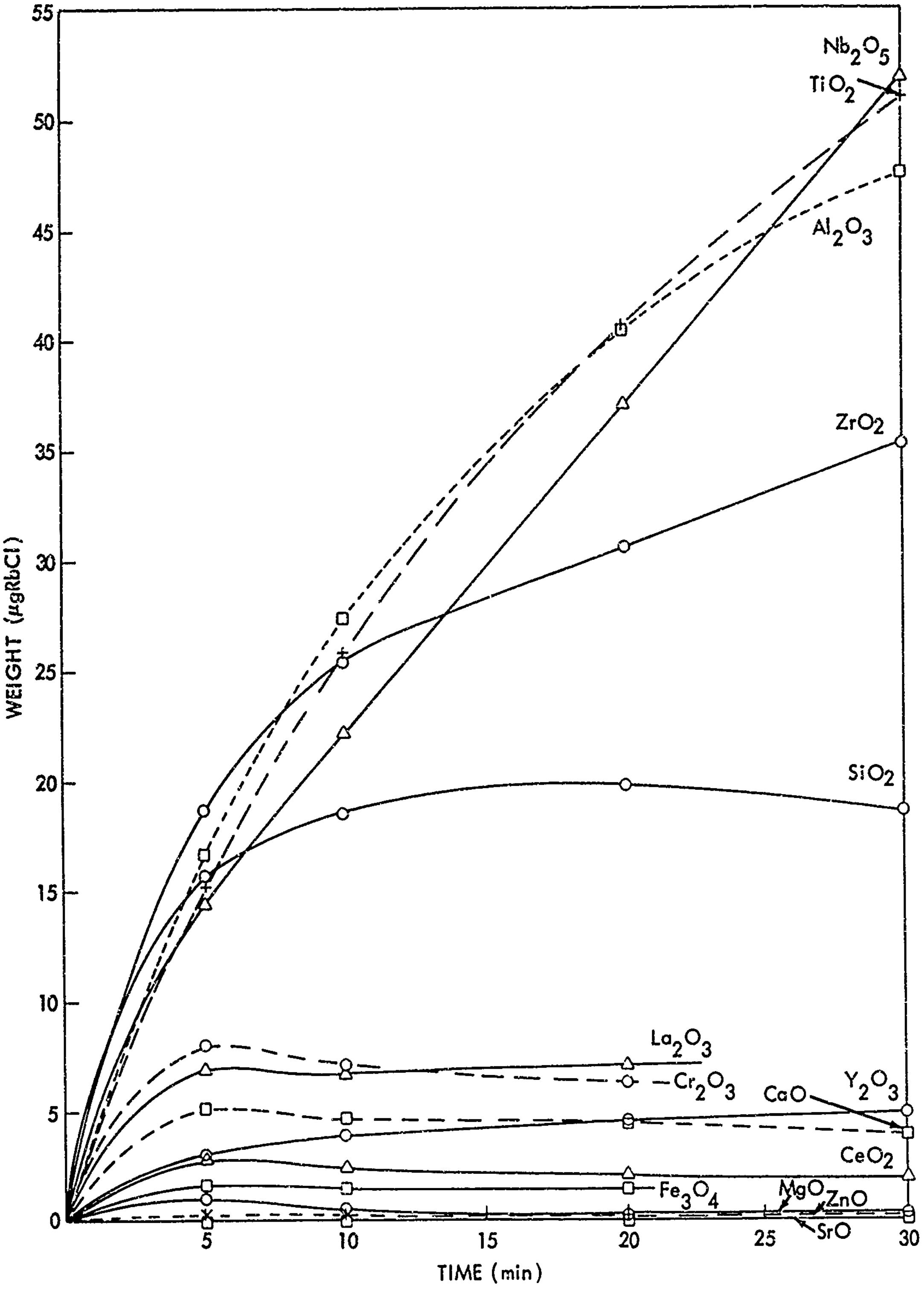

FIG. 8 Uptake of RbCl by Solid Oxide Pellets
$T = 1400°C$, RbCl partial pressure $= 2.3 \times 10^{-5}$ atm.
The area of each pellet exposed to the RbCl vapor was approximately 0.28 cm^2.

uptake of the RbCl 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 RbCl 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 RbCl 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 RbCl and further condensation is governed by the rate at which the RbCl 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 RbCl at a constant concentration. A graphical solution of the mathematical relations for this type of diffusion is given by Crank.[5] At early times in the diffusion process,

$$\frac{M_t}{M_\infty} \sim \frac{(Dt)^{\frac{1}{2}}}{d^2}$$

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,

$$M_t \sim d^2\ t^{\frac{1}{2}}$$

Therefore, if diffusion of RbCl into the particle is rate-determining, the total amount of RbCl 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 RbCl 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 RbCl is Proportional to:	Amount of Uptake of RbCl is Proportional to:
Diffusion of RbCl Vapor Through Air	d	dt
Reaction or Condensation Rate at Surface of the Particle	d^2	d^2t
Diffusion of RbCl into Particle	$\frac{d^2}{\sqrt{t}}$	$d^2\sqrt{t}$

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

Consider first the uptake of RbCl by various sized clay loam particles at 1400°C (Figure 2). The plots are very close to linear, indicating that the RbCl uptake is proportional to the time of exposure of the particles. This suggests that the rate-controlling step may be either diffusion of the RbCl vapor through the air to the surfaces of the particles or the rate of reaction of the RbCl at the surfaces of the particles (see Table I).

