Reactions of Sodium Peroxide with Components of Legacy Plutonium Materials

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Abstract

Plutonium oxide (PuO_2) calcined at >900 °C resists dissolution in nitric acid (HNO_3)-potassium fluoride (KF) solutions, a common method for their dissolution. The Savannah River National Laboratory (SRNL) has developed an alternate method for large samples of PuO_2-bearing materials using sodium peroxide (Na_2O_2) fusion as a pretreatment. The products of the reaction between Na_2O_2 and PuO_2 have been reported in the literature. As part of the SRNL development effort, additional data about the reaction between Na_2O_2 and PuO_2 were required. Also needed were data concerning the reaction of Na_2O_2 with other components that may be present in the feed materials. Sodium peroxide was reacted with aluminum metal (Al), beryllium metal (Be), graphite, potassium chloride (KCl), magnesium chloride ($MgCl_2$), and calcium chloride ($CaCl_2$). The paper reports and discusses the reaction products of these and related compounds with Na_2O_2.

Introduction

Plutonium dioxide calcined at high temperatures (>900 °C) resists dissolution in inorganic acids.[1] As the calcination temperature increases, the specific surface area of PuO_2 decreases, which increases its resistance to dissolution.[2] This behavior is a technical issue in light of standard practices for the storage of PuO_2 which involve calcination at 950 °C or greater for at least two hours.[3] Fusion with Na_2O_2 is a common analytical technique for the dissolution of intractable samples. It is an effective method for the quantitative dissolution of PuO_2 that has been calcined up to 1600 °C.[4]

SRNL developed and identified process parameters for the dissolution of large samples (>50 g) of PuO_2-bearing materials using Na_2O_2 fusion.[5] The Na_2O_2 fusion process is a technology that could provide substantial benefits to the processing of high-fired PuO_2 materials at the Savannah River Site. Those benefits include reduction in dissolution cycle time, decrease in overall residues (especially Pu-bearing residues), and reduction of the potential for generation of a flammable gas mixture during dissolution.

To fuse a sample, Na_2O_2 is mixed with sample in a crucible. The crucible is heated to 600-700 °C where Na_2O_2 reacts with the sample to form a compound that readily dissolves in nitric acid at ambient temperature without the use of potassium. Keller and co-workers report preparing ternary oxides of Np, Pu, and Am by reacting actinide dioxides with lithium oxide (Li_2O) and Na_2O_2 in an oxygen atmosphere at 400-900 °C. The principal products included compounds such as Li_6PuO_6 and Na_4PuO_5.[6,7]

As part of the SRNL development effort, additional data about the reaction with PuO_2 was required. Also needed was an understanding of the reaction of Na_2O_2 with other compounds that might be present in samples, such as Al metal, Be metal, graphite, KCl, $MgCl_2$, and calcium chloride $CaCl_2$. SRNL researchers studied the reaction products of these and related compounds with Na_2O_2.

Experimental Section

Fusion with Sodium Peroxide. Fusion of samples was performed in the following manner. First, a 5-mL zirconium (Zr) metal crucible was weighed on a calibrated balance. In a separate weighing dish, the appropriate amount of granular Na_2O_2 (Fisher Scientific, 96 % pure) was added. Next, the material to be fused was added. Specific test data are listed in Table 1. The materials in the weighing dish were mixed with a spatula and added to the crucible.

Table 1. Parameters for Peroxide Fusion of Non-Pu Components

Material Fused	Mass Fused (g)	Mass Na_2O_2 (g)	Time at 700 °C
Al Metal	0.5016	4.0312	15
Be Metal	0.186	0.930	15
Graphite	0.0992	1.9926	60
NaCl:KCl	0.5076	1.9885	60
$MgCl_2$	0.5011	2.0050	60
$CaCl_2$	0.5007	2.0079	60
$NdCl_3$	0.4990	1.9959	60

The crucible was placed into a standard muffle furnace and heated to 700 ^{o}C. The crucible was typically held at temperature for 30-60 min. The furnace was turned off and allowed to cool. While at 100-300 °C, the crucibles were transferred to a desiccator to limit reaction with moisture in the air. The samples were analyzed using X-ray diffraction (XRD). The detection limit for XRD is ~0.5 wt %. Reaction with air and moisture reduce the effectiveness of X-ray diffraction.

