
The Possible Mechanisms for the Formation of the Observed and Expected Compounds During a Hypothetical Core Disruptive Accident (HCDA)

Prepared by W. A. Zanotelli, G. D. Miller

Mound Facility

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U. S. Nuclear Regulatory
Commission

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The Possible Mechanisms for the Formation of the Observed and Expected Compounds During a Hypothetical Core Disruptive Accident (HCDA)

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ABSTRACT

This report presents results for an evaluation of the thermodynamics and kinetics of the possible chemical reactions which may occur in an HCDA bubble environment during its transport within, and following, its release from the reactor primary system.

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CONTENTS

	<u>Page</u>
ABSTRACT	iii
INTRODUCTION.	3
THE POSSIBLE MECHANISMS OPERATING IN THE FUEL BUBBLE	4
CONTAINMENT MECHANISMS FOLLOWING RELEASE OF FUEL BUBBLE FROM THE PRIMARY SYSTEM.	9
KINETICS OF SODIUM-MIXED URANIUM/PLUTONIUM OXIDE REACTIONS.	14
REFERENCES.	20

THE POSSIBLE MECHANISMS FOR THE FORMATION
OF THE OBSERVED AND EXPECTED COMPOUNDS DURING
A HYPOTHETICAL CORE DISRUPTIVE ACCIDENT (HCDA)

by

William A. Zanutelli, Jr. and Gary D. Miller

INTRODUCTION

In support of the Office of Nuclear Regulatory Research, Nuclear Regulatory Commission, Monsanto Research Corporation has initiated a program to produce and characterize the primary aerosols which could result from a hypothetical core disruptive accident (HCDA) in a Liquid Metal Fast Breeder Reactor (LMFBR). These tests are being conducted under conditions which would probably exist during a postulated excursion. The HCDA event is simulated by employing laser-promoted evaporation technique.

One of the primary objectives of this study is to investigate the chemical reactions and the compounds formed in the short-lived vapor state of the HCDA environment. While there is considerable experimental data available on the generation and behavior of single-component aerosols, and limited information on aerosols containing both uranium and sodium oxides, data is only recently being generated by MRC for multi-component systems containing aerosols generated from $(U,Pu)O_2$, sodium, and stainless steel produced under HCDA conditions.

The resulting data from the aerosol characterization from a simulated HCDA will be used to predict the possible mechanisms for the formation of the observed and expected (thermodynamically possible) compounds formed during a HCDA. This report will discuss the following topics:

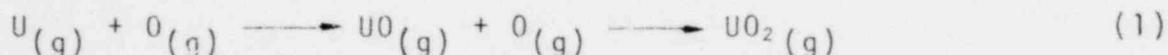
- The possible mechanisms operating in the fuel bubble;
- The possible mechanisms operating in the containment following release of the fuel bubble from the primary system;
- Kinetics of the various sodium-mixed oxide reactions.

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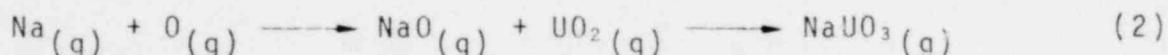
THE POSSIBLE MECHANISMS OPERATING

IN THE FUEL BUBBLE

During the most severe HCDA, caused for example by a transient overpower or loss of flow, substantial amounts of the reactor fuel, stainless steel cladding, and sodium coolant are vaporized. Thermodynamics predicts that all of the components will be atomized at temperatures in excess of 5000 K. The vapor species present will be uranium, plutonium, oxygen, sodium, iron, chromium, nickel and fission products. The vapor species thus formed begin to cool within the "bubble" from a temperature of 3100 K to approximately 1200 K at the liquid sodium walls of the "bubble". The approach to predicting the major products from Figure 1 is to consider the process beginning at a temperature in excess of 5000 K and to simulate a cool-down process by following the temperature axis to the left. Na_2UO_4 and $\text{Na}_2\text{U}_2\text{O}_7$ are anomalies in this analysis; thermodynamically they should be the first products formed. Evidently a kinetic barrier prevents this, since these products were not observed experimentally. Thus, from observation of Figure 1, thermodynamics predicts that UO_2 will form first:

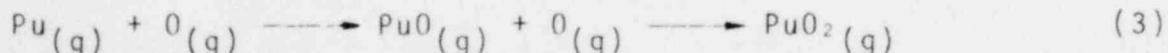


This formation should start at approximately 5800 K. Table 1 represents the principal compounds in the fuel bubble from 5800 K to 1200 K. The compounds are shown in the predicted order of formation based on the thermodynamic data from Figure 1. The next thermodynamically controlled reaction product is NaUO_3 . This compound would start to form at approximately 5300 K, by the following reaction:



