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REACTIONS OF THE SESQUIOXIDES
OF Pm, Nd, AND Sm WITH WATER

H. T. Fullam and F. P. Roberts

June 1970

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OF Pm, Nd, AND Sm WITH WATER

By

H. T. Fullam and F. P. Roberts

Chemical Technology Department
Chemistry and Metallurgy Division

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ABSTRACT

The reactions of Pm_2O_3 , Nd_2O_3 , and Sm_2O_3 with water were investigated. Thermograms were obtained for the reaction products, as well as for the hydroxides of promethium, neodymium, and samarium prepared by precipitation techniques. The solubility and dissolution rates of Pm_2O_3 in distilled water and synthetic seawater were determined.

TABLE OF CONTENTS

LIST OF FIGURES		vi
1.0 INTRODUCTION		1
2.0 SUMMARY		1
3.0 EXPERIMENTAL AND RESULTS		3
3.1 Preparation of Rare Earth Sesquioxides		3
3.2 Solubility of Pm_2O_3 in Water		4
3.3 Dissolution Rates of Promethium Oxide		7
3.4 Hydration of Rare Earth Oxides		10
3.5 Retardation of Oxide Hydration		28
4.0 CONCLUSIONS		30
5.0 REFERENCES		34
DISTRIBUTION		Distr-1

LIST OF FIGURES

1.	Solubility of Rare Earth Hydroxides	6
2.	Disintegration of Sintered Nd_2O_3 Pellets upon Exposure to Atmospheric Moisture (Pellets Prepared by Hot Pressing Nd_2O_3 at 1700 °C to 95% of theoretical Density).	11
	Capsules Containing Rare Earth Oxides After Exposure to Water	13
	A Sm_2O_3 Filled Tungsten Capsule with a Defective Weld After Exposure to Atmospheric Moisture for Several Months	14
5.	Effect of Water Temperature on Rate of Disintegration of Sm_2O_3 Pellets	16
6.	Reaction Rates of Rare Earth Oxides with Atmospheric Moisture	17
	Effect of Crystal Form on Reaction of Nd_2O_3 with Atmospheric Moisture	19
8.	Effect of Calcining Temperature on Rate of Reaction of Nd_2O_3 with Atmospheric Moisture	20
9.	Reaction of Pm_2O_3 with Water at 25 °C	22
10.	Thermograms for Nd_2O_3 and Sm_2O_3 Equilibrated with Atmospheric Moisture	23
11.	Thermograms for Oxides of Nd, Pm and Sm Equilibrated with Water	24
12.	Thermograms for Nd, Pm and Sm Precipitated from Solution with NaOH	26
13.	Comparison of Thermograms for $\text{Nd}_2\text{O}_3\text{-H}_2\text{O}$ Reaction Products	27
14.	Thermograms for Nd_2O_3 Exposed to Atmospheric Moisture for Varying Periods of Time	29
15.	Hydration of $\text{Nd}_2\text{O}_3\text{-WO}_3$ Pellets Sintered at 1400 °C and Exposed to Atmospheric Moisture	31
16.	Hydration of $\text{Nd}_2\text{O}_3\text{-P}_2\text{O}_5$ Pellets Sintered at 800 °C and Exposed to Atmospheric Moisture	32
17.	Hydration of $\text{Nd}_2\text{O}_3\text{-TiO}_2$ Pellets Sintered at 1300 °C and Exposed to Atmospheric Moisture	33

REACTIONS OF THE SESQUIOXIDES
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1.0 INTRODUCTION

A program has been underway at the Pacific Northwest Laboratory (PNL) for a number of years to develop the technology of promethium. One major phase of the program has involved the preparation of high purity promethium sesquioxide (Pm_2O_3), determination of its chemical and physical properties, and development of possible applications for the oxide.