For studies involving graphite, a comparative analysis was performed using thermal gravimetric analysis – mass spectroscopy (TGA-MS). A comparison was made between the behavior of pure graphite (9.522 mg) and 3.5 wt % graphite mixed with Na_2O_2 (273.606 mg). Using nearly equivalent masses of graphite for both tests, the analyses were performed on a Netzsch STA-409-PC-LUXX TGA attached to a Pfeiffer Thermostar QMS 200 MS mass spectrometer. The heating cycle was performed with a purge gas of argon and air. The samples were held at room temperature for 5 min, heated to 740 °C at 15 °C/min, held at 740 °C for 10 min, and then cooled to room temperature.

For the reaction of sodium peroxide (Na_2O_2) and plutonium oxide (PuO_2), a qualitative analysis was performed by TGA-MS. The reaction was investigated at a nominal 5:1 mass ratio, with 502.4 mg PuO_2 and 1721.59 mg Na_2O_2. Portions of the two compounds were added to an alumina crucible in alternate layers to promote mixing. The initial test was repeated on a smaller scale with 25.4 mg PuO_2 and 152.8 mg Na_2O_2, with an additional MS detection point set for Mass 62 to investigate release of Na_2O. In addition, a "process blank", containing only 157 mg Na2O2, was tested using the same temperature profile to gauge Na_2O_2 decomposition versus temperature. The samples were held at room temperature for 5 min, heated to 740 °C at 10 °C/min, then held at nominally 740 °C for 30 min.

Dissolution of Fused Product. Samples of PuO_2 were fused (see Table 2) and dissolved in an apparatus designed to measure temperature change, collect a gas sample, and measure gas generation volume. The dissolution vessel consists of a 250-mL Nalgene^{TM} bottle with a glass thermowell passing through the side wall to the bottom of the vessel; the thermowell was sealed to the side wall of the bottle. A Type-K thermocouple was inserted into the thermowell and attached to a thermocouple reader. The cap of the bottle had a hole drilled through it and a stainless steel bulkhead fitting passed through the hole. Viton™ o-rings created a gas-tight seal on either side of the hole. A 7.5-cm piece of Viton™ tubing passed from the bulkhead fitting to a 1-liter Tedlar™ gas sample bag.

Table 2. Parameters for Peroxide Fusion of Pu Feed

Sample	Sample Mass (g)	Na_2O_2 Mass (g)	Time at 700 °C (min)	HNO_3 Conc (M)	HNO_3 Dissolvent (mL)
Pu-1	0.905	2.700	60	6	125
Pu-2	0.905	2.700	60	5.4	125
Pu-3	0.905	2.700	60	4.9	125
Pu-4	0.905	2.700	60	4.3	125
Pu-5	1.008	3.001	60	4.1	134

Prior to the dissolution, 50 mL of the dissolvent (HNO_3) was placed in the dissolver vessel. With the dissolver cap off, the fused product and its crucible were added to the dissolver vessel. The dissolver cap was immediately put on the vessel and sealed, a timer initiated, and the valve in the Tedlar™ bag opened. Dissolution is complete within one minute. Within 2-5 minutes of dissolution being complete, the Tedlar™ bag was sealed and the gas volume in the bag measured using water displacement. Gas samples were analyzed using gas chromatography (GC).