For distinguishing between these two mechanisms, plots have been made of the initial rates of RbCl uptake vs particle diameter and diameter squared and also the total amounts of RbCl uptake at 25 minutes vs particle diameter and diameter squared (Figure 9). 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 RbCl vapor through the air is the rate-determining step.

The same analysis can be applied to the uptake of RbCl vapor by the clay loam particles at 1175°. At this temperature the clay loam is solid and it might be expected that diffusion of the condensed RbCl into the particles would be slow enough to be the rate-determining step. However, Figure 3 shows that the amount of RbCl uptake by each particle is again proportional to time. Also, the plots of the initial rates of uptake and the total amounts of uptake at 25 minutes vs particle diameter are linear (Figure 10) which again shows that the rate-determining mechanism is the diffusion of the RbCl vapor molecules through the air.

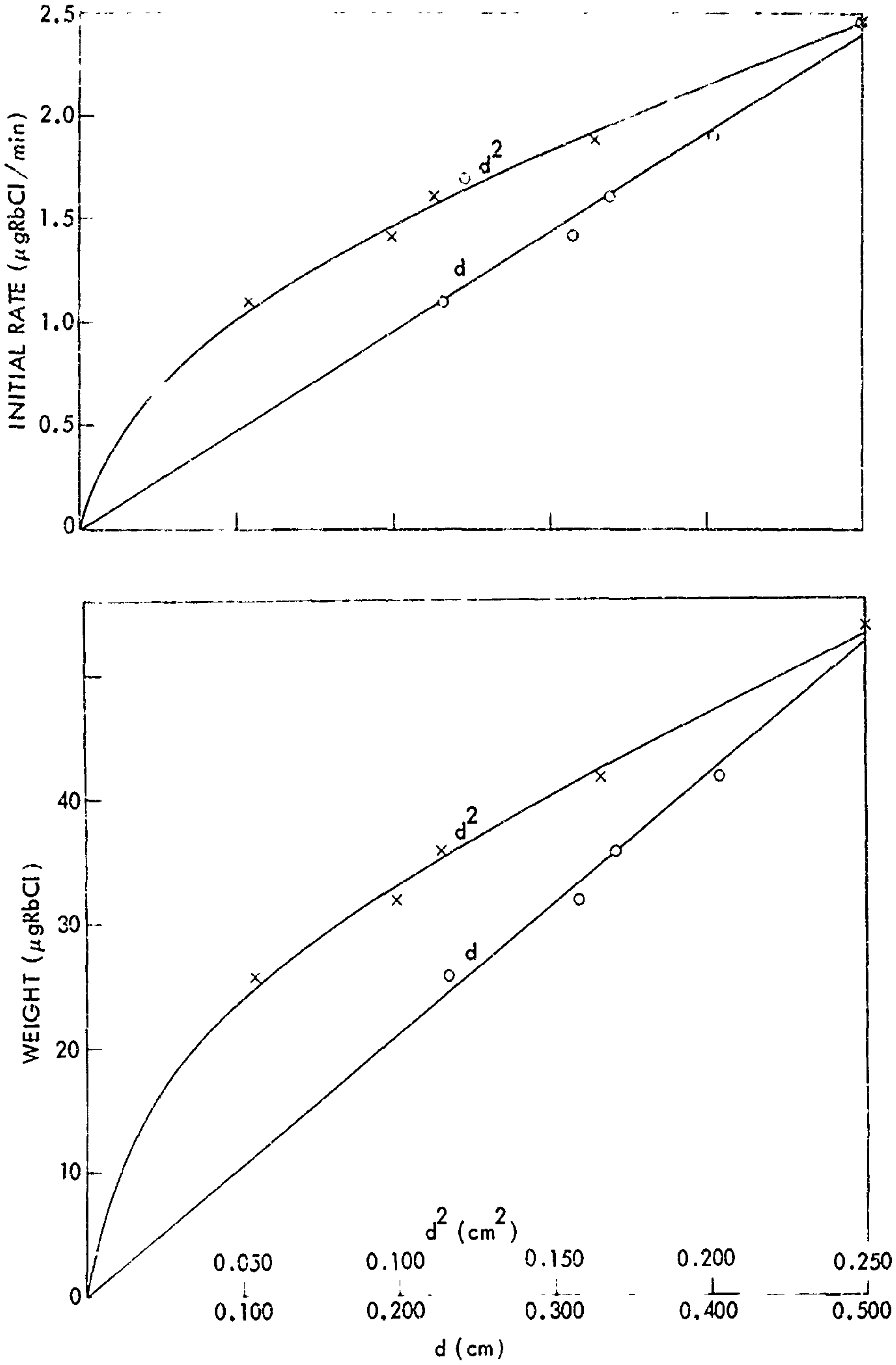

FIG. 9 The Initial Rate of RbCl Uptake and the Amount of RbCl Uptake at 25 minutes by the Clay Loam Particles as a Function of Particle Diameter and Diameter Squared.
T=1400°C, RbCl partial pressure=8.25 x 10^{-6} atm.

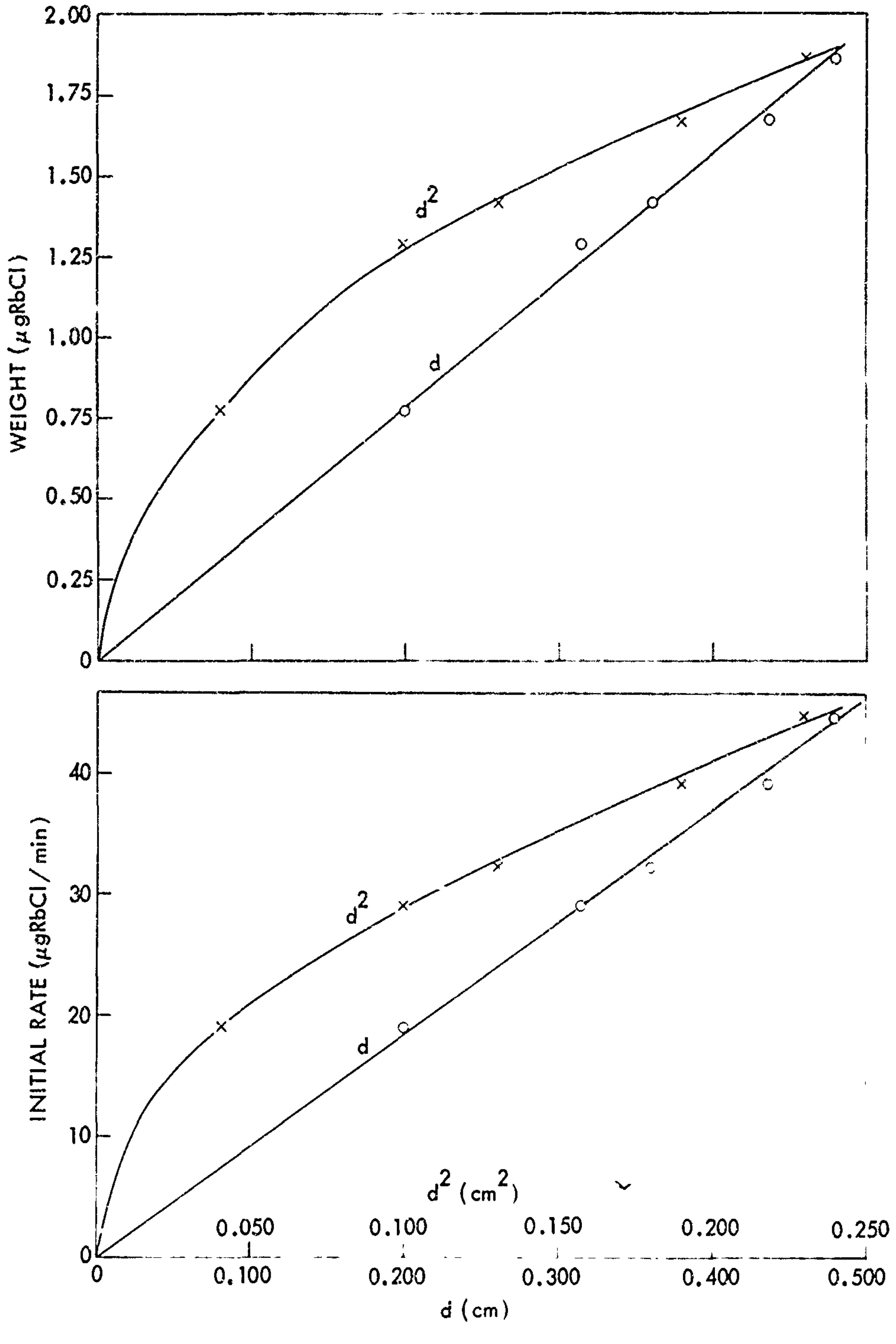

FIG. 10 The Initial Rate of RbCl Uptake and the Amount of Uptake at 25 minutes by the Clay Loam Particles as a Function of Particle Diameter and Diameter Squared.
T = 1175°C, RbCl partial pressure = 7.75×10^{-6} atm.

