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DESORPTION FROM PLUTONIUM DIOXIDE

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Abstract. The outgassing of plutonium dioxide, previously exposed to air, was investigated over the temperature range 25° to 1000°C. This investigation broadened the perspective of the adsorption properties and gas-solid interactions of this material. Plutonium dioxide was found to exhibit a strong gettering action toward water vapor, carbon dioxide, and nitric oxide. Water vapor and carbon dioxide are adsorbed directly from the atmosphere. The nitric oxide is believed either to be adsorbed as a radiolysis product of air or to be the result of radiolytic decomposition of air in the adsorbed state. A qualitative comparison of the adsorption strengths of the major products is $CO_2>NO>H_2O$. Approximately 95% of the adsorbed gases can be removed by outgassing the oxide at 700°C.

INTRODUCTION

Plutonium metal oxidizes so readily that it is always found with an oxide coating. Therefore, when one is interested in reactions which occur at the plutonium metal interface, one also must consider the same reactions involving plutonium oxide. For example, the oxidation of plutonium metal involves the adsorption of a gas onto plutonium oxide followed by diffusion of the anion or cation to the oxide-metal interface. A study of the adsorption properties is particularly important for an understanding of the reactivity of plutonium dioxide.

Several papers have been written describing the adsorption properties of plutonium dioxide (1,2,3). Earlier investigations of the adsorption of water on plutonium dioxide showed that the adsorption of water vapor was irreversible (3). Because of this adsorption property of plutonium dioxide, it has been difficult to define and obtain a dry, clean surface. The present study was carried out to evaluate the outgassing characteristics of plutonium dioxide as well as to provide additional information about its adsorption properties.

The work reported here involves the outgassing of plutonium dioxide samples which have been exposed to drybox atmospheres of air for an extended period of time. The outgassing process was followed thermogravimetrically to provide a quantitative measure of the process. A qualitative measure of the removed gases was obtained by a mass spectrometric analysis of the products. This latter method also provided additional quantitative data to supplement those obtained gravimetrically.

EXPERIMENTAL

Apparatus: The apparatus used for the thermogravimetric studies is shown in Figure 1. The principal component is a Cahn electromagnetic microbalance (4). After loading a sample on the balance, the system was evacuated to less than 10^{-4} torr. The sample was then heated in 100° increments to 1000°C. Weight losses due to sample desorption were followed continuously. The accuracy of the desorption measurements was on the order of ±5 micrograms. Accuracy was limited by the inability to attain a vibration-free mount for the balance.

A second vacuum desorption system was used to collect the desorbed gases. This system is shown in Figure 2. After loading the sample (approximately 2 grams), the system was evacuated to 10^{-5} torr. As the sample was heated in 100°C increments the desorbed gases were removed by means of the Toepler pump. Gas samples were taken at each 100°C increment and analyzed with a CEC Model 104 mass spectrometer.

The third type of apparatus used in this study was a Bendix time-of-flight mass spectrometer. A container for the plutonium dioxide sample was connected directly to the inlet of the spectrometer. Gases evolved by the sample were pumped through the spectrometer during the entire experiment. Sampling of the gas was from a dynamic system with scans