One potential use of Pm_2O_3 is as fuel in radioisotope heat sources. If Pm_2O_3 is used in this application, safety considerations dictate the assurance of adequate containment of the oxide under all foreseeable conditions. One possible environment which the source may encounter is exposure to water. Under such a circumstance, adequate containment of the fuel must be assured by either the integrity of the oxide cladding or by the low solubility or slow dissolution rate of the oxide in the water environment. This requirement led to a study of the solubility and dissolution rate of Pm_2O_3 in fresh and synthetic sea water and to an attempt to define the mechanism by which the oxide reacts with water. The study was expanded to include the reactions of Sm_2O_3 and Nd_2O_3 with water as well. This report summarizes the results of the study.

2.0 SUMMARY

This study had the objective of identifying the problems and evaluating the effects of the reactions of Pm_2O_3 sources when exposed to water or water vapor.

The basicity of promethium lies between that of samarium and neodymium. The solubility of freshly precipitated promethium hydroxide was determined to be about 3×10^{-6} M at 20 °C.

The solubility of Pm_2O_3 was found to be about $5 \times 10^{-7} \text{M}$. Although the value is low on a weight basis, the equilibrium solubility is about 0.1 Ci per liter in terms of radioactivity.

Pleasured dissolution rates for compacted shapes of Pm_2O_3 in water depend on the method of forming the compact. High density pellets formed by hot pressing at 1700°C gave dissolution rates in pure water of $12 \mu\text{g/hr-cm}^2$ of pellet surface, while cold-pressed pellets sintered at 1400°C dissolved at the rate of $4 \mu\text{g/hr-cm}^2$ of pellet surface. The dissolution rates of both types of pellets were about an order of magnitude lower in synthetic seawater.

Reaction of compacted Pm_2O_3 with water results in the cracking and eventual disintegration of the compact into powder in a relatively short time. The disintegration is accompanied by a large increase in volume of the promethium material. If an encapsulated Pm_2O_3 source contacts water as a result of cladding failure, the resultant swelling of the oxide will rupture the cladding. Nd_2O_3 and Sm_2O_3 will react in a similar manner. In fact, Nd_2O_3 and Sm_2O_3 react and swell when exposed to atmospheric moisture.

When Nd_2O_3 and Sm_2O_3 react with atmospheric water, the compounds formed correspond to the formula $\text{R}_2\text{O}_3 \cdot 3 \text{H}_2\text{O}$. Pm_2O_3 and Sm_2O_3 immersed in water also form trihydrates. Nd_2O_3 , however, forms a compound with the formula $\text{Nd}_2\text{O}_3 \cdot 5 \text{H}_2\text{O}$. None of the compounds formed was the rare earth hydroxide (as determined by X-ray diffraction analysis); they are hydrated oxides.

The reaction rates of rare earth oxides with water and water vapor depend on a number of factors including the oxide species and crystal form, the temperature at which the oxide is calcined, and the temperature of the water. Attempts to retard the reaction of the oxides with water by adding other oxides, such as WO_3 , were unsuccessful.

It was concluded from the results of this study that exposure of unclad Pm_2O_3 sources to water will result in the release of substantial amounts of radioactivity to the environment. If the integrity of an encapsulated Pm_2O_3 source is breached and the source is exposed to water, the resultant swelling of the oxide will result in the complete destruction of the source. It is essential, therefore, to maintain integrity of the cladding for the safe containment of Pm_2O_3 .

3.0 EXPERIMENTAL AND RESULTS

3.1 PREPARATION OF RARE EARTH SESQUIOXIDES

All of the rare earth oxides used in the current study were prepared by a standardized process. Fission product promethium, after aging, was purified by chromatographic ion exchange^(1,2) to remove cation impurities. This promethium solution from the ion exchange process contained less than 1% metallic impurities. Oxalic acid was added to the solution to precipitate promethium oxalate which was filtered and washed with distilled water. The oxalate was then calcined in air to form the sesquioxide. The sesquioxides of neodymium and samarium were prepared in a similar fashion. Commercial grades of Nd_2O_3 and Sm_2O_3 (of 99.9% purity) were obtained from the Lindsey Division of American Potash and Chemical Corp. The oxides were dissolved in nitric acid and the oxalates precipitated by the addition of oxalic acid. Each oxalate was filtered, washed with distilled water, and fired in air to form the oxide. The temperatures at which the oxalates were fired determined the crystal forms of the oxides obtained.

