

Thermoseparation of Neutron-Irradiated Tungsten from Re and Os

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Heterogeneous oxidation has been utilized for one-step conversion of metallic W to WO_3 at ~ 750 °C in a stream of air, with simultaneous separation of W from Re and Os impurities which are coproduced during the long neutron irradiation of the W target (~ 50 days). The freshly produced WO_3 is readily soluble in a base for use in a $^{188}\text{W}/^{188}\text{Re}$ biomedical generator. The metallic tungsten target, in the form of small pellets (4×3 mm diameter \times height), was prepared by cold pressing W powder at ~ 3 tons/cm². Sintering (vacuum annealing) the pellets at 1200–1400 °C, under 1–10 μTorr pressure provided good mechanical strength. Analysis of the black residue, which is typically encountered in the dissolution of neutron-irradiated WO_3 targets, indicated that ^{186}W and ^{187}Re were the main constituents. Further, the specific activity of insoluble ^{188}W in the residue was ~ 200 times smaller than that of soluble ^{188}W .

Introduction

Tungsten-188 is in widespread use in the ^{188}W ($t_{1/2} = 69$ days)/ ^{188}Re ($t_{1/2} = 16.9$ h) biomedical generator.^{1,2} W-188 is produced in a nuclear reactor with double neutron capture on highly enriched ^{186}W ($>90\%$). The chemical form of the target can be either metallic or oxide. The main advantage of a metal target is a net increase in the yield per unit target, because a larger amount of W metal can be packed into an irradiation capsule. This is an important factor for the large-scale production of ^{188}W .

The chemical processing of the neutron-irradiated WO_3 targets involves dissolution in excess of hot 1 M NaOH in the presence of H_2O_2 or NaOCl or both.³ This process typically takes several hours and is repeated a number of times in order to ensure complete dissolution of W, because a clear solution is not obtained. The solution always contains a black residue which resists dissolution in alkaline media and must be filtered out. The black residue is only visible for relatively large targets (≥ 100 mg), which have been exposed to a neutron fluence of $\geq 10^{20}$ neutrons/cm⁻² (i.e., 1×10^{15} neutrons/cm⁻²·s⁻¹ \times 24 days).

Because of the chemical inertness of metallic W, processing metal W targets remains a challenge. One approach, however, is to take advantage of the reactivity of molecular oxygen toward metallic W powder at elevated temperatures^{4,5} and subsequent dissolution of the WO_3 as above. This approach has an additional benefit in that the technique can be used for simultaneous separation of W from Re and Os which form volatile oxides.^{6–9}

The goal of our research was to evaluate self-supporting metallic W targets for large-scale production of ^{188}W and to report the effects of various parameters (including temperature, heating period, and sintering temperature), on the conversion of metallic W to WO_3 . We also report on the degree of separation of W from Re and Os impurities which are coproduced during the long neutron irradiation of the W target. In addition, the

preliminary results from ICP-MS and NAA analysis of the black residue produced in a WO_3 target are also presented.

Experimental Section

Metallic tungsten targets in the form of small pellets (4 mm in diameter \times 3 mm in height) were prepared by cold pressing W metal powder at ~ 3 tons/cm² and vacuum annealing (sintering) the pellets at 800–1400 °C under 1–10 μTorr pressure. During the sintering process, the oven temperature was maintained at a given maximum temperature for 3 h. The rates of heatup and cooldown were controlled at ~ 7.5 °C/min. Molybdenum foil was used to support the pellets. For a comparison experiment, a bead of tungsten was prepared by the arc-melting technique.

For development and testing purposes, the apparatus was of a conventional horizontal design using a quartz tube placed into a split tube furnace.¹⁰ A quartz boat containing a W pellet was introduced into the tube and placed at the position of the maximum temperature at the center of the furnace. The furnace temperature was monitored with a thermocouple placed close to the center of the oven. A Variac was used to control the furnace temperature. The volume flow rate of the carrier gas (air) was 15–20 mL/min, and it was monitored by a flowmeter. The apparatus intended for hot-cell operations was of a different vertical design, as shown in Figure 1. This apparatus was a modified version of a system used for the separation of ^{211}At from Bi targets.¹¹

Irradiations were performed at position #1 of the hydraulic tube facility (HT) of the ORNL-High Flux Isotope Reactor (HFIR) for 24 days at a neutron flux of 1×10^{15} neutrons·s⁻¹·cm⁻². The irradiated ^{186}W pellet (~ 180 mg, ^{186}W 96.2%, ^{184}W 2.2%, ^{183}W 0.33%, and ^{182}W 0.45%) target was transferred to a quartz tube (tube A, Figure 1), which was then placed in the assembly. While an air flow rate of 10–20 mL/min was maintained, the furnace was turned on. ReO_3 and Re_2O_7 formed were sublimed and deposited as a thin film on the upper part of the tube assembly (tube B), and OsO_4 was carried by the air and trapped in 2 mL of 1 M NaOH placed downstream (Figure 1). Note that both Re and Os are formed through nuclear transmutations on the ^{186}W