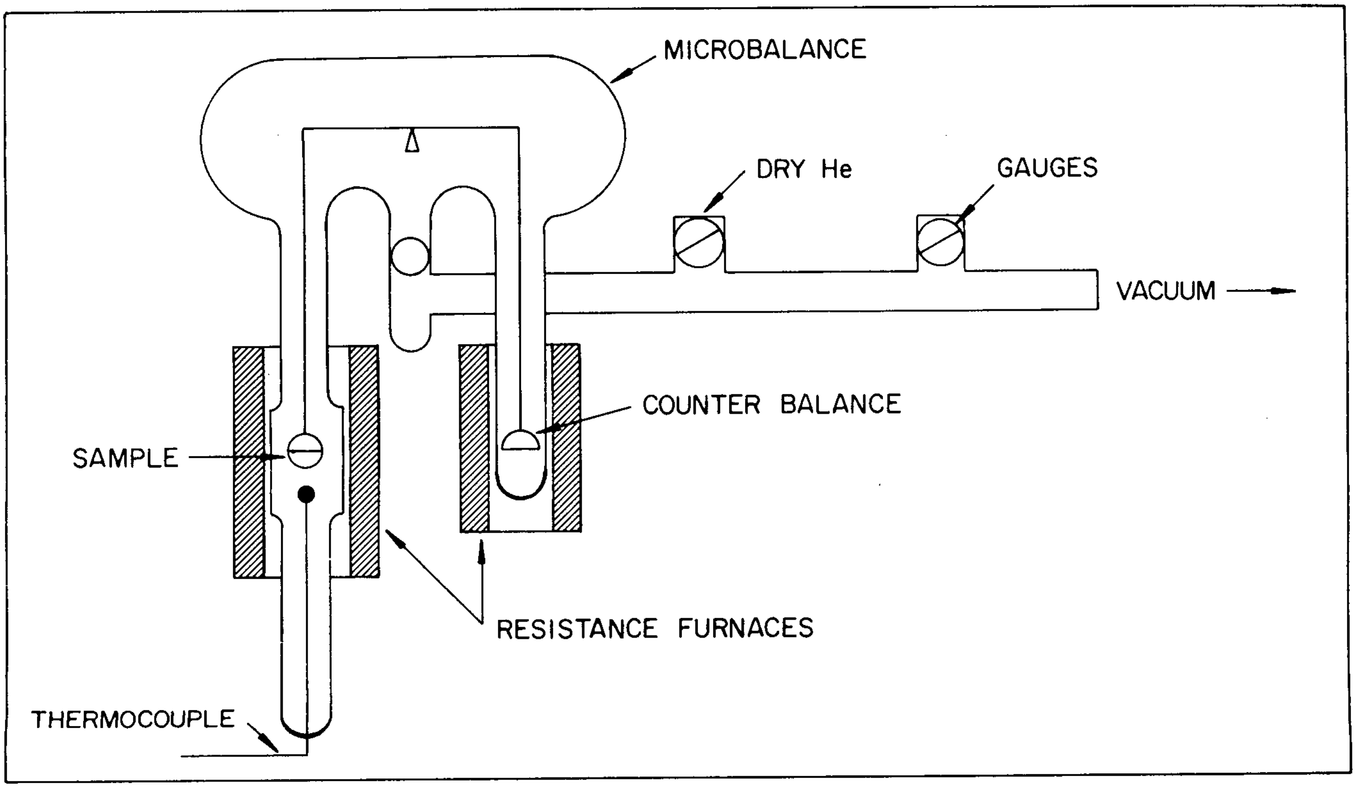
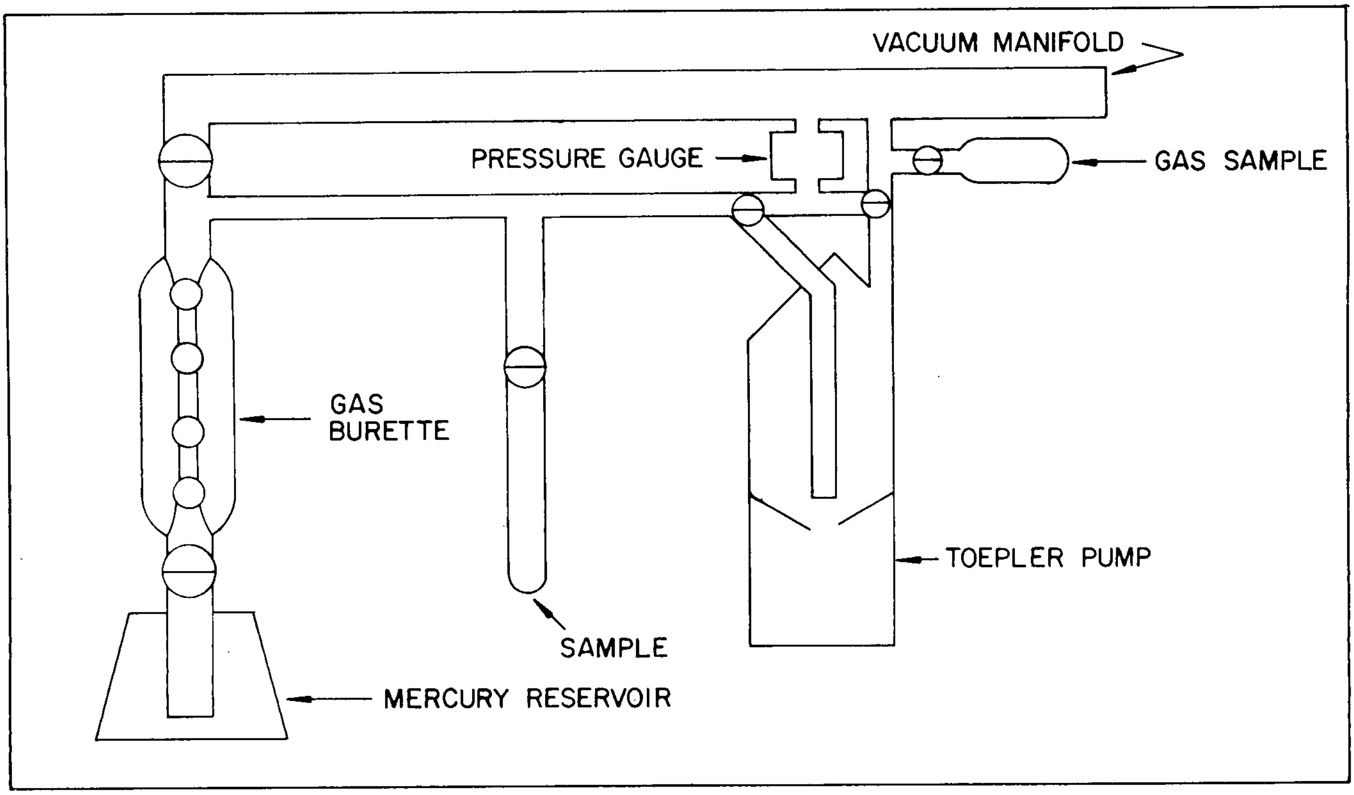


Figure 1. Thermogravimetric system.

Figure 2. Plutonium dioxide degassing system.



every 2 minutes. The system was maintained at 10^{-6} to 10^{-7} torr as the temperature was increased. An exception occurred in the 150° to 200°C range where the pressure increased to 10^{-5} torr.

Sample: The plutonium dioxide (I) used in this study was prepared by the air oxidation of electrorefined alpha plutonium metal at 27°C. The physical properties of this oxide are shown in Table I and the elemental analysis in Table II. Prior to this study the oxide had been exposed to drybox atmospheres for about 5 years. The high iron content of the oxide probably can be attributed to the can in which the oxide was stored. So far as can be determined, this oxide had not been exposed to any liquid or vapor other than air and water vapor. Before beginning the degassing studies, the air was removed from the sample chamber by freezing the sample in liquid nitrogen and evacuating to 10^{-5} torr.

Table I. Physical properties of low temperature plutonium dioxide (I).

Composition	$PuO_{1.87}$
Surface Area	16.1 m^2/g
Particles <1μ	3.1%
1-5μ	96.9%
Crystallite Size	97 Å
Lattice Parameter	5.404 ±.001 Å

Table II. Elemental analysis of low temperature plutonium dioxide (I).