The following table shows the temperature at which each phase of the three oxides was formed. The high temperature forms of the oxide are stable and upon cooling do not revert to the low temperature forms. A temperature of at least 700 °C is necessary to completely decompose the oxalates.

It is therefore evident that the cubic forms of the oxides probably contain small amounts of carbon contamination, probably in the form of carbonate. Small amounts of water are probably also present in oxide fired below 800 °C.

TABLE 1. Temperatures at Which Each Phase of the Oxides was Formed

<u>Oxide</u>	<u>Calcining Temp, °C</u>	<u>Crystal Form</u>
Nd ₂ O ₃	≤ 700 °C	Cubic
	> 700 °C	Hexagonal
Pm ₂ O ₃	≤ 750 °C	Cubic
	> 750 < 2100 °C	Monoclinic
Sm ₂ O ₃	≤ 750 °C	Cubic
	> 750 °C	Monoclinic

3.2 SOLUBILITY OF Pm₂O₃ IN WATER

It has long been recognized that the basicities of the rare earths decrease with increasing atomic numbers.⁽³⁾ The solubility of Pm(III) would therefore be expected to lie between Nd(III) and Sm(III). To verify this assumption the solubility product of Pm(III) in water was measured using the titrimetric method described by Moeller.⁽⁴⁾

In this technique, a solution containing a known amount of the rare earth is titrated with a standard base using a pH meter to observe the pH after each increment of base added. If the reaction

is assumed, the Pm(III) in solution can be estimated from the titration curve, and the hydroxyl ion concentration is given by the pH.

An apparent solubility product is given by:

$$K = [\text{Pm}^{+3}] [\text{OH}^-]^3. \quad (2)$$

For our measurements, a 0.100M solution of Pm(III) was prepared by dissolving a weighed amount of Pm_2O_3 in a slight excess of perchloric acid and diluting it to a measured volume. Aliquots of this were titrated with standardized 0.1M sodium hydroxide in a thermostatted vessel held to within $\pm 0.2^\circ\text{C}$ of the desired temperature. After each increment of base was added, the mixture was stirred 10 min with a magnetic stirrer, and the pH was measured with a glass electrode. Titrations were carried out at 10, 20, 30, and 40°C . In addition to the measurements with Pm(III), titrations were made with Nd(III) and Sm(III) under identical conditions.

Figure 1 shows the data obtained. As expected, the values for Pm(III) are between those for Nd(III) and Sm(III). Increasing the temperature gives lower apparent solubility products which agrees with the observations made by Meloche.⁽⁵⁾

Solubilities based on these apparent solubility products calculated from the equation

$$S = \sqrt[4]{K/27}$$

are given in Table 2

TABLE 2. Solubilities of Rare Earth Hydroxides

Temperature, $^\circ\text{C}$	Solubility, $\text{M} \times 10^6$		
	<u>Nd</u>	<u>Pm</u>	<u>Sm</u>
10	5.7	3.5	2.7
20	3.9	2.8	2.0
30	2.8	1.8	1.5
40	2.0	1.4	1.1

The data obtained by the titrimetric method give, at best, a measure of the relative solubility of the freshly precipitated solid formed on reaction with hydroxyl ions. Further experiments were carried out to get solubilities for the reaction product of anhydrous promethium oxide and water. These were

FIGURE 1 Solubility of Rare Earth Hydroxides

done by equilibrating Pm_2O_3 with water for extended time periods and measuring the ^{147}Pm in solution. The equilibration was done in a closed thermostatted vessel to prevent absorption of carbon dioxide from the atmosphere. The Pm_2O_3 , prepared by ignition of promethium oxalate at 900°C , was washed exhaustively with carbon dioxide-free water. About 0.5 g was placed in the vessel with 400 ml water and mixed continuously with a magnetic stirrer. The temperature was held at $20 \pm 0.2^\circ\text{C}$. Samples were periodically removed and filtered. The ^{147}Pm content was determined by beta counting aliquots of the filtrate.