Results and Discussion

A reaction for the formation of an Na_2O_2-PuO_2 fusion product has been proposed.[8]

$$PuO_2 + 2\,Na_2O_2 \rightarrow Na_4PuO_5 + \tfrac{1}{2}\,O_2 \qquad (1)$$

The reaction products for Al metal powder reacting with Na_2O_2 were identified using XRD. The XRD did not detect either Al metal or Al_2O_3 (from air-oxidized metal). Aluminum was present only as a Na_2O_2 reaction product (Na_5AlO_4), which is analogous to the compound formed (Na_4PuO_5) when Na_2O_2 reacts with PuO_2.

For the Be metal fusion tests, pieces of Be metal coupons were used due to the unavailability of Be metal powder. The coupon completely dissolved into the Na_2O_2 and produced the product shown in Figure 1. XRD shows that Be metal reacted with Na_2O_2 to form BeO. No other Be compounds were identified.

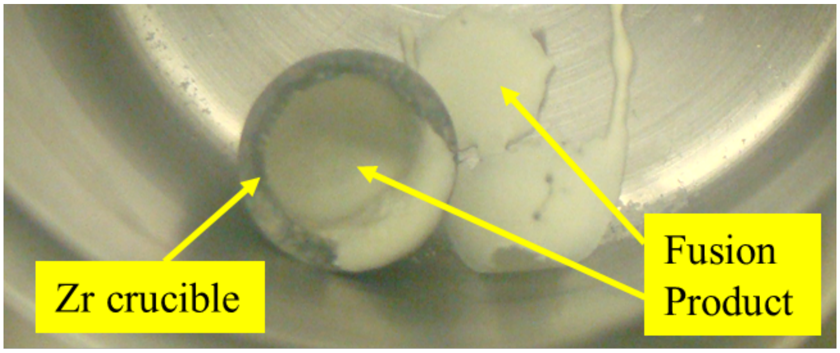

Figure 1. Product from Be Metal Coupon Reaction with Na_2O_2.

Sodium peroxide was reacted with four different chloride salt matrices: $NdCl_3$, $MgCl_2$, $CaCl_2$, and 50:50 mole% NaCl-KCl. The analyses demonstrate that the higher valence cations (i.e., neodymium [Nd], magnesium [Mg], and calcium [Ca]) exchanged chloride with Na_2O_2. Neodymium chloride reacted to form $NaNdO_2$, $MgCl_2$ reacted to form MgO, and $CaCl_2$ reacted to form CaO; in all three samples, the chloride was present as NaCl. Sodium peroxide did not react with KCl (Reaction 2) because the formation of potassium oxide (K_2O) is not thermodynamically favorable.[9]

$$Na_2O_2 + 2\,KCl \rightarrow K_2O + 2\,NaCl + \tfrac{1}{2}\,O_2 \qquad \Delta H_f^\circ = +200 \text{ kJ/mol} \qquad (2)$$

For the reaction between Na_2O_2 and graphite, graphite powder was blended with Na_2O_2 in varying ratios. When the graphite concentration exceeded 10 wt % of the total bulk for fusing, some the contents of the crucible foamed out of the crucible after the Na_2O_2 had melted (melting point = 675 °C). Similar foaming was not observed at 4.7 wt % or less graphite. The products for 4.7 wt % graphite reacting with Na_2O_2 were identified using XRD. The XRD showed no residual graphite. Rather, carbon was present as a Na_2O_2 reaction product, sodium carbonate (Na_2CO_3). The presence of the carbonate was somewhat surprising as CO_2 gas from the oxidation of carbon was the expected reaction product.