Element	Concentration (ppm)
Be	0.1
Ca	10
Cr	25
Cu	20
Fe	600
K	200
Mg	100
Mn	5
Ni	5
Si	25
Sn	100
C	512

Traces of: Ag, Al, B, Ba, Bi, Cd, In, Mo, P, Pb, Pd, Sb, Sr, Ti, V, Zn, Au, As.

It is assumed that the desorption products are derived from adsorbed gases and vapors and not from impurities in the oxide such as carbon. To verify this, a second sample, plutonium dioxide (II), was prepared by hydriding a gallium stabilized delta-plutonium sample and then burning the hydride in air to form plutonium dioxide. This oxide was exposed to the dry box atmosphere for 9 weeks and then outgassed via the time-of-flight mass spectrometer. The elemental analysis of this oxide is shown in Table III.

Table III. Elemental analysis of Plutonium Dioxide (II).

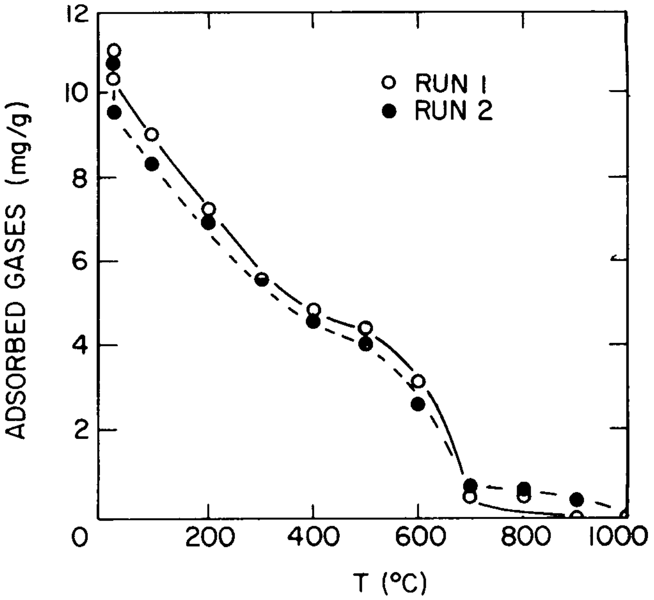
Element	Concentration (ppm)
Al	103
Be	0.18
Cr	70
Cu	46
Fe	329
Mn	12
Mo	15
Ni	167
C	138

Traces of: B, Ca, Cd, Pb, Pd, Sn, Ti, V, Zn, Au.

RESULTS

Thermogravimetric: The results from the thermogravimetric desorption are shown in Figure 3. It is assumed that after heating the sample to 1000°C all of the adsorbed gases were either removed or had reacted with the oxide. It is evident from the desorption curves (Figure 3) that there are three different zones of adsorption involving different

Figure 3. Thermogravimetric degassing of PuO_2.



types of adsorption or possibly different adsorption sites. Zone 1 contains physically adsorbed molecules which can be removed under vacuum at the temperature of adsorption, 27°C. The average of two desorption runs indicates that 0.90 mg of gas/g PuO_2 was physically adsorbed on the oxide. This amount is approximately 8 percent of the total adsorbed gases.

The second zone is bounded by the discontinuities in the curves at 27° and 500°C. Adsorption in this zone involves from 1 to 3 molecular layers with a high probability of lateral bonding between adsorbed molecules. This adsorption is a type of chemisorption which probably involves hydrogen bonding between water molecules.

Zone 3 occurs between 500° and 1000°C and consists of less than one molecular layer of chemisorbed molecules. The discontinuity at 700°C is indicative of the removal of all but about 0.1 monolayer of adsorbed gases. The possibility also exists that this discontinuity is evidence of total desorption and any further weight loss is the result of oxygen being removed from the oxide lattice. However, we have no conclusive evidence for this reasoning.