Samples taken during the first 48 hr contained a colloidal dispersion which passed through the filter and gave high values. After 7 days, agglomeration had occurred, and fairly reproducible results were obtained. A value for the solubility was obtained, based on ten measurements, of $5 \times 10^{-7} \text{M} \pm 30\%$.

3.3 DISSOLUTION RATES OF PROMETHIUM OXIDE

Several experiments were performed to observe the dissolution of Pm_2O_3 in water. The objective was to ascertain if low dissolution rates could be relied on to minimize the spread of radioactivity in the event that the integrity of the cladding material was lost when the source was immersed in water. As evident in the following discussion, dissolution rates of compact Pm_2O_3 are reasonably low, but after relatively short times the compacts disintegrate, resulting in rapid dissolution limited only by the solubility.

Compact Sources of Pm_2O_3

Tests were carried out to measure the dissolution of compacted Pm_2O_3 pellets in distilled water and in synthetic sea water. Both low density and high density pellets were tested.

Pellets prepared by cold pressing Pm_2O_3 and sintering at 1400°C resulted in compacts of 84% of theoretical density,

while hot pressing at 1700 °C gave compacts of > 95% of theoretical density. The Pm_2O_3 used contained 22.5% Sm_2O_3 as the result of the decay of ^{147}Pm .

The test procedure consisted of placing the Pm_2O_3 pellet of known surface area in a small glass vessel fitted with a glass frit at the exit. Next, a flow of either distilled water or synthetic seawater⁽⁶⁾ was directed through the vessel at a uniform rate. The effluent was collected in a graduated cylinder, and the time required to collect a measured volume was noted. The amount of ^{147}Pm collected was determined by beta counting. The rate of dissolution per cm^2 of pellet surface area could then be calculated.

The duration of each test was at least 8 hr with measurements taken at 1-hr intervals. At the conclusion of the tests, the flow of water was terminated and the pellets were left immersed in the water and their behavior was observed.

The results obtained are presented in Tables 3 and 4.

TABLE 3. Dissolution Rates of Pm_2O_3 Pellets in Distilled Water

Time, hr	Dissolution Rate, $\mu\text{g}/\text{cm}^2/\text{hr}$	
	Low Density Pellets	High Density Pellets
1	4.0	12.1
2	3.7	12.1
3	3.5	12.6
4	4.0	11.7
5	3.8	11.8
6	3.5	11.9
7	3.0	12.1
8	4.5	11.8

TABLE 4. Dissolution Rates of Pm_2O_3 Pellets in Seawater

Time, hr	Dissolution Rate $\mu\text{g}/\text{cm}^2/\text{hr}$	
	Low Density Pellets	High Density Pellets
1	0.06	0.51
2	0.05	0.57
3	0.05	0.60
4	0.04	0.58
5	0.04	0.58
6	0.05	0.53
7	0.05	0.57
8	0.03	0.57

The high density pellets developed cracks after approximately 48 hr immersion, and during the following 3 days completely disintegrated. The low density pellets showed no indication of disintegration until the fifth day. At that time, cracks formed and the pellets began to fall apart. In both cases, the disintegration resulted in the formation of very fine crystalline particles.