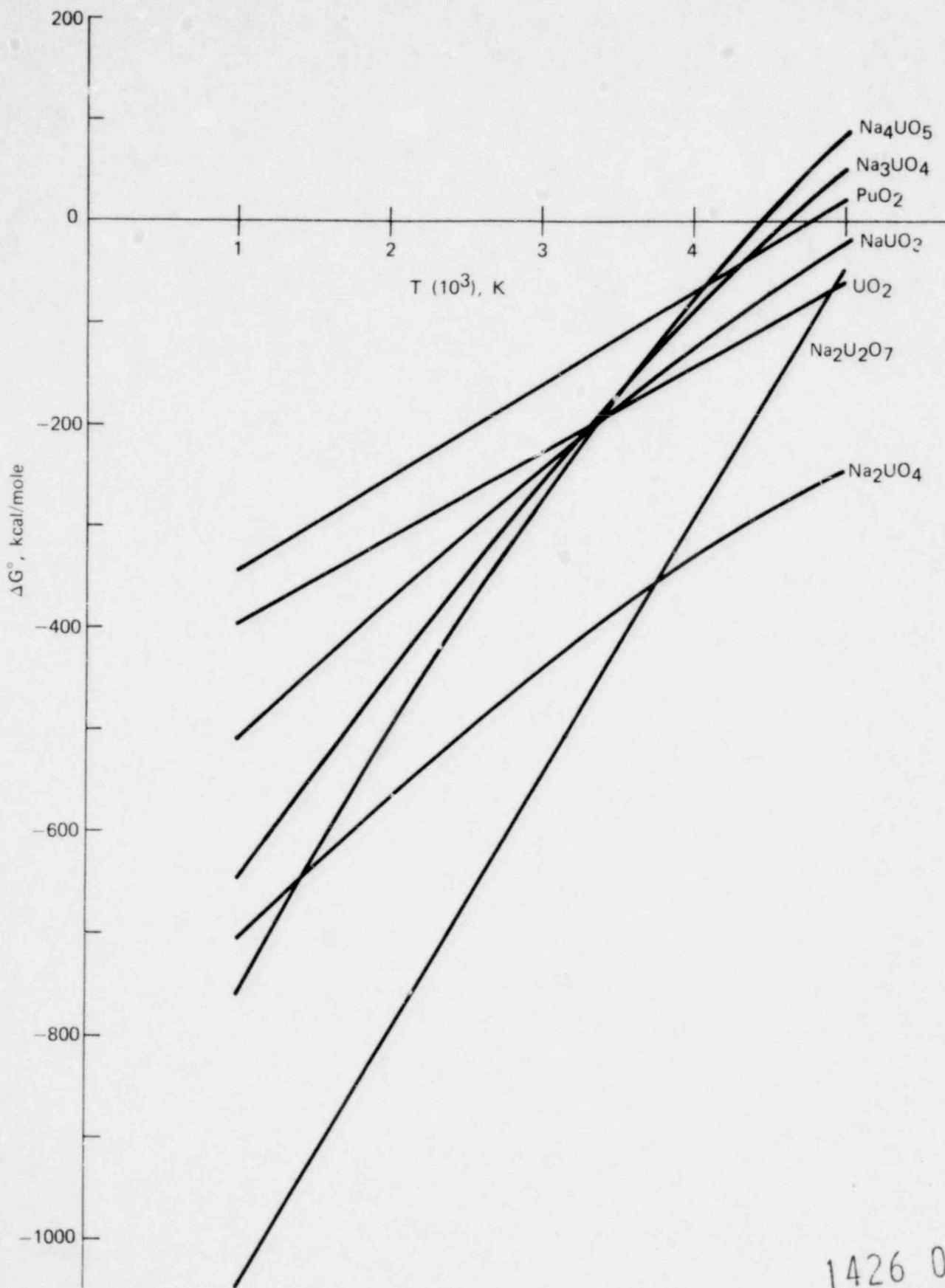
The sodium vapors are expected to react with oxygen to form NaO at temperatures greater than 2000 K, and then react with oxygen and UO_2 to form the sodium uranates. At temperatures below 2000 K, Na_2O is expected to form and then react with UO_2 to form sodium uranates, since sodium itself does not react with UO_2 (Pepper, 1964, Addison, 1965, Chasanov, 1969). The unreacted sodium vapors cool, move to the wall of the bubble, and condense into liquid sodium.

Thermodynamically the next compound to form would be PuO_2 . The following reaction would start at approximately 4800 K:



Experiments using ZrO_2 as a simulant for PuO_2 have indicated that PuO_2 would indeed be formed.

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FIGURE 1 - Behavior of free energy change as a function of temperature calculated for various potential products.

The compounds Na_3UO_4 and Na_4UO_5 would form after PuO_2 as shown from Figure 1. Na_3UO_4 would start to form at approximately 4600 K by the following reaction:

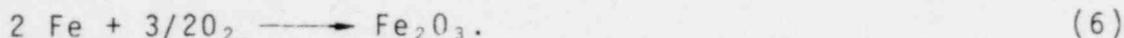


Na_4UO_5 would start to form at approximately 4400 K by the following reaction:

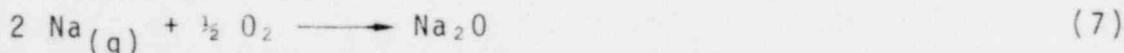


These compounds have been observed experimentally and along with NaUO_3 appear to be the principal sodium uranates formed.

The stainless steel products did not react with sodium or fuel. The stainless steel is composed of iron, chromium, and nickel in vapor form above 3300 K, liquid below 2800 K. Some constituents of stainless steel were observed, such as FeC and a combination product FeNi . The only compound formed was Fe_2O_3 . From Table 1 the formation of Fe_2O_3 starts at 3000 K by the following reaction:



At 2000 K the compound Na_2O is expected to form as follows:



The FeNi compound is expected to combine at 1500 K by the following mechanism:



Table 1 summarizes the principal mechanisms and compounds formed using the thermodynamic data from Figure 1. In summary, at 6000 K the atomized constituents of the fuel "bubble" are uranium, plutonium, oxygen, sodium, iron, chromium, and nickel. The compounds that are formed in the bubble are shown at various temperatures when they become thermodynamically possible. The principal compounds that would cool down and mix with the sodium liquid when the bubble collapses are: UO_2 , PuO_2 , NaUO_3 , Na_3UO_4 , Na_4UO_5 , Fe_2O_3 , Na_2O , FeNi , and FeC , along with some elemental iron, chromium, nickel and sodium(g).