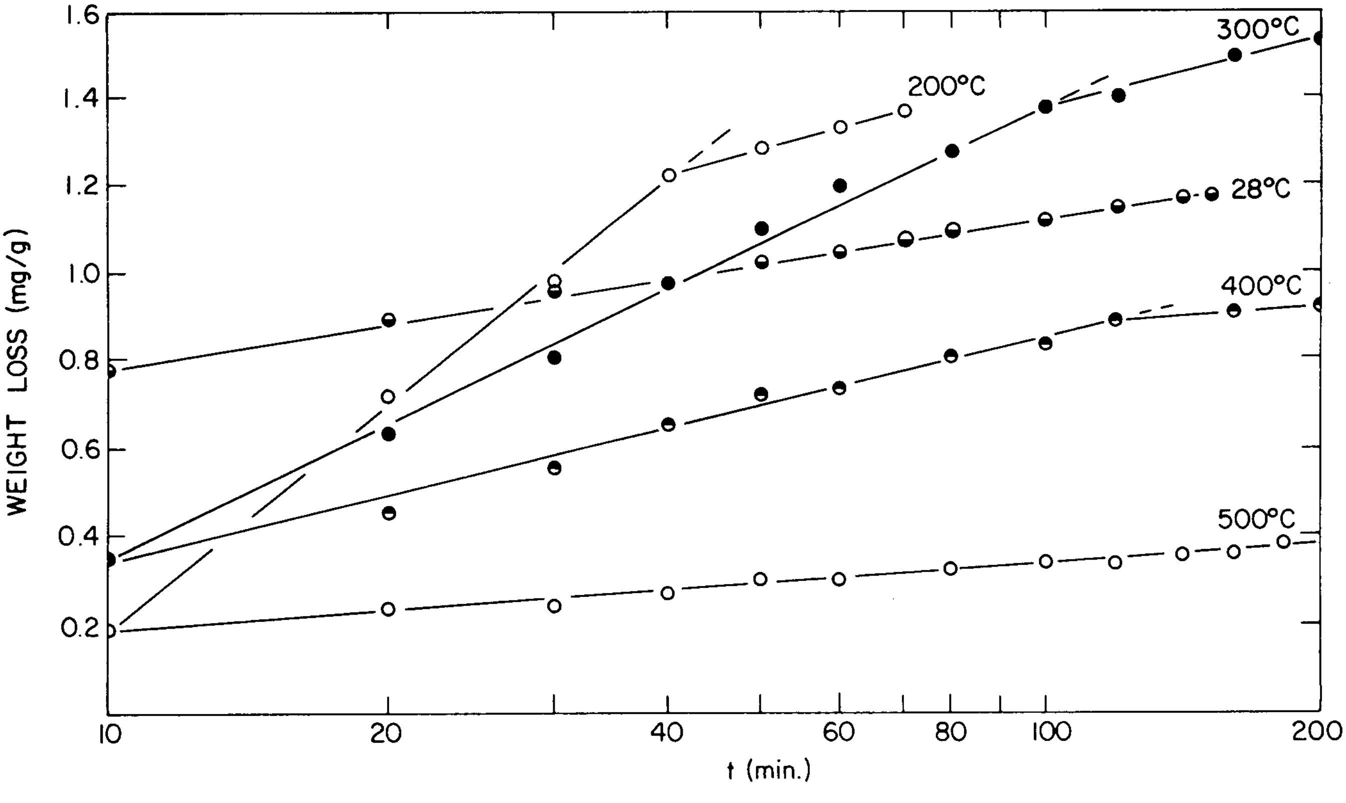
During the desorption process the samples were heated at a given temperature until no further weight loss was observed. The temperature was then increased by 100°C and the sample allowed to reach equilibrium. Because of the nature of this procedure, the amount of adsorbed gases initially present decreased as the temperature was increased. This is reflected in the desorption rates which decrease with temperature instead of increasing as would be expected. The one exception occurred at 28°C where the desorption of physically adsorbed molecules was involved.

The rate of desorption can best be described by a logarithmic rate law such as that provided by the Elovich Equation,

$$\frac{dq}{dt} = ae^{-\alpha t} ,$$

where q is the amount desorbed in time, t, and a and α are constants. This equation has been used extensively to explain the kinetics of chemisorption (5,6). Figure 4 shows an Elovich plot of the desorption data obtained in this experiment.

Figure 4. Elovich plot for the degassing of PuO_2.



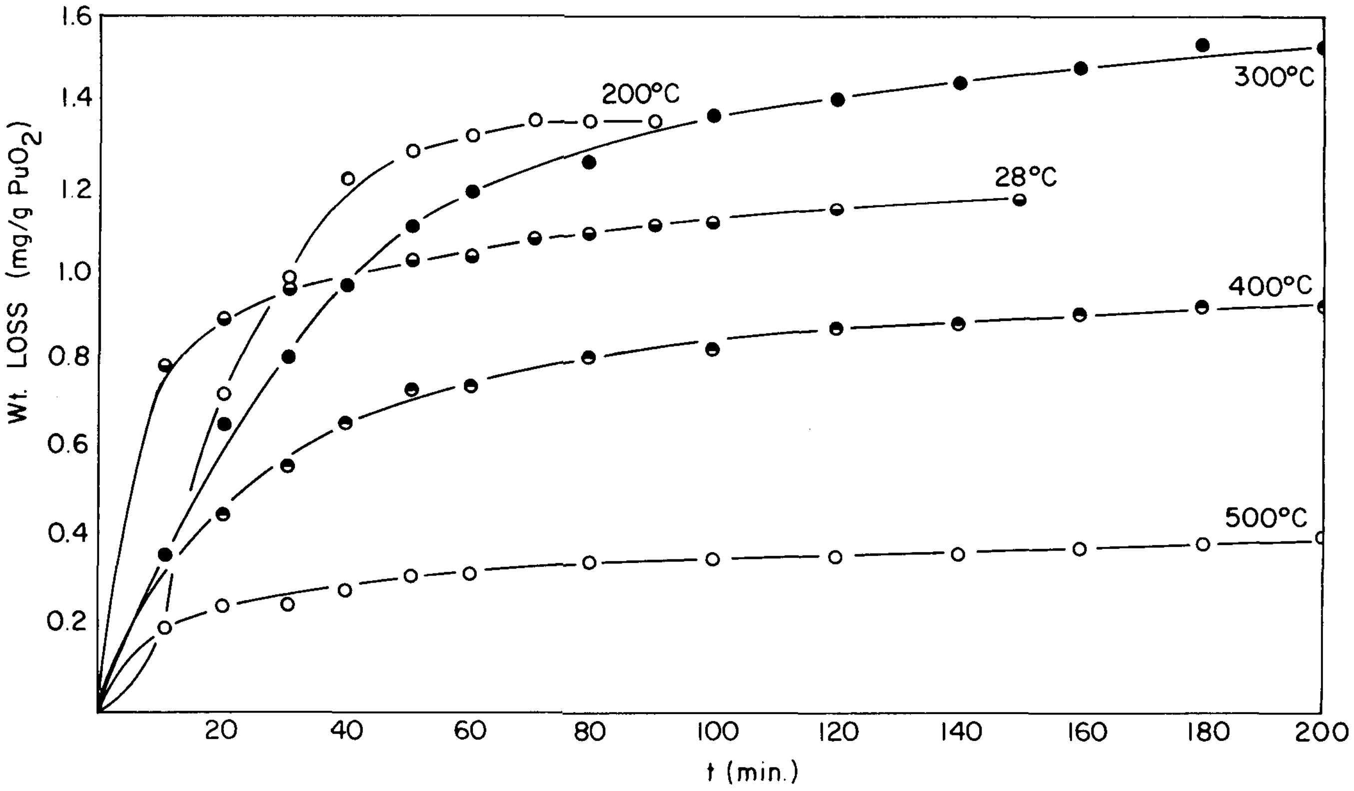
There is no ready explanation for the breaks in some of the curves. However, they might be caused by surface contamination or surface heterogeneity.