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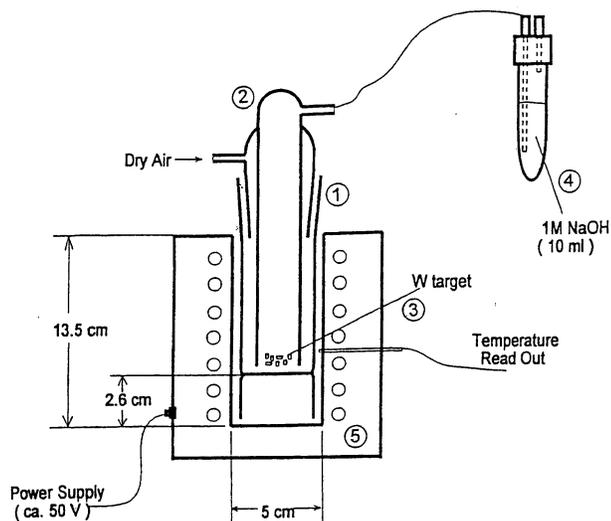


Figure 1. Apparatus for one-step conversion of a neutron-irradiated W target to WO_3 and subsequent separation from Re and Os in air at $750\text{ }^\circ\text{C}$: (1) tube A, containing tungsten pellets; (2) tube B, where rhenium oxide deposits at the cooler end of this tube; (3) tungsten pellets; (4) trap C, containing 1 M NaOH; (5) oven.

target in the reactor.¹² The oven ramp temperature was $\sim 12\text{ }^\circ\text{C}/\text{min}$ from 25 to $750\text{ }^\circ\text{C}$, where distillation was continued for $\sim 15\text{ h}$. At this point, conversion was considered complete, and the furnace was turned off. The air flow was continued for an additional 3 h until the unit cooled to room temperature (the rate of cooldown was $\sim 5\text{ }^\circ\text{C}/\text{min}$). This was to ensure that all of OsO_4 had been transferred to the NaOH trap prior to opening the apparatus. WO_3 was dissolved in 3-fold molar excess of 1 M NaOH directly added to tube A within an hour as the mixture was gently heated. The rhenium oxide deposited at the cooler part of tube B was dissolved in 20 mL of 0.1 M NaOH at room temperature.

Analysis of the Black Residue. A 530-mg target of ^{186}W , with an enrichment of 97% (3% of the other W isotopes) and in oxide form, was irradiated at the HT-HFIR at a neutron flux of $\sim 1 \times 10^{15}$ (with a thermal-to-epithermal ratio of ~ 40) for 2713 h (5 reactor cycles). After ~ 4 years of cooling, the target was dissolved in hot $\text{NaOH}/\text{H}_2\text{O}_2$ and the dissolution repeated two additional times. The residue was then washed with water and methanol and air-dried. Known portions of the residue were then subjected to ICP-MS analysis and NAA/ γ -ray analysis. The sample for ICP-MS was solubilized in 10 mL of aqua regia by microwave digestion at $\sim 200\text{ }^\circ\text{C}$. NAA were performed at the ORNL-HFIR NAA Facility #1 having a neutron flux of 4×10^{14} neutrons $\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$ with a thermal-to-epithermal ratio of ~ 40 , and samples were irradiated for 30 s.

Results and Discussion

Under our experimental conditions, the sintered pellets lost 1–6% of their weights and had a sintered density of 11–13 $\text{g}\cdot\text{cm}^{-3}$ ($\sim 60\%$ of the solid tungsten), depending on the maximum sintering temperature. The physical dimensions of the pellets also decreased $\sim 2\%$ upon sintering. Pellets of natural W and isotopically enriched ^{186}W (96%) metal powder sintered at and above $1200\text{ }^\circ\text{C}$ exhibited good mechanical strength, and they typically retained their integrity during neutron irradiation, receiving a neutron fluence of up to 2×10^{21}

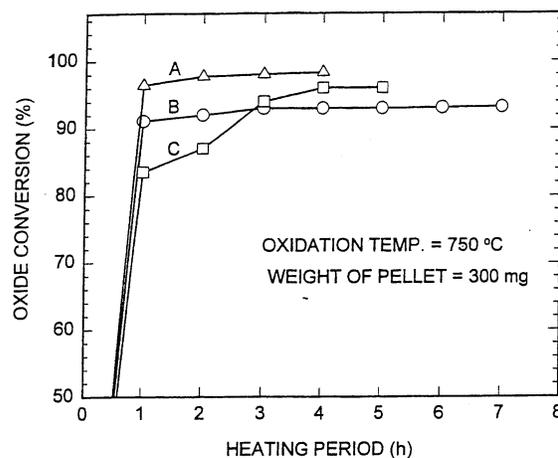


Figure 2. Effect of the heating period on the degree of oxidation at a constant temperature of $750\text{ }^\circ\text{C}$. Sintering temperature: (A) $1000\text{ }^\circ\text{C}$, (B) $1200\text{ }^\circ\text{C}$, (C) $1400\text{ }^\circ\text{C}$.