Table 2 represents the possible mechanisms and the compounds that are expected (thermodynamically possible) for a HCDA. At high temperatures uranium dioxide can form superstoichiometric compounds such as $\text{UO}_{2.25}$ (U_4O_9) and $\text{UO}_{2.67}$ (U_3O_8). Plutonium dioxide is known to form substoichiometric oxide above 1700 K. The stoichiometric ratios possible range from $\text{PuO}_{1.5}$ to $\text{PuO}_{1.99}$. The counterpart

Table 1 - PRINCIPAL COMPOUNDS
AND MECHANISMS IN THE FUEL BUBBLE

Temperature, K	Substances Present
6000	- U, Pu, Na, O, Fe, Cr, Ni
5800	- $U(g) + O(g) \longrightarrow UO(g) + O(g) \longrightarrow UO_2(s)$
5300	- $Na(g) + O(g) \longrightarrow NaO(g)$ + $UO_2(s) \longrightarrow NaUO_3(s)$
4800	- $Pu(g) + O(g) \longrightarrow PuO(g)$ + $O(g) \longrightarrow PuO_2(s)$
4600	- $3Na(g) + 2O(g) + UO_2(s) \longrightarrow Na_3UO_4(s)$
4400	- $4Na(g) + 3O(g) + UO_2(s) \longrightarrow Na_4UO_5(s)$
3000	- $2Fe(l) + 3O(g) \longrightarrow Fe_2O_3(s)$
2000	- $2Na(g) + 1/2 O_2 \longrightarrow Na_2O$
1500	- $Fe(l) + Ni(l) \longrightarrow FeNi(s)$ - $Fe(l) + C(s) \longrightarrow FeC$
1300	- $UO_2, PuO_2, NaUO_3, Na_3UO_4, Na_4UO_5, Fe_2O_3,$ $FeNi, FeC, Cr, Ni, Na_2O$ (solids) and $Na(g)$
1200	- $Na(l)$

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Table 2 - POSSIBLE COMPOUNDS
AND MECHANISMS IN THE FUEL BUBBLE

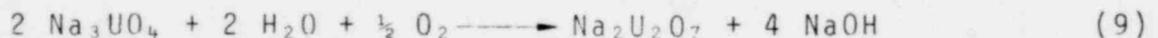
Temperature, K	Substances Present
6000	- U, Pu, O, Na, Fe, Cr, Ni (gases)
5800	- $UO_2 + 0.25 O_{(g)} \longrightarrow UO_{2.25}(s)$ $UO_2 + 0.67 O_{(g)} \longrightarrow UO_{2.67}(s)$
5300	- $Na_{(g)} + O_{(g)} \longrightarrow NaO_{(g)}$ $+ PuO_2(s) \longrightarrow NaPuO_3(s)$
4800	- $PuO_2 \longrightarrow PuO_{1.5}(s) + \frac{1}{2} O_{(g)}$
4600	- $3 Na_{(g)} + 2 O_{(g)} + PuO_2(s) \longrightarrow Na_3PuO_4(s)$
4600	- $3 Na_{(g)} + 2 O_{(g)} + (U,Pu)O_2(s) \longrightarrow$ $Na_3(U,Pu)O_4(s)$
4400	- $4 Na_{(g)} + 3 O_{(g)} + PuO_2(s) \longrightarrow$ $Na_4PuO_5(s)$
1300	- $UO_{2.25}, UO_{2.67}, PuO_{1.5}, NaPuO_3, Na_3PuO_4,$ $Na_3(U,Pu)O_4, Na_4PuO_5$ (solids)
1200	- $Na_{(l)}$

plutonium compounds NaPuO_3 , Na_3Pu_4 , and Na_4PuO_5 are possibly formed. The mixed oxide compound $\text{Na}_3(\text{U,Pu})\text{O}_4$ has been observed in some experiments and could possibly form (Adamson, 1973).

In summary, Table 1 represents the observed and principal compounds that form based on the experimental work done at Mound. Table 2 represents the possible mechanisms and compounds that could form during a HCDA, since their thermodynamic properties should closely approximate those of the principal compounds in most cases.

CONTAINMENT MECHANISMS FOLLOWING RELEASE OF FUEL BUBBLE FROM THE PRIMARY SYSTEM

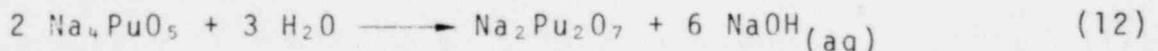
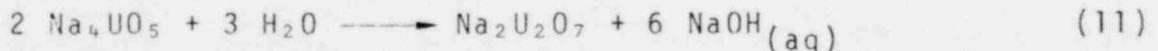
When the fuel bubble breaks the primary system containment it will be exposed to an air atmosphere composed of excess O_2 , CO_2 and H_2O vapors. Table 3 is a summary of the principal compounds formed and the mechanisms expected. Table 1 shows that the sodium uranates with uranium in the oxidation state of +5, with the exception of NaUO_3 , are very hygroscopic and sensitive to oxidation, yielding ultimately $\text{Na}_2\text{U}_2\text{O}_7$ (Cordfunke, 1971). Thus the following sodium uranates and expected plutonates, Na_3UO_4 , Na_3PuO_4 , $\text{Na}_3(\text{U,Pu})\text{O}_4$, when exposed to air, would follow the general reaction:



The NaUO_3 and the expected NaPuO_3 would be stable at approximately 650 K in air, but would decompose to $\text{Na}_2\text{U}_2\text{O}_7$ if exposed to air at greater than 650 K according to the following reaction (Cordfunke, 1971):



From Table 1, the Na_4UO_5 and the expected Na_4PuO_5 would remain stable at >1200 K in air, but on cooling below this temperature these compounds in the presence of moist air react with H_2O to form $\text{Na}_2\text{U}_2\text{O}_7$ by the following reaction (Cordfunke, 1971):



When the components of stainless steel from the bubble are exposed to air, the compounds Fe_2O_3 , FeNi , Fe , Ni and FeC are not expected to be affected by air but to remain in this form (Johnson, 1977). The chromium is expected to combine with oxygen to form Cr_3O_4 by the following reaction (Johnson, 1977).



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Table 3 - OBSERVED AND EXPECTED COMPOUNDS FORMED
WHEN THE FUFL BUBBLE ESCAPES TO THE AIR ATMOSPHERE

I. Reactions of Sodium Uranates and Plutonates Present in Bubble

1. Excess O₂, H₂O and CO₂ in the Containmentment
2. $2 \text{Na}_3\text{UO}_4 + 2 \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \longrightarrow \text{Na}_2\text{U}_2\text{O}_7 + 4 \text{NaOH}$
3. $2 \text{Na}_3\text{PuO}_4 + 2 \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \longrightarrow \text{Na}_2\text{Pu}_2\text{O}_7 + 4 \text{NaOH}$
4. $2 \text{Na}_3(\text{U,Pu})\text{O}_4 + 2 \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \longrightarrow \text{Na}_2(\text{U,Pu})_2\text{O}_7 + 4 \text{NaOH}$
5. $2 \text{NaUO}_3 + \frac{1}{2} \text{O}_2 \longrightarrow \text{Na}_2\text{U}_2\text{O}_7$
6. $2 \text{NaPuO}_3 + \frac{1}{2} \text{O}_2 \longrightarrow \text{Na}_2\text{Pu}_2\text{O}_7$
7. $2 \text{Na}_4\text{UO}_5 + 3 \text{H}_2\text{O} \longrightarrow \text{Na}_2\text{U}_2\text{O}_7 + 6\text{NaOH}_{(\text{aq})}$
8. $2 \text{Na}_4\text{PuO}_5 + 3 \text{H}_2\text{O} \longrightarrow \text{Na}_2\text{Pu}_2\text{O}_7 + 6 \text{NaOH}_{(\text{aq})}$

II. Reactions of Stainless Steel Components Present in Bubble

1. Excess O₂, H₂O and CO₂ in the Containmentment
2. $3 \text{Cr} + 2 \text{O}_2 \longrightarrow \text{Cr}_3\text{O}_4$

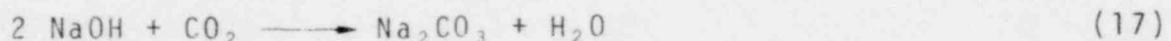
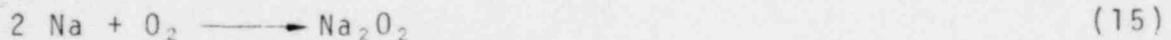
III. Reactions of Sodium Components Present in the Bubble

1. Excess O₂, H₂O and CO₂ in the Containmentment
2. $2 \text{Na} + \frac{1}{2} \text{O}_2 \longrightarrow \text{Na}_2\text{O}$
3. $2 \text{Na} + \text{O}_2 \longrightarrow \text{Na}_2\text{O}_2$
4. $\text{Na}_2\text{O} + \text{H}_2\text{O} \longrightarrow 2 \text{NaOH}$
5. $2 \text{NaOH} + \text{CO}_2 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$
6. $3 \text{NaOH} + 2 \text{CO}_2 \longrightarrow \text{Na}_2\text{CO}_3 + \text{NaHCO}_3 + \text{H}_2\text{O}$

IV. Reactions of Uranium and Plutonium Present in the Bubble

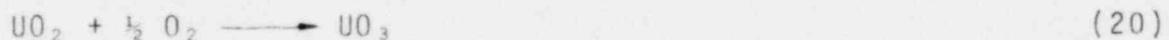
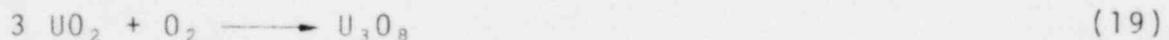
1. Excess O₂, H₂O and CO₂ in the Containmentment
2. $3 \text{UO}_2 + \text{O}_2 \longrightarrow \text{U}_3\text{O}_8$
3. $\text{UO}_2 + \frac{1}{2} \text{O}_2 \longrightarrow \text{UO}_3$
4. $\text{PuO}_2 - \text{X} + \text{XO} \longrightarrow \text{PuO}_2$

From the experiments conducted in air previously and from a knowledge of sodium chemistry, a sodium fire would be initiated on contact with moisture in the air. According to the two previous references, the following reactions are expected to occur:



These sodium species are expected to be available for further reaction.