Figure 5 shows the degassing of PuO_2 as a function of time at several temperatures. It can be seen that nearly 100 percent of the removable gases are desorbed within the first 60 to 100 minutes. Again it should be remembered that the quantity of adsorbed gases varies for each temperature.

Product Analyses: The second phase of this study was to follow the desorption process by a mass spectrometric analysis of the products. By collecting and analyzing the desorbed gases we obtained the data shown in Figures 6, 7, and 8. Figure 6 shows that the number of moles of gas removed is affected by temperature. Degassing was assumed to be complete after heating the sample to 1000°C since the amount of gas evolved reached a constant at this temperature. It is evident that very high temperatures are necessary in order to obtain a "clean," dry plutonium dioxide surface. These data compare favorably with the results obtained thermogravimetrically, Figure 3, and indicate that heating the oxide under vacuum to 700°C is required to remove 95 to 100 percent of the removable gases.

An analysis of the gaseous products revealed that plutonium dioxide in addition to being hygroscopic readily adsorbs other gases from the atmosphere. The results of the gas analyses from a typical sample at various temperatures are shown in Figures 7 and 8. Figure 7 shows the products resulting from air adsorbed on the sample and Figure 8 the products emanating from adsorbed water. From Figure 7, the high concentration of carbon dioxide in the gas samples tends to indicate that plutonium dioxide preferentially adsorbs this gas from the atmosphere. It is proposed that the presence of nitrogen oxides is due to the radiolysis of air over an extended period of time. After formation the nitrogen oxides are adsorbed on the surface of the plutonium dioxide. Another possibility is that the radiolysis of air may occur in the adsorbed state. In either case results show the presence of adsorbed nitrogen and nitrogen oxides at temperatures up to 1000°C. The fact

Figure 5. Degassing of PuO_2 as a function of evacuation time.



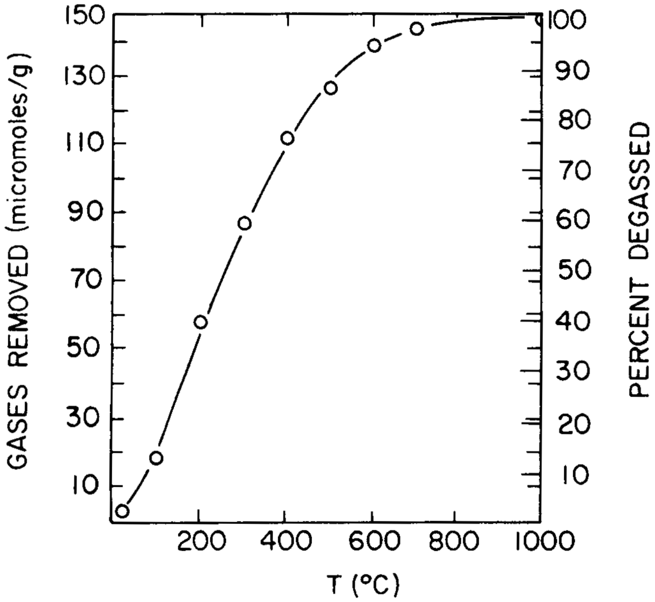


Figure 6. Effect of temperature on desorption.

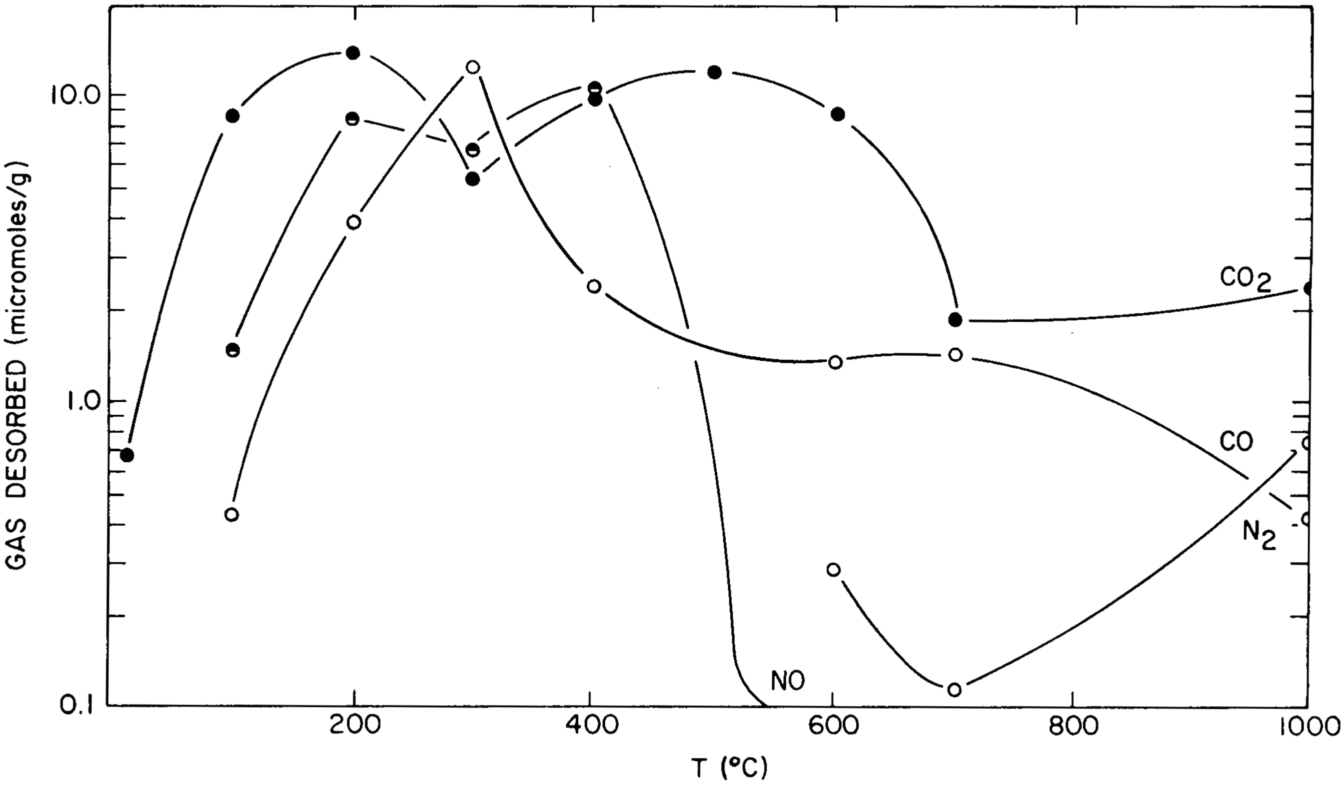
that nitrogen is still present at these temperatures suggests a leak in the system.