Figure 4 shows the uptake of RbCl 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 RbCl into the particles. However, it has been pointed out that the criteria of Table I are valid only when the uptake of the RbCl is relatively small compared with the final uptake at equilibrium. Figure 4 shows that the smaller calcium ferrite particles reach equilibrium in a few minutes. For application of the criteria of Table I, the initial rate of RbCl uptake has been plotted against diameter and diameter squared. Because of the lack of data and the pronounced curvature of the graph at early times in the uptake process, there is uncertainty in determining the rate of uptake at $t = 0$. The degree of uncertainty is indicated by the length of the vertical bars in the graph (top half of Figure 11). Although there is considerable scatter in the points, the plot of initial rate vs diameter squared conforms roughly to a straight line while the plot using particle diameters is definitely curved.

Plotted on the lower graph of Figure 11 is the amount of RbCl uptake at 1 minute vs particle diameter and diameter squared. At 1 minute the smaller particles have taken up an appreciable fraction of their final equilibrium uptake, but nevertheless, it is apparent that the amount of RbCl taken up is proportional to the square of the particle diameter.

These results suggest that the rate of RbCl uptake by the calcium ferrite particles is governed either by the reaction rate at the surface of the particle or by the diffusion of the condensed RbCl (or of the compound or complex that RbCl forms when reacting with calcium ferrite) into the particle. According to the scheme of Table I it should be possible to distinguish between these two mechanisms by observing whether, for any single particle, the amount of RbCl taken up is proportional to t or to $\sqrt{t}$. However, these criteria are applicable only at early times in the uptake process when the amount taken up is a small fraction of the final equilibrium uptake. Because of the rapid approach to equilibrium, the experimental data at these early times is not adequate to distinguish between these two possibilities.

If diffusion of the condensed RbCl into the particles is rate-determining, it is necessary that the viscosity of the melted calcium ferrite be high enough so that mixing by convection is not important. Calcium ferrite melts, in contrast to those of clay loam, are quite fluid and it is quite possible that at high temperatures there is considerable mixing by convection.

A qualitative test of this effect was made by exposing to RbCl vapor at about 1400°C two similar sized particles of calcium ferrite (dia. = 0.35 cm). The first particle was exposed for 2½ and the second for 3 3/4 minutes. These times are sufficient for the first particle to pick up about 40% and the second particle about 54% of