The UO_2 should react with O_2 in the air and produce the following compounds:



The PuO_2 should be relatively stable in an air atmosphere and remain as PuO_2 . Any substoichiometric PuO_2 that may be formed would be oxidized to PuO_2 (Keller, 1971) as follows:



With the exception of substoichiometric PuO_2 and the sodium plutonates, the compounds of Table 3 are the principal compounds formed from the "bubble" when it escapes and collapses in the primary containment. The sodium plutonates were included because their thermodynamic properties are similar to the sodium uranates and because when PuO_2 is added to the system, there is a very good probability that these compounds will be observed experimentally.

Table 4 represents the mechanisms at work and the compounds that could possibly form upon release of the bubble to the containment. From previous experiments in air atmosphere, the reaction of sodium oxide and sodium carbonate with uranium compounds have produced the following compounds: β - Na_2UO_4 , $\text{Na}_2\text{U}_2\text{O}_7$, $\text{Na}_2\text{U}_2\text{O}_5$ ($\text{Na}_2\text{O} \cdot 2 \text{ UO}_2$), $\text{Na}_2\text{U}_{2.5}\text{O}_{8.5}$ ($\text{Na}_2\text{O} \cdot 2.5 \text{ UO}_3$), NaUO_3 , and $\text{Na}_4\text{UO}_2(\text{CO}_3)_3$.

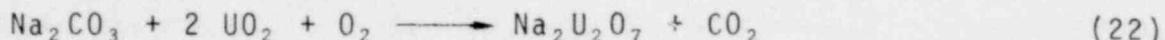
Sodium itself does not react with UO_2 (Pepper, 1974, Chasanov, 1971). The NaUO_3 has been previously discussed as being oxidized to $\text{Na}_2\text{U}_2\text{O}_7$ in air. $\text{Na}_2\text{U}_2\text{O}_7$ has been discussed as being formed from the

Table 4 - POSSIBLE COMPOUNDS FORMED WHEN THE FUEL BUBBLE ESCAPES TO THE AIR ATMOSPHERE

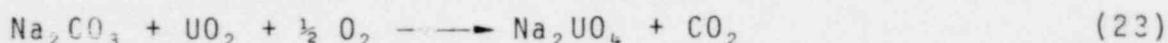
Reactions that form Sodium Uranates and Plutonates in the Containment.

1. Excess O_2 , H_2O and CO_2 in the Containment
2. $Na_2CO_3 + 2 UO_2 + O_2 \longrightarrow Na_2U_2O_7 + CO_2$
3. $Na_2CO_3 + 2 PuO_2 + O_2 \longrightarrow Na_2Pu_2O_7 + CO_2$
4. $Na_2CO_3 + UO_2 + \frac{1}{2} O_2 \longrightarrow Na_2UO_4 + CO_2$
5. $Na_2CO_3 + PuO_2 + \frac{1}{2} O_2 \longrightarrow Na_2PuO_4 + CO_2$
6. $Na_2O + 2 UO_2 \longrightarrow Na_2U_2O_5 (Na_2O \cdot 2 UO_2)$
7. $Na_2O + 2 PuO_2 \longrightarrow Na_2Pu_2O_5 (Na_2O \cdot 2 PuO_2)$
8. $Na_2O + 2.5 UO_3 \longrightarrow Na_2U_{2.5}O_{8.5} (Na_2O \cdot 2.5 UO_3)$
9. $Na_2O + 2.5 PuO_3 \longrightarrow Na_2Pu_{2.5}O_{8.5} (Na_2O \cdot 2.5 PuO_3)$
10. $2 Na_2O + UO_3 \longrightarrow Na_4UO_5$
11. $3 Na_2O + PuO_2 \longrightarrow Na_4PuO_5 + 2 Na$
12. $Na_2UO_4 + UO_2 \longrightarrow 2 NaUO_3 + \frac{1}{2} O_2 \longrightarrow Na_2U_2O_7$
13. $Na_2PuO_4 + UO_2 \longrightarrow 2 NaPuO_3 + \frac{1}{2} O_2 \longrightarrow Na_2U_2O_7$
14. $3 Na_2CO_3 + UO_2 + H_2O + \frac{1}{2} O_2 \longrightarrow Na_4 (UO_2) (CO_3)_3 + 2 NaOH$
15. $3 Na_2CO_3 + PuO_2 + H_2O + \frac{1}{2} O_2 \longrightarrow Na_4 (PuO_2) (CO_3)_3 + 2 NaOH$

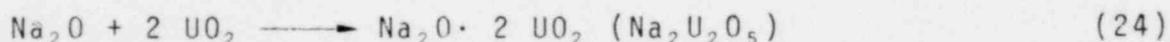
oxidation of NaUO_3 , but a previous study (Johnson, 1977) showed that the following reaction produced $\text{Na}_2\text{U}_2\text{O}_7$ in the air:



In the same study the $\beta\text{-Na}_2\text{UO}_4$ compound was formed in air by reacting Na_2CO_3 with either UO_2 or $\text{Na}_2\text{U}_2\text{O}_7$. Since heating $\beta\text{-Na}_2\text{UO}_4$ at 1250 K causes a partial decomposition to $\text{Na}_2\text{U}_2\text{O}_7$ in an air atmosphere, and since the temperatures are predicted to be <1250 K for the cool-down in air, the production of $\beta\text{-Na}_2\text{UO}_4$ is attributed (Johnson, 1977) to the following reaction:

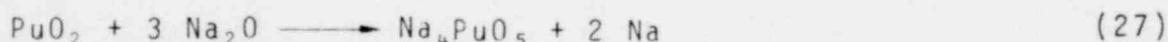
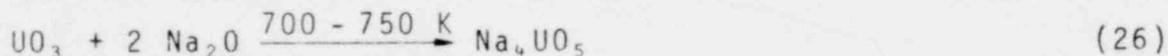