In Figure 8, the high hydrogen concentration cannot be explained in terms of adsorption. It is believed that the hydrogen is the result of a reaction between water and plutonium dioxide. Since the plutonium dioxide used was substoichiometric this reaction was simply an oxidation process to attain a stoichiometric condition. That is:

$$PuO_{2-x} + H_2O \rightarrow PuO_2 + H_2$$

This reaction accounts for the low concentration of oxygen as well as the high hydrogen concentration. This reaction is further supported by the fact that the oxide crystal lattice parameter decreased from 5.404 Å ±0.001 Å to 5.396 Å ±0.001 Å indicating the oxide has picked up oxygen. Part of the oxygen remaining in the gas phase may have resulted from the adsorption of oxygen from the atmosphere. The Toepler pump used for this portion

Figure 7. Air desorption products.



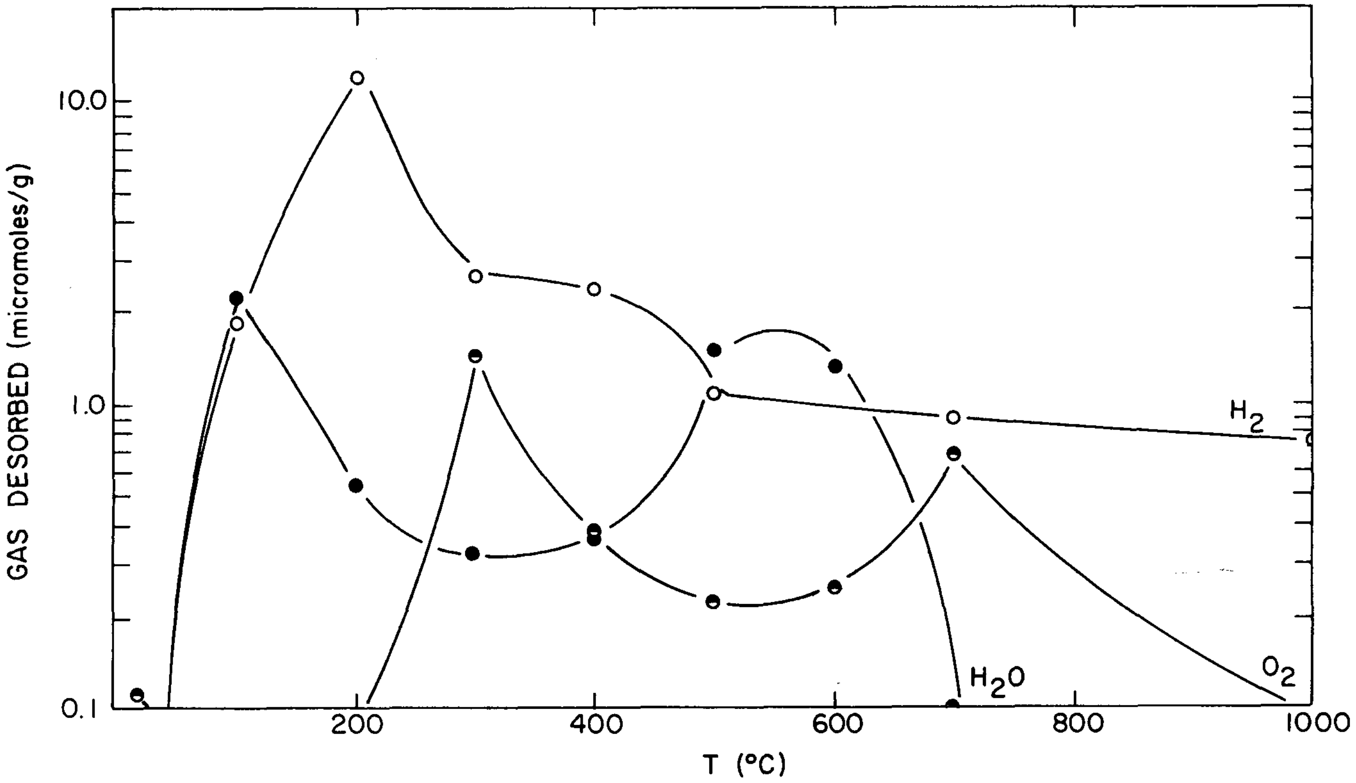


Figure 8. H_2O desorption products.

of the investigation was capable of maintaining a vacuum of only about 10^{-3} torr. This could have allowed enough water vapor to remain in the system at each temperature to support the oxidation of the oxide.