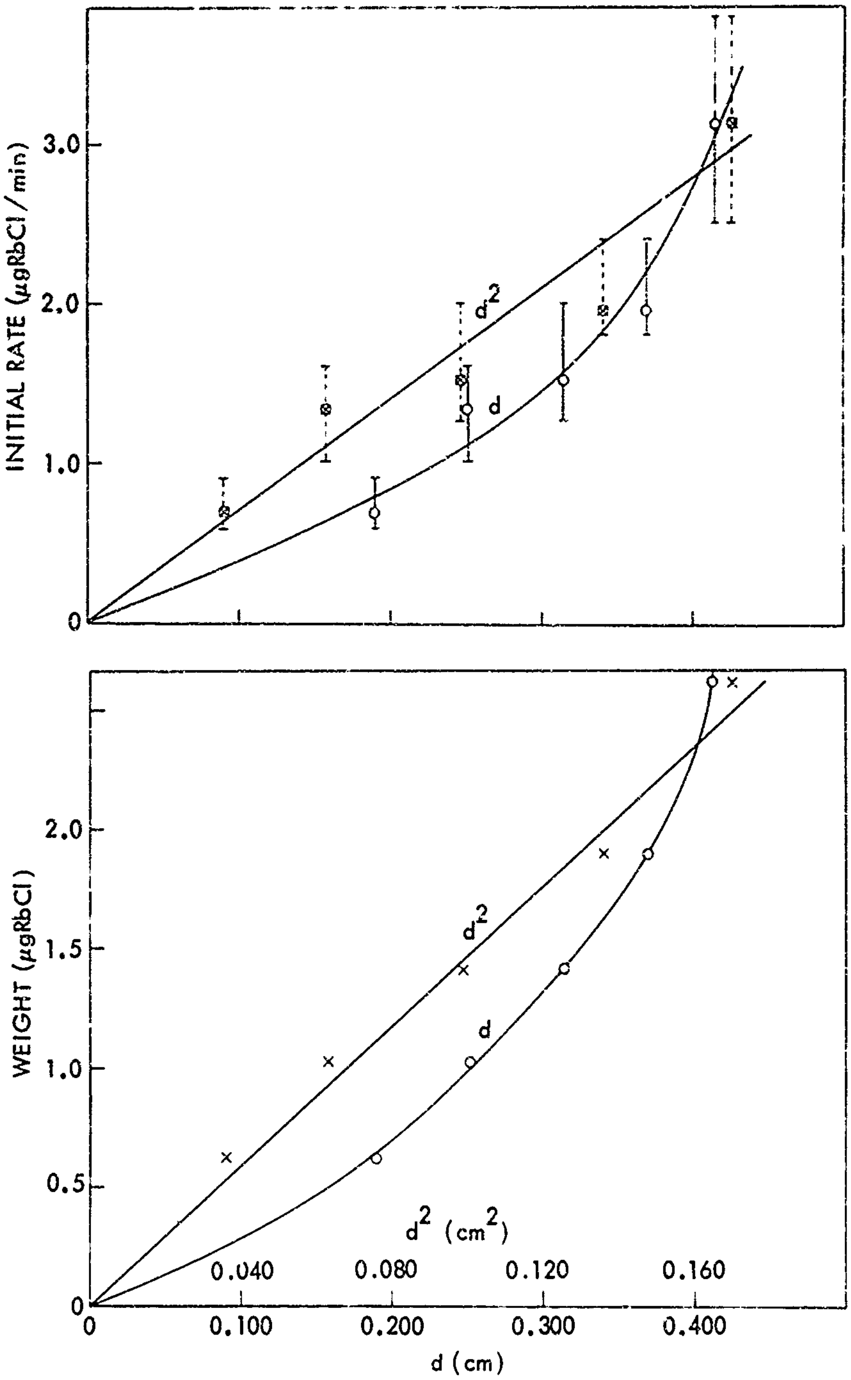

FIG. 11 The Initial Rate of RbCl Uptake and the Amount of Uptake at 1 Minute by the Calcium Ferrite Particles as a Function of Particle Diameter and Diameter Squared.
T=1400°C, RbCl partial pressure=3.80 x 10^{-5} atm.

their final equilibrium uptake. The particles were then embedded in plastic and the plastic ground away until sections through the centers of the particles were exposed. Radioautographs of these sections were made by pressing pieces of Eastman NTB stripping film against them for several days.

The radioautographs showed that in both cases the rubidium was evenly distributed throughout the particles and that there was no evidence of a diffusion gradient. This indicates that in the case of RbCl vapor uptake by calcium ferrite particles, the rate-determining step is the rate of reaction of the vapor at the surface of the particle.

The RbCl uptake data of the calcium aluminum silicate samples at 1400° (Figure 5) have also been analyzed in the manner just described. The results (Figure 12) are similar to those for the clay loam and indicate that the rate-determining step is the diffusion of the RbCl vapor through the air to the surfaces of the particles.

Uptake of RbCl as a Function of Pressure

If, in the case of the clay loam particles, the rate-determining step is the diffusion of RbCl vapor through the air, it should be possible to predict the rate of RbCl 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 RbCl molecules in air. This interdiffusion constant is not known, but it can be estimated by use of the Stefan-Maxwell equation,

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

where σ_{12} is the mean collision diameter of the two vapor species, in this case RbCl 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 RbCl molecules 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 internuclear distance of the gaseous RbCl molecule[6], the collision diameter was crudely estimated as about 7.2×10^{-8} cm.

Maxwell's equation was used to calculate the mass of RbCl 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