Powdered Pm_2O_3

Experiments to measure the dissolution rate of powdered Pm_2O_3 were limited to batch equilibrations in which a small amount of Pm_2O_3 was placed in water, stirred, and periodically sampled. Three samples of Pm_2O_3 , prepared by calcining promethium oxalate at 700, 850, and 1000 °C, were placed in glass filters and washed with CO_2 free water. About 25 mg of each was placed in 150 ml of CO_2 -free water in a closed glass vessel thermostatted at 25 ± 0.1 °C. The mixture was agitated by means of a magnetic stirrer and sampled periodically. The samples were centrifuged to remove the solids, and the ^{147}Pm content was determined by beta counting.

The results given in Table 5 show the promethium in the supernate quickly reaches a limiting value. The values are much higher than would be predicted from the solubility

of Pm_2O_3 (discussed in the preceding section) and may be attributed to the formation of a colloid which is not removed by centrifuging.

TABLE 5. Dissolution of Pm_2O_3 Powder

Promethium Concentration in Solution, mg/liter			
Time, hr	Pm_2O_3 Calcined at 700 °C	Pm_2O_3 Calcined at 850 °C	Pm_2O_3 Calcined at 1000 °C
0.5	19	28	28
1.0	18	28	29
5.5	20	30	31
55.0	20	30	30
80.0	25	31	30
104.0	21	32	31

3.4 HYDRATION OF RARE EARTH OXIDES

As stated previously, when a compacted shape of Pm_2O_3 contacts water, the shape cracks and disintegrates in a relatively short time even though the dissolution rate is very slow. Given sufficient time, the oxide ends up as finely divided particles dispersed throughout the system. Compacted shapes of Nd_2O_3 and Sm_2O_3 exhibit the same type of reaction with water. In fact, Nd_2O_3 and Sm_2O_3 shapes exposed to atmospheric moisture will, given sufficient time, disintegrate in the same way. Figure 2 shows a number of hot-pressed Nd_2O_3 pellets which had been exposed to atmospheric moisture for varying periods of time. Cracking and disintegration of the pellets as they react with moisture is readily apparent. Promethium sesquioxide shapes do not appear to react with atmospheric moisture at any appreciable rates, probably because of the heat generated by radioactive decay.

The disintegration of the compacted oxide shape by reaction with water results in a large increase in volume. If oxide enclosed in a container comes in contact with water, the resultant swelling of the oxide can destroy the container.

Exposure Time In Hours

Exposure Time In Days

FIGURE 2. Disintegration of Sintered Nd_2O_3 Pellets upon Exposure to Atmospheric Moisture (Pellets Prepared by Hot Pressing Nd_2O_3 at 1700 °C to 95% of Theoretical Density).

Figure 3A shows a Haynes 25 capsule which originally contained Sm_2O_3 at 90% of theoretical density. A small hole was drilled in one end of the capsule, and the capsule was placed in water. After several days, swelling of the oxide was sufficient to rupture the capsule at the end opposite the drilled hole.

Figure 3B shows a stainless steel capsule which originally contained Pm_2O_3 at 50% of theoretical density. Pressure generated when the oxide contacted the water was sufficient to swell the capsule but not rupture it. If the initial oxide density had been higher, the capsule would undoubtedly have ruptured. Figure 4 shows a tungsten capsule which had been filled with Sm_2O_3 to a density of 75% of theoretical by step pressing. After the capsule lid had been welded in place, a pin hole leak was detected in the weld area. The defective capsule was allowed to sit on a shelf for several months. Reaction of the oxide with atmospheric moisture resulted in capsule rupture as shown.

These data show that containment of the promethium oxide must be assured through the integrity of the heat source cladding, even though the dissolution rate in water is very slow.

A number of factors affect the rate at which the oxides react with water or water vapor. They include:

- The oxide species under consideration.
- The oxide crystal structure.
- The temperature at which the oxide is calcined prior to exposure to water.

The water temperature.