Dynamic Outgassing of Plutonium Dioxide (I): This portion of the investigation was carried out using the Bendix time-of-flight mass spectrometer. Results of this experiment for the plutonium dioxide (I) are shown in Figure 9. The three principal desorption products obtained in the range 50° to 550°C were water, carbon dioxide, and nitric oxide. The major desorption peak for water vapor occurred at 180°C. This peak is derived mainly from physically adsorbed water. A minor desorption peak was observed at 400°C and could have been caused by an adsorption involving chemical or hydrogen bonding.

The carbon dioxide desorption peak is quite broad ranging from about 250° to 400°C. The peak for nitric oxide, on the other hand, is quite sharp. Maximum desorption occurred at 250°C and decreased to zero at approximately 300°C. It is interesting to note that significant amounts of nitrogen and hydrogen were obtained during the Toepler pump degassing but only trace amounts were observed with the Bendix dynamic system. Two possible explanations for this observation exist. First, the nitrogen was due to a leak in the system. Second, the minimum pressure obtained with the Toepler system was 10^{-3} torr thus permitting enough water vapor to remain on the oxide to undergo the oxidation reaction previously discussed and resulting in the production of hydrogen. The Bendix dynamic system, on the other hand, maintained a pressure of about 10^{-8} torr and consequently removed the water vapor before it had a chance to react.

Outgassing of Plutonium Dioxide (II): This oxide was outgassed via the time-of-flight mass spectrometer in order to verify the results obtained with the plutonium dioxide (I). The results are shown in Figure 10 and indicate that after only a limited exposure to air plutonium dioxide will adsorbed significant quantities of gas. The primary desorption product was water vapor followed by carbon dioxide. A small amount of nitric oxide was found to be present and reached a desorption

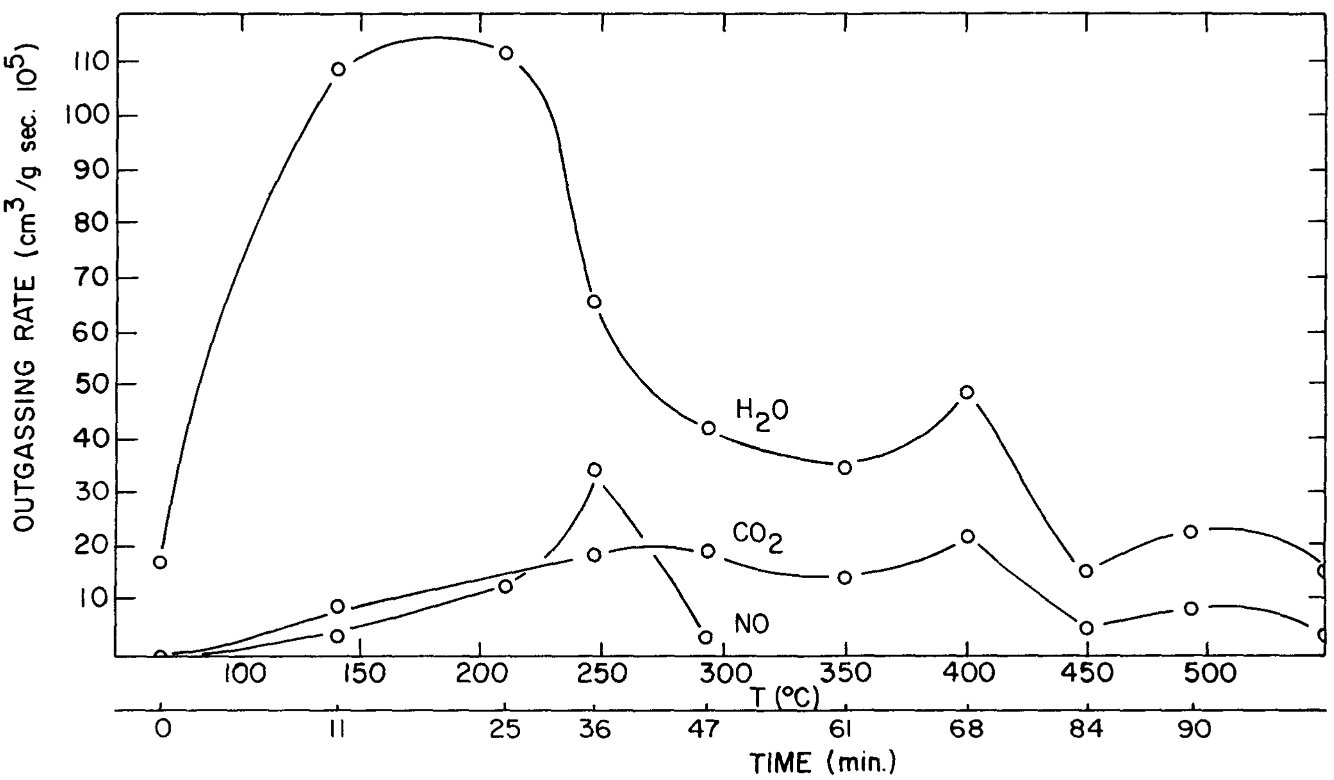


Figure 9. Dynamic outgassing of PuO_2.

peak at 250°C. The magnitude of this peak is highly dependent upon the period of time the oxide is exposed to air since the nitric oxide is formed by a radiolytic process. The results obtained with this oxide support the conclusion that the gases emitted from plutonium dioxide originate from adsorbed gases and not from contaminants.