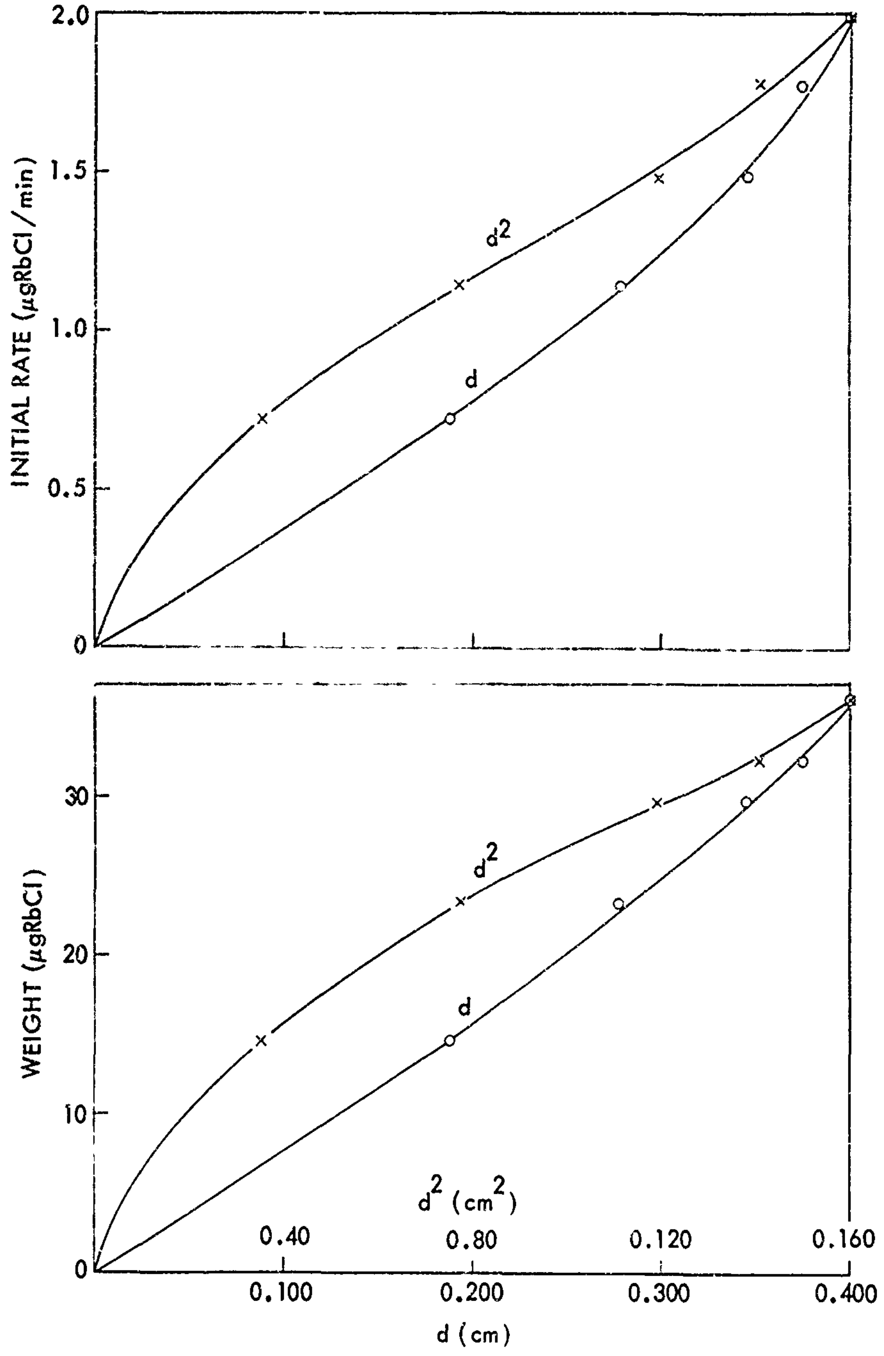

FIG. 12 The Initial Rate of RbCl Uptake and the Amount of Uptake at 25 Minutes by the Calcium Aluminum Silicate Particles as a Function of Particle Diameter and Diameter Squared. T=1400°C, RbCl partial pressure=7.70 x 10^{-6} atm.

assumed that the term P_o in Maxwell's equation is zero. This term refers to the RbCl partial pressure at the surface of the particle. If all of the RbCl molecules that strike the surface remain, the assumption that $P_o = 0$ is probably acceptable.

The calculated rate of RbCl uptake over the range of experimental pressures has been plotted as a dashed line in Figure 6. It is apparent that there is a reasonable correspondence between the experimentally measured rates of RbCl uptake by the clay loam particles with those predicted by the use of Maxwell's equation. This supports the hypothesis that, in the case of the RbCl vapor uptake by the clay loam (and calcium aluminum silicate) particles, the uptake rate is determined by the rate of diffusion of the RbCl vapor molecules through the surrounding air.

The behavior of the plot of the initial rate of uptake of RbCl vapor by the calcium ferrite particles is quite different. Over most of the range of RbCl partial pressures studied, the measured initial rates fall substantially below those predicted by use of Maxwell's equation. This is consistent with the conclusion presented above, that the uptake rate is determined by a slow reaction rate of the RbCl vapor at the surfaces of the calcium ferrite particles.

At the lowest RbCl partial pressures, the initial uptake rates approach those predicted by Maxwell's equation. Presumably, at these low pressures, the rate of arrival of the RbCl molecules at the calcium ferrite surfaces is slow enough so that the rate is not determined exclusively by the rate of surface reaction but also by the rate of arrival, or diffusion through the air, of the RbCl vapor molecules. A second series of experimental runs was made which again measured the initial rates of RbCl vapor uptake by a series of various sized calcium ferrite particles at a RbCl partial pressure of 7.5×10^{-6} atm ($T = 1400^{\circ}$). At this lower pressure, neither the plots of initial uptake rate and amount of uptake at 1 minute vs particle diameter nor diameter squared were linear. That is, the results of these measurements could not be interpreted as favoring a rate determined either by a slow surface reaction or by diffusion of the RbCl vapor through the air.