In general, it can be stated that Nd_2O_3 will react with water at the fastest rate, Sm_2O_3 at the slowest rate, and Pm_2O_3 at an intermediate rate. Qualitative data on the rates at which compacted shapes of the three oxides react with water are shown in Table 6. The data were obtained by placing oxide pellets in water and watching for the first visible evidence

(a) Sm_2O_3 Capsule

(b) Pm_2O_3 Capsule

FIGURE 3. Capsules Containing Rare Earth Oxides After Exposure to Water

Neg 0690988

FIGURE 4. A Sm_2O_3 Filled Tungsten Capsule with a Defective Weld After Exposure to Atmospheric Moisture for Several Months

of cracking. Reproducibility of results was quite poor, and the data are presented only to show the trend of lowered rate of reactivity with water from Nd_2O_3 to Sm_2O_3 .

TABLE 6. Disintegration of Oxide Pellets in Water

Oxide	Method of Preparing Pellets, °C	Initial Pellet Density, % of Theoretical	Time to Initial Evidence of Disintegration
Nd_2O_3	Sintered at 1500	94 to 95	4 to 12 hr
Nd_2O_3	Hot Pressed at 1700	95 to 96	4 to 12 hr
Pm_2O_3	Sintered at 1400	84	5 days
Pm_2O_3	Hot Pressed at 1700	95	48 hr
Sm_2O_3	Sintered at 1500	95 to 96	10 to 20 days
Sm_2O_3	Hot Pressed at 1700	96 to 97	8 to 20 days

The data presented in Table 6 were obtained from compacts exposed to water at 25 to 30 °C. When the water temperature was increased, the disintegration of the oxide compacts was much more rapid. Cold pressed and sintered Sm_2O_3 pellets were exposed to water at various temperatures and observed for the first visual evidence of disintegration. The results obtained are shown in Figure 5. Again there was significant variation in the data for a given set of conditions. However, the trend of increasing disintegration rate with increasing water temperature is readily apparent.

Nd_2O_3 reacts with atmospheric moisture at a much faster rate than Sm_2O_3 . Weighed samples of each oxide (in powder form) were placed in open beakers, exposed to the atmosphere, and weighed periodically to determine the weight increase. The results obtained are presented in Figure 6. The relative humidity of the air was fairly constant at about 50% during the test period. Pm_2O_3 samples tested in a similar fashion (in an air atmosphere glove box) showed no measurable weight increase.

FIGURE 5. Effect of Water Temperature on Rate of Disintegration of Sm_2O_3 Pellets

FIGURE 6. Reaction Rates of Rare Earth Oxides
with Atmospheric Moisture

The Nd_2O_3 and Sm_2O_3 samples, after exposure to the atmosphere until equilibrium was obtained, were heated to 1000 °C in a vacuum system and the off-gas from each sample collected and analyzed. Water was the only volatile species found. This shows the weight increases observed with the oxides were due to reaction with atmospheric moisture and not to reactions with carbon dioxide.

The failure of Pm_2O_3 to react with atmospheric moisture is probably due to the heat generated at the oxide particle surface by the radioactive decay of the ^{147}Pm .

The rate at which a given oxide reacts with water generally depends on its crystal form. The low temperature cubic forms of Nd_2O_3 , Pm_2O_3 , and Sm_2O_3 react with water at significantly faster rates than the high temperature forms (monoclinic Pm_2O_3 and Sm_2O_3 and hexagonal Nd_2O_3). This is illustrated by the data presented in Figure 7 which show the rates at which the cubic and hexagonal forms of Nd_2O_3 react with atmospheric moisture. Similar differences were observed for the cubic and monoclinic forms of Sm_2O_3 upon exposure to the atmosphere.

The temperature at which a given crystal form of an oxide is fired also affects the rate at which it reacts with water. However, the temperature effect will vary depending on the oxide under consideration. For example, with hexagonal Nd_2O_3 the rate of reaction with atmospheric moisture increases with increasing calcining temperature (see Figure 8); hexagonal Nd_2O_3 fired at 1400 °C shows approximately the same reaction rate as cubic Nd_2O_3 fired at 700 °C. Monoclinic Sm_2O_3 reacts with water in a like fashion and low fired oxides show a greater stability to water than high fired oxide. Curtis and Johnson⁽⁷⁾ have reported similar results with Sm_2O_3 .

