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ABSTRACT

A method was developed to produce $^{238}Pu^{16}O_2$ depleted in oxygen-18 and oxygen-17 on a routine production basis. The method is a gas phase-packed bed method which was used successfully on both low-fired and high-fired $^{238}PuO_2$ particles. Average neutron emission rates of 4.6×10^3 n/sec/g of plutonium-238 were obtained on production batches with average weights of 250 g plutonium-238.

INTRODUCTION

Plutonium dioxide containing natural abundance oxygen emits $\sim 23 \times 10^3$ n/sec/g of plutonium-238. This emission rate is relatively high compared to the neutron emission rate of plutonium-238 metal. The metal containing no light element impurities emits $\sim 2.8 \times 10^3$ n/sec/g of plutonium-238.[1] These neutrons are produced by the spontaneous fission of plutonium-238. The difference in the emission rates of the metal and the oxide is due mainly to the (α,n) reaction with the oxygen-18 and oxygen-17 present in the oxide. The normal amount of oxygen-18 present in the natural form is 0.204% while that of oxygen-17 is 0.037%.[2,3] The reduction of the oxygen-17 and oxygen-18 present in plutonium dioxide will result in a much lower neutron emission rate for the oxide; this can be accomplished by a gas phase $^{16}O_2$ exchange method. Regular production batches of $^{238}PuO_2$ particles precipitated as a hydroxide were used to show that large production batches could be effectively $^{16}O_2$-exchanged on a routine basis. High-fired $^{238}PuO_2$ microspheres were successfully $^{16}O_2$-exchanged showing that an exchange will take place regardless of the previous heat treatment history of the $^{238}PuO_2$.

METHOD OF GASEOUS EXCHANGE

Regular production batches of $^{238}PuO_2$ particles precipitated as the hydroxide were used except in the case of the plasma-fired microspheres. The average size of batches exchanged each time was about 245 g of plutonium-238 (340 g of $^{238}PuO_2$) in the 125-297μm size range. The particles were $^{16}O_2$ exchanged by a gas phase - packed bed method and had resulting neutron emission rates averaging 4.6×10^3 n/sec/g of plutonium-238.

In this method the sized particles are placed in a specially built platinum crucible; two alumina tubes, connected to a $^{16}O_2$ supply, are inserted into the material; and the material is allowed to self-heat from the radioactive decay of plutonium-238. After the temperature reaches equilibrium (700-1100°C, depending on batch size), the $^{16}O_2$ is flowed through the $^{238}PuO_2$ particles. After the exchange is completed, the crucible is placed in a furnace, and the temperature is increased to 1600°C for 4 hr. During sintering and cooling, a positive flow (~ 50 cm^3/min) of $^{16}O_2$ is maintained to ensure an atmosphere of enriched $^{16}O_2$ at all times.

The volume of $^{16}O_2$ gas used for each exchange depends upon several factors, such as length of exchange time, length of sintering time, and size of batch. A larger volume will be consumed if the sintering time is lengthened from 4 to 12 hr because during sintering a positive flow

is maintained through the material. The size of batch is critical in determining the volume of $^{16}O_2$ used; that is, the larger the batch size, the greater the volume used. The total volume will also depend upon the length of cooling time since the positive flow is maintained during this time. For example, if a batch is air cooled rather than water cooled, it will require a greater volume of $^{16}O_2$. The average amount of $^{16}O_2$ gas used per batch is about 80 liters at standard conditions using a 250 g $^{238}PuO_2$ batch and allowing to air cool, but excellent results have been obtained with smaller volumes.

DISCUSSION AND RESULTS

Neutron spectral measurements were used to determine the source of neutrons in both unsintered and sintered samples of $^{238}PuO_2$. The (α,n) reaction with light element impurities of boron and fluorine contributed considerably to the total neutrons emitted from an unsintered $^{238}PuO_2$ sample. The neutron energy spectrum revealed neutrons from the spontaneous fission of plutonium-238 and the (α,n) reaction with boron and fluorine. Based on the neutron measurements, the boron concentration was estimated to be 125 ppm by weight with an uncertainity of 20-50% and thus contributed about 30±15% of the total neutron flux. The fluorine concentration was estimated to be 600±200 ppm and accounted for 45±15% of the total neutron flux. The remaining neutrons were produced by the oxygen-17 and oxygen-18 (α,n) reactions.

A sample was then enriched in $^{16}O_2$ and sintered at 1600°C. Although the spectral measurements by themselves did not rule out other (α,n) neutrons, the number of fissions and the oxygen-17 and oxygen-18 (α,n) neutrons were thought to be sufficient to account for all of the measured neutron flux. Thus, the number of neutrons produced by the fluorine-19 (α,n) and natural boron (α,n) reactions can be reduced or eliminated by sintering. Also, the oxygen-17 and oxygen-18 concentration in the oxide can be nearly depleted, resulting in a reduction of the total number of neutrons emitted from the $^{238}PuO_2$.