SUMMARY AND CONCLUSIONS

From a study of the desorption characteristics of plutonium dioxide we have gained a broader perspective of its adsorption properties and the possible gas-solid interactions which can occur upon storage of the oxide. Plutonium dioxide has been found to exhibit strong gettering actions toward water vapor as well as carbon dioxide and nitric oxide. The water vapor and carbon dioxide were found to be adsorbed directly from the atmosphere which is in agreement with the results of other workers (7,8). Nitric oxide is believed to be adosrbed as a radiolysis product of air.

Degassing of the oxide was viewed from three different experimental approaches: (a) a thermogravimetric method; (b) a static method where the products from outgassing at ten temperature intervals were removed and analyzed; (c) a dynamic method utilizing the Bendix time-of-flight mass spectrometer. It is evident from the thermogravimetric results (Figure 3) that there are three distinct desorption zones: <25°C; 25° to about 500°C, and 500° to 800°C. Adsorption in these zones can be attributed to different types of adsorption and/or different adsorption sites. Subsequent studies (10) indicate that the third zone is caused by the desorption of CO beginning at about 500°C.

From the dynamic desorption experiments (Figure 9) the major products were found to be CO_2, NO, and H_2O. The ratios of their maximum outgassing rates were approximately 1:1.7:, 1:5.7, respectively. The desorption rate of water vapor decreases fairly evenly to about 450°C where it levels off corresponding to the upper boundary of the second adsorption zone. In the case of the dynamic system we have no data beyond 550°C.

The results obtained with the static system defy a strict interpretation in terms of the zone adsorption theory. However, two things may be said about

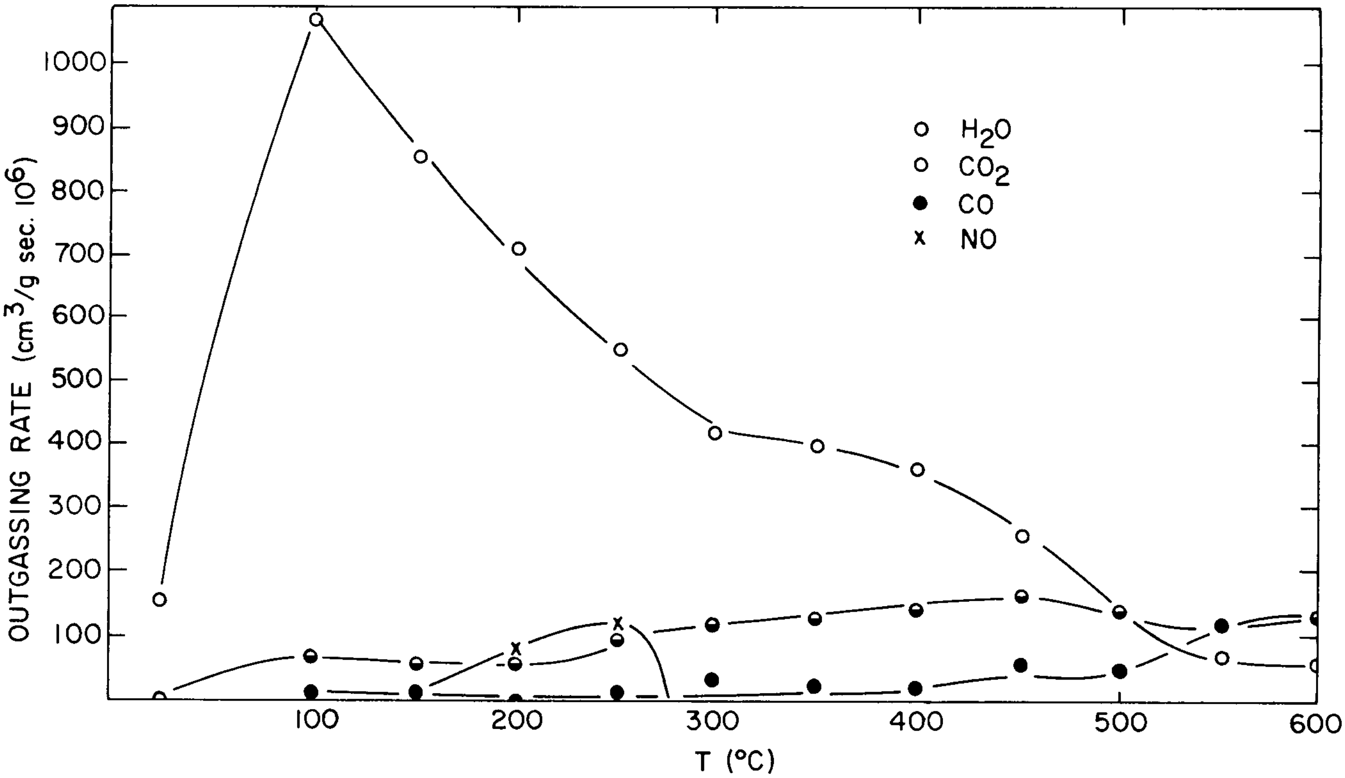


Figure 10. Outgassing of plutonium dioxide (II).

these results. First, the major portion of the desorption takes place between 25° and 300°C. Second, a secondary desorption peak occurs in the region 500° to 700°C. The one exception is carbon dioxide which has a broad degassing band between 200° and 500°C. Basically, these results support the theory that there are different zones of adsorption.

A qualitative comparison of the adsorption strengths of the major components is $CO_2 > NO > H_2O$. The relatively weak binding strength of the NO molecules is in conflict with other work (9) where NO was found to adsorb more strongly than either CO or CO_2. It was found that 95 percent of the gases adsorbed from the atmosphere could be removed by outgassing the plutonium dioxide at 700°C. The subsequent effect of this heat treatment on the surface properties of plutonium dioxide has not been fully investigated. Some studies, however, have shown the surface area to be decreased by about 36 percent (10).

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