The compounds $\text{Na}_2\text{U}_2\text{O}_5$ ($\text{Na}_2\text{O} \cdot 2 \text{UO}_2$) and $\text{Na}_2\text{U}_2.5\text{O}_{8.5}$ ($\text{Na}_2\text{O} \cdot 2.5\text{UO}_3$) are expected to form in air by combining the following compounds:

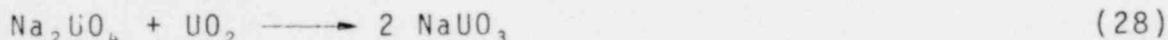


The plutonium analog of the compound from reaction (24) could be expected to form likewise, since the thermodynamic properties of the two substances are similar; however, similar studies in an air atmosphere using plutonium have not been conducted.

The NaUO_3 and the sodium VI uranates can also be formed between 1000 K and 1300 K by reacting Na_2CO_3 with either UO_3 or U_3O_8 , since the compounds are available for reaction (Adamson, 1973). The reaction mechanisms cited seem to follow the most direct path to the final product. There are also other side reactions that can be expected to occur. The products Na_4UO_5 and Na_4PuO_5 , which have been shown to hydrolyze to $\text{Na}_2\text{U}_2\text{O}_7$ and NaOH according to reaction (11) can also be formed by the following reactions (Cordfunke, 1971):



Another reaction route for NaUO_3 to be formed is the following:



The compound $\text{Na}_4(\text{UO}_2)(\text{CO}_3)_3$ has been observed in reactions of Na_2CO_3 and Na_2O with UO_2 in an air atmosphere (Cordfunke, 1971). This compound has been observed when sodium-mixed UO_2/PuO_2 aerosols were exposed to water vapor (Allen, 1978). The following reaction mechanism is predicted for this compound (Johnson, 1977):



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The plutonium analog could possibly be expected to form in a similar manner, but studies with PuO_2 have not been conducted.

Other compounds that have been observed in an air atmosphere from reaction of Na_2CO_3 and UO_2 are the hyperstoichiometric compounds $\text{UO}_{2.92}$ and U_4O_9 . These are possibly formed along with their UO_2 , UO_3 and U_3O_8 counterparts in an enriched air atmosphere.

Tables 3 and 4 are summary tables of the reactions and compounds observed and expected for the escape of the fuel bubble from the primary containment into the air atmosphere.

KINETICS OF SODIUM-MIXED

URANIUM/PLUTONIUM OXIDE REACTIONS

The sodium-mixed uranium/plutonium oxide reaction is represented by



with $M = \text{U} + \text{Pu}$ in the ratio $\text{Pu}/(\text{U}+\text{Pu}) = 0.20$. In the best experimental work presently available on the kinetics of this reaction, the volume change of the mixed oxide pellet was followed as a function of time at three temperatures, 700, 800, and 900°C (Martin, 1972). Because the volume change is related to the reaction extent, Martin's data contained sufficient information to allow a temperature-dependent rate law for Reaction 30 to be extracted. This section of this report discusses how the rate law was extracted, its implications, its limitations, and methods for determining a more reliable rate law.

The theoretical maximum increase in the volume of the mixed oxide pellet after completion of reaction is 4.44%. The longest time data (Martin, 1972) confirm this theoretical value. Some pellets were observed to expand more than 4.44%, but these observations could be explained by cracks and fissures found in the pellets. The reaction extent, α , may then be taken to be the observed volume expansion divided by its theoretical maximum value.

The next step in the analysis was to find a rate law based on a physical reaction model which fits the data. Three integral rate laws were examined. Using a first order rate law,

$$\ln(1-\alpha) = -kt, \quad (31)$$

where k is the rate constant and t is the time, the fit of the data to a linear function of t was poor. In addition, there was no physical basis for using a first order rate equation for the reaction of interest here. Second, using the equation:

$$-\ln(1-\alpha) = kt^3 \quad (32)$$

which corresponds physically to the growth of spherical nuclei,

the fit of the data was very poor. This law would apply if the reaction involved a gas-solid interaction at the pellet surface. Finally, the expression,

$$1 - (1-\alpha)^{1/3} = kt, \quad (33)$$

which corresponds physically to movement of a spherical phase boundary was tried (Sestak, 1971). This rate law seems most plausible for a liquid-solid reaction at the pellet surface. When the data at 700°C were plotted (see Figure 2) using Equation 33, a straight line was obtained except in the region representing the last stages of reaction where deviation might be expected because of side reactions and possible sublimation. At 800 and 900°C, the fit (see Figure 2) is hard to evaluate because most of the data points were taken after the major part of the reaction had already occurred. The experiments at 800 and 900°C should be repeated with measurements made at much shorter intervals so that the early stages of reaction can be observed.

The rate constants were determined at 700, 800 and 900°C from the slopes of the best fit lines. The values are poor at 800 and 900°C for the reasons discussed above. Table 5 shows the rate constants extracted at each temperature. Using Arrhenius analysis, the data in Table 5 were fitted to a straight line according to the linear least squares method, which gave a coefficient of determination, r^2 (measure of goodness of fit), of 0.899. From the coefficients a temperature-dependent rate constant,

$$k = 10^{16.88} \exp(-40,272/T) \quad (34)$$

could be written, the kinetic parameters of which are:

$$E_a = 80.0 \text{ kcal-mol}^{-1} \text{ and } A = 10^{16.88} \text{ day}^{-1} \text{ or}$$

$$A = 8.8 \times 10^{-11} \text{ sec}^{-1}$$

From equations 33 and 34, the time for 90% completion of reaction, $t_{0.9}$ was easily obtained as:

$$t_{0.9} = \frac{0.54}{10^{16.88} \exp(-40,272/T)} \quad (35)$$

where $t_{0.9}$ is in days. From Equation 35, times were calculated for several temperatures of interest: 5000 K, 3100 K (inside bubble temperature), and 1200 K (outside bubble temperature). These times are shown in Table 6.