To determine whether there were other reaction products released as carbon gases, comparative TGA-MS tests were performed on graphite only and graphite mixed with Na_2O_2. The results are provided in Figure 2 and Figure 3. The data for the graphite-only test (9.52 mg) show that graphite begins to react with air at about 500 °C (~45 min) with the accompanying weight loss and release of CO_2. The reaction rate accelerates above 625 °C. Conversely, when 9.58 mg of graphite was reacted with 264 mg of Na_2O_2, no significant weight loss was observed at any temperature and no release of CO_2, carbon monoxide, or oxygen gases was detected. The TGA-MS data imply that, consistent with the XRD data, all of the graphite reacts with Na_2O_2 to form Na_2CO_3. Once Na_2CO_3 forms, because it is in a highly caustic medium, it does not decompose to release CO_2. It cannot be known for certain whether the graphite reacted directly with Na_2O_2, or whether the graphite reacted with oxygen in the air to form CO_2 which was subsequently absorbed by Na_2O_2. Recalling that the tests of Figure 2 and Figure 3 had essentially the same mass of graphite, the almost-complete absence of CO_2 in Figure 3 seems to imply that the graphite reacted directly with Na_2O_2 to form Na_2CO_3,

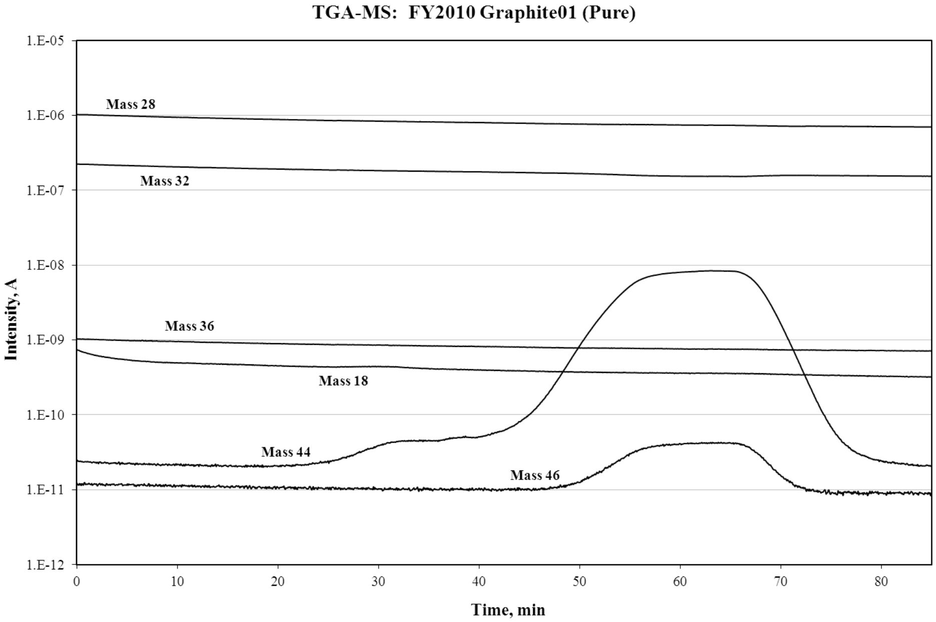

Figure 2. TGA-MS Data for Graphite Oxidation in Air,
Heat at 15 °C/min to 740 °C

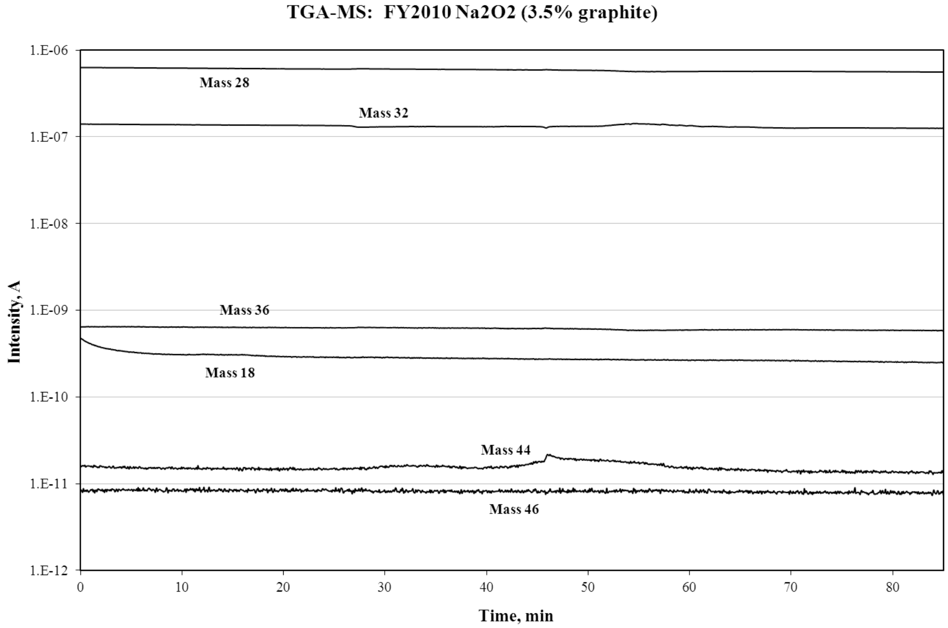

Figure 3. TGA-MS Data for Graphite Reaction with Na_2O_2,
Heat at 15 °C/min to 740 °C

In the reaction of PuO_2 with Na_2O_2 (Reaction 1), Na_4PuO_5 and oxygen gas (O_2) are produced. The reaction indicates that the release of O_2 occurs during the fusion reaction. Gas measurements made during the dissolution of fused-PuO_2 products have shown that O_2 is released during dissolution. Test data are listed in Table 3. For these tests, the head space of the reaction vessel was not purged prior to the dissolution reaction. Therefore, 116-125 mL of air space is present in the apparatus when the sample is added and the cover sealed. Consequently, nitrogen (N_2) and O_2 from air are expected in samples and are diluted by gas generated during dissolution.