In reducing the neutron emission rate of $^{238}PuO_2$, various methods and techniques were used. Changes in equipment design and variation of parameters drastically improved the methods of neutron flux reduction. An average of 4.6×10^3 n/sec/g of plutonium-238 was obtained on large batches on a routine production basis. Table 1 shows results obtained for production batches of $^{238}PuO_2$ of various weights.

Table 1
NEUTRON EMISSION AFTER OXYGEN EXCHANGE - PRODUCTION BATCHES

Batch	^{238}Pu (g)	Neutron Emission (n/sec/g ^{238}Pu)
P-134	244	4.4×10^3
P-138	259	4.8×10^3
P-142	221	4.6×10^3
P-143	250	4.8×10^3
P-147	245	4.7×10^3
P-152	230	4.2×10^3
P-153	230	4.2×10^3

Batches which had previously been fired to a temperature of 1600°C in $^{16}O_2$ for 4 to 12 hr were resintered at a temperature of 1600°C for 2 to 12 hr with ∿75 cm^3/min flow of $^{16}O_2$ during heating and cooling. The resulting neutron emission rates are comparable to those rates on the original $^{238}Pu^{16}O_2$ (see Table 2). For example, a batch (P-91, -94) of $^{238}PuO_2$ particles (105-177 μm) was resintered in air without a flow of $^{16}O_2$ for ∿168 hr at 1450°C and had a resulting neutron emission rate of $17x10^3$ n/sec/g of plutonium-238. This material was again sintered for 4 hr at 1600°C, but with a flow of ∿75 cm^3/min $^{16}O_2$ during heating and cooling, and had a resulting neutron emission rate of $6x10^3$ n/sec/g of plutonium-238. Another batch (P-139) which had been $^{16}O_2$-exchanged had a neutron emission rate of $5.2x10^3$ n/sec/g of plutonium-238 but had to be resintered because of low density. During resintering, approximately 75 cm^3/min of $^{16}O_2$ was allowed to flow through the material during heating and cooling. The neutrom emission rate of the oxide after 24 hr of resintering at 1600°C was $4.7x10^3$ n/sec/g of plutonium-238.

Table 2
EFFECT OF RESINTERING ON NEUTRON EMISSION

Batch	Time and Temperature of Sintering	Atmosphere	Neutron Emission (n/sec/g ^{238}Pu)
P-91, -94	168 hr at 1450°C	Air	17 $x10^3$
Resinter P-91, -94	4 hr at 1600°C	$^{16}O_2$	6 $x10^3$
P-139	4 hr at 1600°C	$^{16}O_2$	$5.2x10^3$
Resinter P-139	24 hr at 1600°C	$^{16}O_2$	$4.7x10^3$

High-fired, plasma-torch microspheres obtained from the SNAP-27 (FCA-4) heat source were successfully $^{16}O_2$-exchanged by flowing 45 cm^3/min of $^{16}O_2$ through the material while increasing the temperature at the rate of 235°C/hr up to 1400°C. At this temperature, the $^{16}O_2$ flow was increased to 200 cm^3/min and held for 2 hr. After the 2 hr at 1400°C the flow of $^{16}O_2$ was maintained while the material was rapidly cooled by removing it from the furnace, allowing it to air cool to ∿700°C, and then submerging the crucible in a water bath to further cool it to a temperature of 450°C. Two grades of material from the SNAP-27 heat source were exchanged. The first was nonspherical material which was the original plasma-fired microspheres from the SNAP-27 (FCA-4) which were crushed by handling in the remake of SNAP-FCA-4. The second was production grade, plasma-fired (high-fired) microspheres. Table 3 shows the resulting emission rates of these samples.

Table 3
EFFECT OF OXYGEN EXCHANGE ON FUEL RECOVERED FROM SNAP-27(FCA-4) CAPSULE

Sample	Emission Before Exchange (n/sec/g ^{238}Pu)	Emission After Exchange n/sec/g ^{238}Pu)
Spheres I (nonspherical)	∿18.8x10^3	3.5x10^3
Spheres II	∿18.8x10^3	4.9x10^3
Spheres II-A[a]	4.9x10^3	3.7x10^3

[a]The Spheres II-A sample represents the results obtained after re-exchanging the same batch of microspheres represented by the Sphere II sample.

CONCLUSION

A method of $^{16}O_2$-exchanging large production batches of $^{238}PuO_2$ particles was developed and used successfully to produce low-neutron-emitting $^{238}PuO_2$ on a routine basis. It was also found that previously high-fired material could be exchanged just as effectively as low-fired material.

An important factor that was established is that different grades or levels of neutron-emitting plutonium dioxide material can be produced to meet specific needs. For example, a batch that has been normally exchanged to a neutron flux of 5x10^3 n/sec/g of plutonium-238 can be re-exchanged to yet a lower final neutron emission rate of 3.7x10^3 n/sec/g of plutonium-238.

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