Inspection of Table 6 shows that at the temperature of the inner part of the bubble, the reaction can proceed essentially to completion in less than a microsecond. The formation and subsequent observation of Na_2MO_4 is, therefore, explicable from the kinetic data.

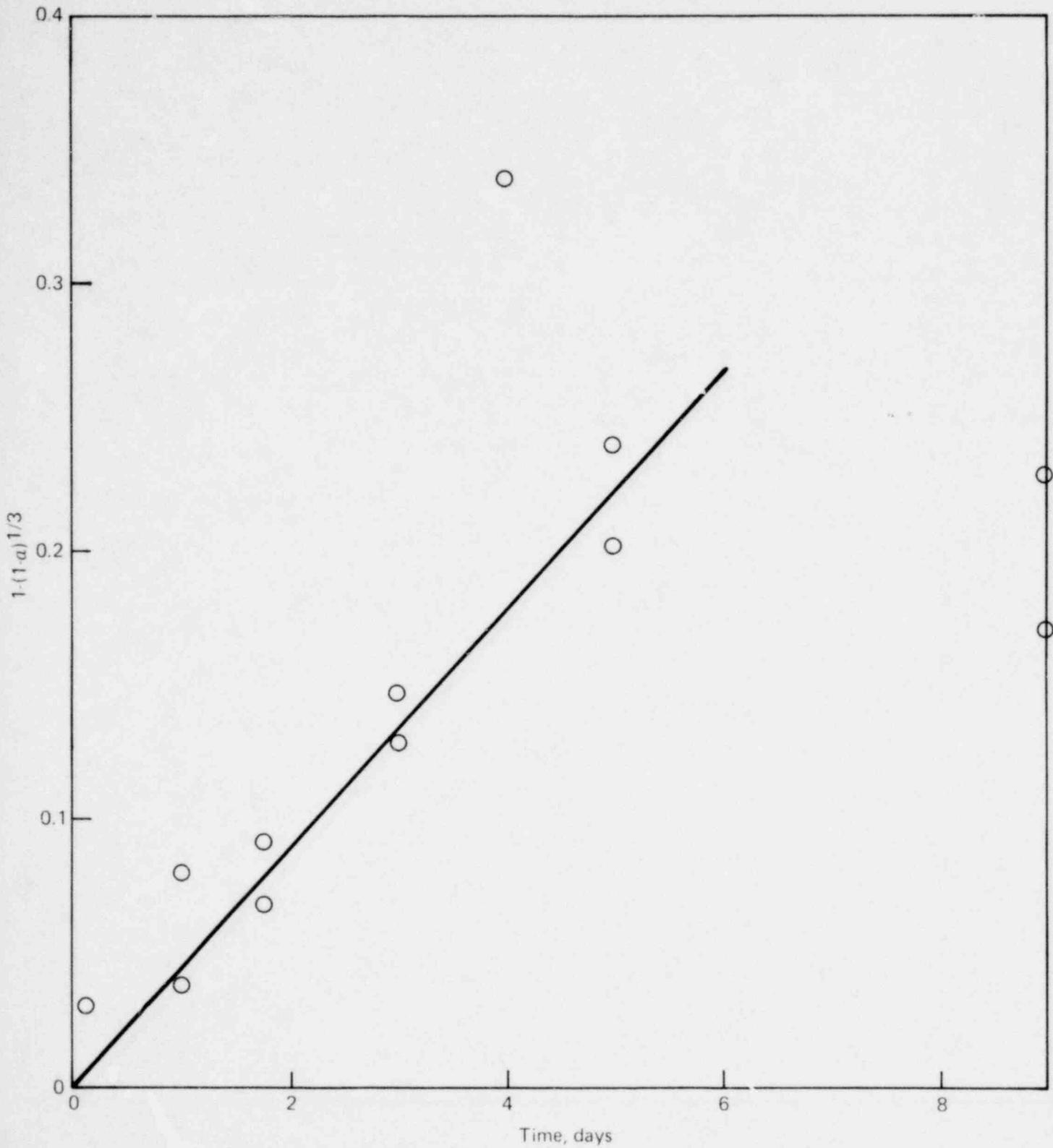


FIGURE 2 - Three-dimensional phase boundary movement at 700°C yielded a straight line except in the last stages of reaction.