Uptake of RbCl as a Function of Temperature

Maxwell's equation was used to calculate rates of uptake for the series of runs in which the sample temperatures were varied but the RbCl partial pressure was held constant (Figure 7). The initial rates of RbCl uptake by the clay loam particles conform reasonably closely over the temperature range of 1100 to 1450°C with the rates predicted by assuming that diffusion of the RbCl vapor through the air is rate-determining.

The initial rates of RbCl uptake by the calcium ferrite particles are again markedly lower than those of the clay loam particles and there is also a sharp decrease in the rate as the temperature drops below the melting point of the calcium ferrite. It is surprising that there is not a corresponding decrease in the uptake rate by the clay loam as the temperatures drop below its softening point (about 1300°C). At lower temperature one might expect that, because the rate of diffusion within the solid clay loam is appreciably slower than in the liquid, the surface would soon become saturated and the rate of uptake would decrease. This absence of a rate decrease below the softening, or melting point, has been observed before in some cases of uptake of oxide vapors of molybdenum, tellurium and rubidium by both the clay loam and calcium ferrite where the uptake rate was governed by the rate of diffusion of the oxide vapors through the air.

Possible Chemical Reactions During the RbCl Uptake Process

It is of interest to speculate upon the chemical changes that occur when the RbCl is taken up by either the clay loam, calcium ferrite, or solid oxide samples. At high temperatures, RbCl is stable relative to rubidium oxide. Furthermore, the alkali chlorides are somewhat soluble in silicate melts containing basic oxides so that it is possible that some of the RbCl could be taken up by solution in the clay loam and perhaps in the calcium ferrite.

However, alkali chlorides do not react appreciably with acidic oxides in the absence of basic oxides. Figure 8 shows that RbCl is taken up extensively by several single, acid oxides. While it is not likely that RbCl would react with these oxides at high temperatures to form a complex oxy-chloride, it is known that Rb_2O will form stable complex oxides with acidic oxides at high temperatures[3]. There is, in fact, a close resemblance between the uptake behavior of RbCl and Rb_2O by the same solid oxide substrates.

Referring to Figure 8, the uptake of the RbCl vapor by the solid oxides can be qualitatively divided into three groups: (1) oxides with which RbCl reacts extensively, (2) oxides with which RbCl reacts to an intermediate degree, and (3) oxides with which RbCl reacts only in trace amounts. The same groups are also evident in the reactions of Rb_2O with the solid oxides[3]. These groups for both the RbCl and Rb_2O uptake are compared below:

See next page for Table II

TABLE II

LARGE UPTAKE		INTERMEDIATE UPTAKE		SMALL UPTAKE	
RbCl	Rb_2O	RbCl	Rb_2O	RbCl	Rb_2O
Nb_2O_5	Nb_2O_5	Y_2O_3	Y_2O_3	SrO	SrO
SiO_2	SiO_2	Cr_2O_3	Cr_2O_3	MgO	CaO
ZrO_2	ZrO_2	Fe_3O_4	Fe_3O_4	ZnO	
Al_2O_3	Al_2O_3	CeO_2	CeO_2		
TiO_2	TiO_2	La_2O_3	La_2O_3		
		CaO	ZnO		
			MgO		

The degrees of uptake of RbCl and Rb_2O by the various solid oxides are remarkedly similar. When allowance is made for the differences in partial pressures in the two cases, the actual amounts of RbCl and Rb_2O taken up by each solid oxide are comparable although there is some variation in the order of uptake by the individual oxides in each group. These similarities suggest that the reaction proceeds by the conversion of the RbCl to Rb_2O and the formation of a stable complex oxide.

Possible reactions in the conversion of RbCl to Rb_2O are:

$$2x\,RbCl(g) + MO_x(s) \longrightarrow xRb_2O(s,l) + MCl_{2x}\uparrow$$

$$2\,RbCl(g) + H_2O(g) \longrightarrow Rb_2O(s,l) + 2\,HCl\uparrow$$

$$2\,RbCl(g) + 1/2\,O_2(g) \longrightarrow Rb_2O(s,l) + Cl_2\uparrow$$

The Rb_2O then reacts with the oxide substrate to form a stable complex oxide. None of the above reactions proceed to any appreciable degree under equilibrium conditions at the temperatures and pressures of the experiments. However, equilibrium does not exist under the experimental conditions because of the flow of carrier gas and RbCl vapor. By the continual removal of the gaseous products of reaction, some of the reactions might proceed to a much greater extent than would be predicted.

Influence of Humidity on the Uptake Process

To check the effect of moisture on the uptake of RbCl vapor, a few experimental runs were made using air saturated with water vapor at 25° as the carrier gas. There was no observable difference between the rates of evaporation of the RbCl source with either dry or humid air. Furthermore, there was no appreciable change in the uptake rates of RbCl vapor by either the clay loam or the calcium ferrite (at 1400°C) with either dry or moist air.