The data in Table 3 indicate that O_2 is released during dissolution and dilutes the N_2 concentration. In all tests, the gas released during dissolution was colorless. The calculated O_2 value in the table assumes that only O_2 was released during dissolution. In the first four tests, the measured O_2 value was higher than the calculated value, which suggests that the gas released during dissolution is not well-mixed with the gas in the head space. The calculated O_2 value shows that the gas released is primarily O_2. No measurable quantities (<0.2 vol %) of hydrogen gas (H_2) were detected.

Table 3. Gas Generation from the Dissolution of Fused PuO_2

			Measured with GC			**Calc**
Test #	**Head Space (mL)**	**Gas Generated (mL)**	**H_2 (vol %)**	**N_2 (vol %)**	**O_2 (vol %)**	**O_2 (vol %)**
Pu-1	125	90	<0.2	40	60	53
Pu-2	125	120	<0.2	24	75	59
Pu-3	125	190	<0.2	24	74	68
Pu-4	125	210	<0.2	21	78	70
Pu-5	116	500	<0.1	23	75	85
Analytical uncertainty = 10%						

The generation of O_2 during dissolution does not mean that O_2 is released only during dissolution. Testing using thermogravimetric analysis with mass spectroscopy (TGA-MS) has shown that during the fusion of PuO_2 with Na_2O_2 at 700 ^oC, O_2 is released between 200 and 400 °C and then again above 600 °C (Figure 4). Based on the TGA-MS results obtained with only Na_2O_2 (Figure 5), which showed release of Mass 32 (presumably O_2) starting at ~625 °C, the release of O_2 between 200 and 400 °C corresponds to the reaction of PuO_2. The release of O_2 above 600 °C corresponds primarily to the decomposition of Na_2O_2, although a reaction between Na_2O_2 and PuO_2 is likely as Na_2O_2 melts and diffuses through the system. TGA-MS did not detect the release of any Mass 62, which would correspond to sodium oxide (Na_2O).