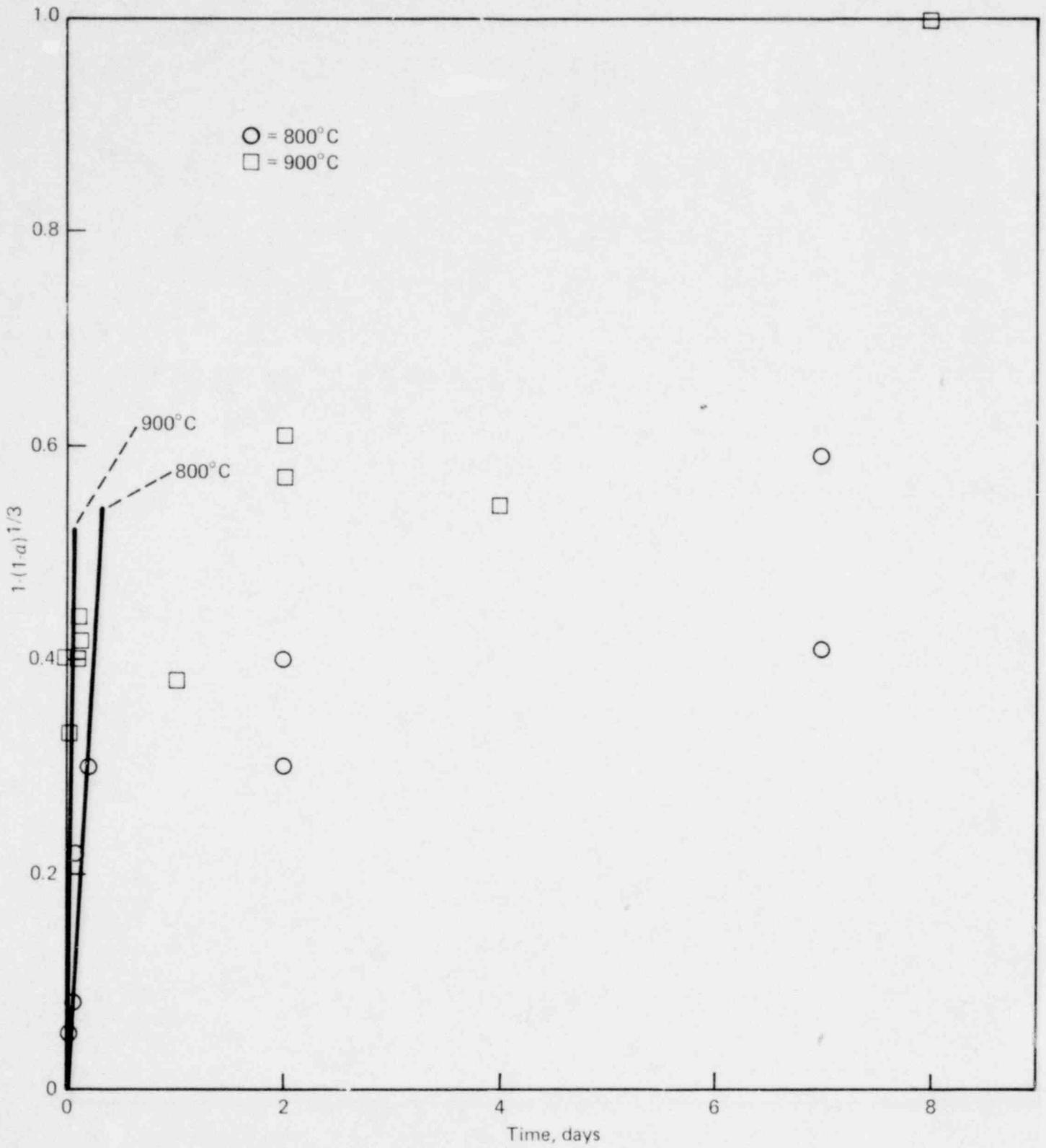


FIGURE 3 - Three-dimensional phase boundary movement at 800 and 900°C was difficult to evaluate with the present data.

Table 5 - THE RATE CONSTANT, k , FOR SODIUM-MIXED OXIDE REACTIONS WAS DETERMINED FROM THE DATA PLOTTED IN FIGURES 2 AND 3

Temperature (°C)	Temperature (K)	$1/T(K^{-1})$	$k(\text{day}^{-1})$	$\ln k$
700	973	10.277×10^{-4}	4.40×10^{-2}	-3.12
800	1073	9.320×10^{-4}	15.0	2.71
900	1173	8.525×10^{-4}	45.0	3.81

Table 6 - THE TIME REQUIRED FOR COMPLETION OF SODIUM-MIXED OXIDE REACTIONS WAS DETERMINED FROM EQUATION 35

Temperature (K)	Time (days)	Time (sec)
1200	2.67×10^{-3}	230
3100	3.12×10^{-12}	2.7×10^{-7}
5000	2.24×10^{-14}	1.9×10^{-9}

The rate constant in equation 34 may be in considerable error for several reasons. First, as mentioned previously, the data at 800 and 900°C were such that accurate rates could not be extracted. Second, and perhaps more serious in nature, is the fact that we have attempted to extrapolate kinetic data over a temperature range of about 2000 K, that is, from ~ 1000 K to ~ 3000 K. Such extrapolation is questionable even over a range of a few hundred degrees, and we are not aware of any chemical rate laws which take the same form over a range of more than a hundred or so degrees. When temperatures of ~ 3000 K are approached, we are dealing with the chemistry of excited states, which almost always display radically different kinetics from ground states of the same species. We must therefore conclude that the kinetic predictions made here are the best possible given the present data; however, application of these predictions to temperatures higher than ~ 1500 K is very questionable.

The need for kinetic data at temperatures approximating the bubble conditions is clear from the foregoing discussion. Experimental kinetics at these high temperatures with this system will probably

have to be studied by atom beam techniques. A variable temperature sodium beam incident on the mixed oxide pellet under high vacuum conditions with subsequent surface analysis of the pellet after different beam exposure times would yield empirical rate laws. Mass spectrometric detection of reflected reactants, products and intermediates would provide additional information which would possibly lead to the elucidation of the reaction mechanism.

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