FIGURE 7. Effect of Crystal Form on Reaction of Nd_2O_3 with Atmospheric Moisture

FIGURE 8. Effect of Calcining Temperature on Rate of Reaction of Nd_2O_3 with Atmospheric Moisture

When compacted pellets of monoclinic Pm_2O_3 were exposed to water, the pellets formed at the higher temperature reacted more rapidly than low fired pellets (see Table 6). When monoclinic Pm_2O_3 powder was exposed to water, however, a different temperature effect was observed; oxide fired at lower temperatures reacted more rapidly than high fired oxide (see Figure 9). The data were obtained by firing the oxide at the desired temperature, exposing the resulting powder to water, sampling the slurry periodically, filtering and drying the resultant powder at 100 °C, and then determining the water content by thermogravimetric analysis using a Cahn electrobalance.

Several experiments were performed in an attempt to determine the products formed when the three oxides react with water. Thermogravimetric analysis was carried out on the various reaction products using a Cahn electrobalance and a Mosely X-Y recorder. Figure 10 shows typical thermograms for Nd_2O_3 and Sm_2O_3 which had been equilibrated with atmospheric moisture. In each case, the reaction product appears to be a compound with the empirical formula $\text{R}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The water in excess of 3 moles per mole of oxide is apparently adsorbed water and is not part of the compound structure. X-ray diffraction analysis indicates the two products are not hydroxides - $\text{R}(\text{OH})_3$ ^(8,9) - but rather hydrated oxides of some type. The hydrated Nd_2O_3 exhibits a slightly greater temperature stability than the Sm_2O_3 product, as well as a more complex dehydration curve.

Figure 11 shows typical thermograms for the oxides of neodymium, promethium, and samarium after equilibration with water. For neodymium, the thermogram indicates a more complex structure (empirical formula $\text{Nd}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) than was obtained with Nd_2O_3 exposed to atmospheric moisture. The thermogram for promethium is less well defined than those obtained with

FIGURE 9. Reaction of Pm_2O_3 with Water at 25 °C

FIGURE 10. Thermograms for Nd_2O_3 and Sm_2O_3 Equilibrated with Atmospheric Moisture

FIGURE 11. Thermograms for Oxides of Nd, Pm and Sm Equilibrated with Water

samarium and neodymium. However, the equilibrium product appears to have the empirical formula $\text{Pm}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. Again, X-ray diffraction analysis shows the products do not have the typical hydroxide structure, but are probably hydrated oxides.

When neodymium, promethium, and samarium were precipitated from nitric acid solutions with sodium hydroxide, the products obtained after washing and drying gave much more complex thermograms than those obtained by reacting the corresponding oxides with water (see Figure 12). The empirical formulas for the three products are $\text{Nd}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$, $\text{Sm}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$, and $\text{Pm}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. Again promethium gives a less well-defined thermogram than either samarium or neodymium. X-ray diffraction analysis of each product indicates that the basic structures correspond to the hydroxide $\text{R}(\text{OH})_3$ with a number of extraneous lines which could not be identified. Unfortunately, time and budget limitations did not permit a more detailed study to determine the exact structures of the various reaction products or the intermediate compounds formed during dehydration.

In comparing the thermograms for the three neodymium reaction products under consideration (see Figure 13), it is interesting to note that the products appear distinctly different. In addition, intermediate compounds formed during dehydration of the various products show little, if any, similarity. Comparable differences were noted for the three samarium products and the two promethium products.

One general similarity was noted for the various products formed between neodymium, samarium, promethium, and water. In each case, a temperature of approximately 800 °C was required to convert the material to the anhydrous oxide.