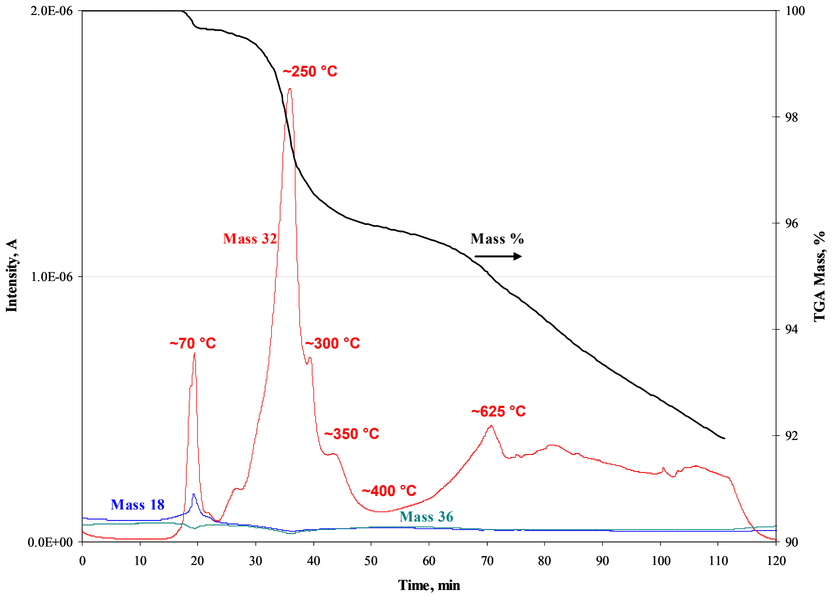

Figure 4. TGA-MS Data for PuO_2 Reaction with Na_2O_2

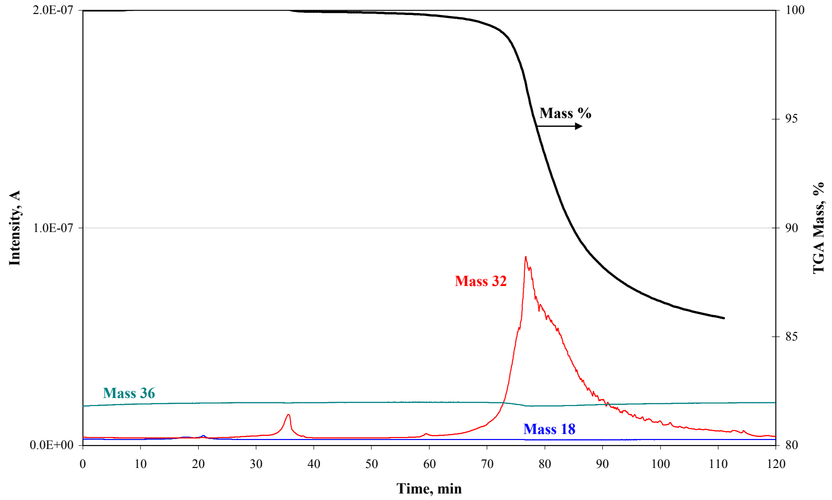

Figure 5. TGA-MS Data for Na_2O_2 with Same Temperature Profile as Figure 4

Conclusions

SRNL researchers evaluated the reaction products of several non-radioactive chemical compounds with Na_2O_2 at 700 °C. Aluminum metal, Be metal, graphite, $NdCl_3$, $MgCl_2$, and $CaCl_2$ are oxidized by Na_2O_2 and form reaction products which dissolve in 4-8 M HNO_3; KCl does not react with Na_2O_2 at the conditions studied. Graphite powder reacted with Na_2O_2 to form Na_2CO_3 rather that CO_2. Data demonstrate that no measurable amount of graphite reacted with air to form CO_2. PuO_2 reacts with Na_2O_2 to release O_2 both during fusion and dissolution. TGA-MS data show that the reaction between PuO_2 and Na_2O_2 begins below 350 °C, but may not complete until the reaction vessel is above 600 °C. Complete reaction of PuO_2 with Na_2O_2 may be dependent upon Na_2O_2 reaching its melting point and diffusing throughout the reaction vessel.

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