Experimental runs with humid air were made on five of the solid oxide samples. Substrates of SiO_2, Cr_2O_3 and ZrO_2 showed little change in the uptake rates with either dry or moist air. Al_2O_3 took up RbCl at about a 50% lower rate and Nb_2O_5 at about a 50% greater rate with humid air as compared with dry air.

The lack of a pronounced effect on the uptake rate by a significant increase in H_2O vapor content of the carrier gas indicates the improbability of the reactions of RbCl with H_2O to form Rb_2O as postulated in the previous section.

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FIGURE CAPTIONS

Fig. 1 - Two-Temperature Furnace

Fig. 2 - Uptake of RbCl by Clay Loam as a Function of Particle Diameter and Time
$T = 1400^\circ C$, RbCl partial pressure = 8.25×10^{-6} atm.

Fig. 3 - Uptake of RbCl by Clay Loam as a Function of Particle Diameter and Time
$T = 1175^\circ C$, RbCl partial pressure = 7.75×10^{-6} atm.

Fig. 4 - Uptake of RbCl by Calcium Ferrite as a Function of Particle Diameter and Time
$T = 1400^\circ C$, RbCl partial pressure = 3.80×10^{-5} atm.

Fig. 5 - Uptake of RbCl by Calcium Aluminum Silicate as a Function of Particle Diameter and Time
$T = 1400^\circ C$, RbCl partial pressure = 7.70×10^{-6} atm.

Fig. 6 - Initial Rates of Uptake of RbCl at 1400°C as a Function of RbCl 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 0.272 cm.

Fig. 7 - Initial Rates of Uptake of RbCl as a Function of Temperature at a Constant RbCl Partial Pressure of 2.0×10^{-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 0.272 cm.

Fig. 8 - Uptake of RbCl by Solid Oxide Pellets
$T = 1400^\circ C$, RbCl partial pressure = 2.3×10^{-5} atm.
The area of each pellet exposed to the RbCl vapor was approximately 0.28 cm^2.

Fig. 9 - The Initial Rate of RbCl Uptake and the Amount of RbCl Uptake at 25 minutes by the Clay Loam Particles as a Function of Particle Diameter and Diameter Squared.
$T = 1400^\circ C$, RbCl partial pressure = 8.25×10^{-6} atm.

Fig. 10- The Initial Rate of RbCl Uptake and the Amount of Uptake at 25 minutes by the Clay Loam Particles as a Function of Particle Diameter and Diameter Squared
$T = 1175^\circ C$, RbCl partial pressure = 7.75×10^{-6} atm.

Fig. 11- The Initial Rate of RbCl Uptake and the Amount of Uptake at 1 Minute by the Calcium Ferrite Particles as a Function of Particle Diameter and Diameter Squared
T = 1400°C, RbCl partial pressure = 3.80×10^{-5} atm.

Fig. 12- The Initial Rate of RbCl Uptake and the Amount of Uptake at 25 Minutes by the Calcium Aluminum Silicate Particles as a Function of Particle Diameter and Diameter Squared
T = 1400°C, RbCl partial pressure = 7.70×10^{-6} atm.

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1 ORIGINATING ACTIVITY *(Corporate author)* U. S. Naval Ordnance Laboratory White Oak Silver Spring, Maryland 20910	2a REPORT SECURITY CLASSIFICATION UNCLASSIFIED 2b GROUP

3 REPORT TITLE

High-Temperature Measurements of the Rate of Uptake of Rubidium Chloride Vapor by Selected Oxides

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5 AUTHOR(S) *(Last name, first name, initial)*

Charles E. Adams, M. H. Rowell, and J. T. Quan

6 REPORT DATE 27 January 1970	7a TOTAL NO. OF PAGES 31	7b. NO OF REFS 6

8a CONTRACT OR GRANT NO. AT(49-7)-1963	9a ORIGINATOR'S REPORT NUMBER(S) NOLTR 69-191
b PROJECT NO.	
c	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

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13 ABSTRACT In a program for the 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 chloride. The rate measurements were made in air from 1100° to 1450°C and over a rubidium chloride partial pressure range of about 1×10^{-6} to 5×10^{-4} atm. The clay loam took up rubidium chloride vapor at a rate determined by the rate of diffusion of the rubidium chloride vapor through the surrounding air. The calcium ferrite took up the rubidium chloride at a slower rate which was governed by the rate of reaction of the rubidium chloride with the calcium ferrite at the substrate surface. The uptake of rubidium chloride vapor by a series of simple, unmelted oxides at 1400°C was also measured. In general, the rubidium chloride reacted most with acidic oxides such as Nb_2O_5 and TiO_2 and least with basic oxides such as SrO and MgO.

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