One other factor concerning the reaction of the oxides with water should be mentioned. Limited data obtained with Nd_2O_3 indicate that when the oxide reacts with atmospheric

FIGURE 12. Thermograms for Nd, Pm and Sm Precipitated from Solution with NaOH

FIGURE 13. Comparison of Thermograms for $\text{Nd}_2\text{O}_3\text{-H}_2\text{O}$ Reaction Products

moisture, intermediate compounds are not formed. Instead, each molecule of oxide reacts to form the equilibrium product $\text{Nd}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. This can be seen from the data presented in Figure 14 which makes it apparent that the thermograms for oxide, not at equilibrium with atmospheric moisture, show the same structural detail as oxide at equilibrium.

3.5 RETARDATION OF OXIDE HYDRATION

The data presented in the previous section have shown that hydrates will form when Nd_2O_3 , Sm_2O_3 and Pm_2O_3 are exposed to water. This can be a serious problem when Pm_2O_3 is considered for use as a heat source fuel, since oxide hydration could have a catastrophic effect on the integrity of the source. If the hydration problem could be eliminated, the use of Pm_2O_3 as a heat source fuel would be much more attractive.

Earlier work at PNL had indicated that sintered compacts of $\text{Sm}_2\text{O}_3\text{-WO}_3$ had greater stability in water than sintered Sm_2O_3 compact alone. Therefore, a study was undertaken to see if the hydration of Pm_2O_3 could be retarded or eliminated by the use of oxide additives. Several oxides including WO_3 , TiO_2 , Ta_2O_5 , P_2O_5 and Cr_2O_3 were evaluated as hydration inhibitors. Sm_2O_3 and Nd_2O_3 were used as stand-ins for Pm_2O_3 in the study.

The test procedure consisted of:

- Mixing the rare earth sesquioxide with a specific amount of additive oxide.
 - a Pressing the mixture into pellets at 60 to 80 TSI.
- Sintering the pellets at 800 to 1700 °C.
- Exposing the sintered pellets to water.
 - a Following the hydration as a function of time.

None of the oxides tested were effective in stopping the hydration of Nd_2O_3 or Sm_2O_3 upon exposure to water. Only tungstic oxide (WO_3) served to reduce the rate of hydration, and even then, a large percentage of WO_3 (>10 wt%) was required

FIGURE 14. Thermograms for Nd_2O_3 Exposed to Atmospheric Moisture for Varying Periods of Time

before the rate was reduced significantly (see Figure 15). Furthermore, the use of large amounts of WO_3 in fabricating the oxide source is precluded by the need to maintain a high power density in the source.

The other oxides tested were almost completely ineffective in reducing the rate of oxide hydration and in some instances actually increased the rate (see Figures 16 and 17).

4.0 CONCLUSIONS

Experimental measurements have shown that the solubility of Pm_2O_3 in water is quite low on a weight basis. On a curie basis, however, the solubility is high, amounting to about 0.1 Ci/liter. The dissolution rates of compacted Pm_2O_3 in distilled and synthetic sea water are also quite high on a curie basis. These results show that one can not rely on low solubility or slow dissolution of the oxide as a means of containing Pm_2O_3 if it is exposed to a water environment. Instead, one must rely on the integrity of the oxide cladding for adequate containment.

When Pm_2O_3 is encapsulated in a metal cladding and exposed to water complete integrity of the cladding is essential. If a minute hole develops in the cladding, the reaction between the oxide and the water can result in complete destruction of the encapsulated source.

FIGURE 15. Hydration of Nd_2O_3 - WO_3 Pellets Sintered at 1400 °C and Exposed to Atmospheric Moisture

FIGURE 16. Hydration of Nd₂O₃-P₂O₅ Pellets Sintered at 800 °C and Exposed to Atmospheric Moisture

FIGURE 17. Hydration of Nd_2O_3 - TiO_2 Pellets Sintered at 1300 °C and Exposed to Atmospheric Moisture

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