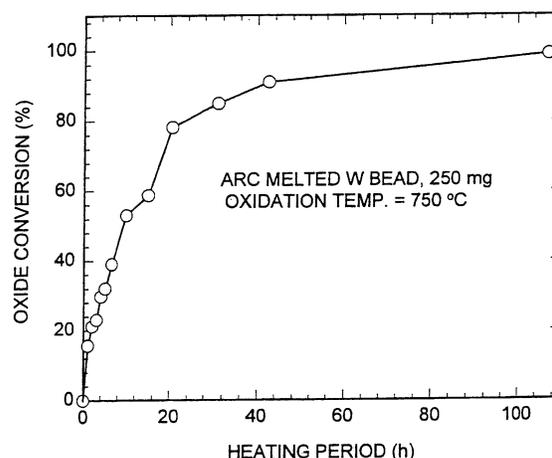


Figure 3. Plot of the degree of the oxide conversion vs duration of the heating for arc-melted beads of tungsten.

neutrons $\cdot\text{cm}^{-2}$ (24 days at a flux of 1×10^{15} neutrons $\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$). The failed sintered pellets were found broken into a few pieces but not completely shattered.

In the experiments involving oxidation of cold W, the degree of oxide conversion was calculated by mass analysis of the boat containing tungsten before and after the oxidation process and assuming WO_3 as the final compound. The effect of the heating period on the degree of the oxidation process at a constant temperature of $750\text{ }^\circ\text{C}$ was measured for a number of pellets which were sintered at various temperatures, all having a mass of $\sim 300\text{ mg}$. The data for three sets of pellets sintered at 1000, 1200, and $1400\text{ }^\circ\text{C}$ are given in Figure 2. In all three cases, $>90\%$ oxide conversion was achieved within the first 3 h. Over 3 h, the results are probably statistically identical. Oxidation of pellets which were not sintered or sintered at $800\text{ }^\circ\text{C}$ was essentially complete ($>98\%$) within 30 min at $750\text{ }^\circ\text{C}$ (data not shown). A similar plot of the degree of the oxide conversion vs duration of the heating for arc-melted beads of tungsten is shown in Figure 3. At $750\text{ }^\circ\text{C}$, $>100\text{ h}$ was required to completely oxidize a solid bead of W. The decrease in the rate of oxidation at constant temperature with time is consistent with the fact that progressively fewer atoms are available as the oxidation proceeds. For oxidation periods of less than 3 h, the trend in the oxidation rate of W can be given in order of "arc-melted beads" $\ll 1400 < 1200 < 1000 \ll 800\text{ }^\circ\text{C}$.

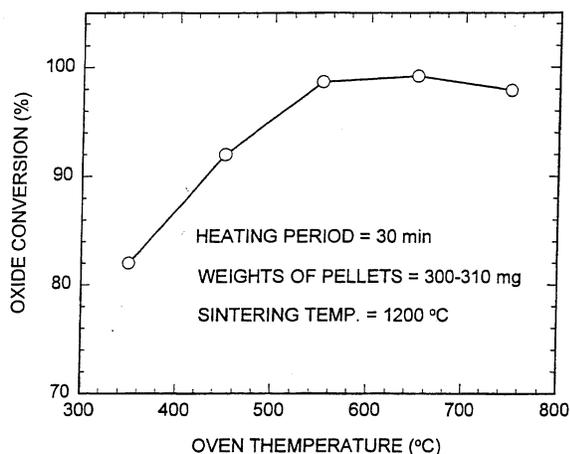


Figure 4. Effect of temperature on the degree of oxidation at a constant heating period. Sintering temperature: 1200 °C.

Table 1. Processing Summary of the Sintered Tungsten Metal Targets^a

target	radioactivity at the end of irradiation (mCi)		
	tube A ^b	tube B	trap C
¹⁸⁸ W	219 ± 11	0.14	ND
¹⁸⁸ Re	0.16	243 ± 13	0.24
¹⁹² Ir	ND	0.01	ND
¹⁹¹ Os	ND	0.15	0.20

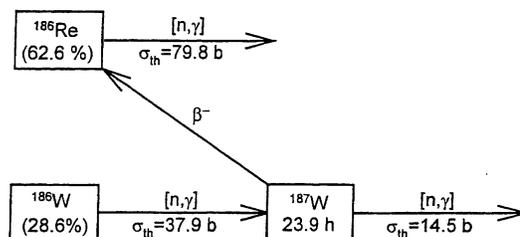
^a The average weight of the targets was 183.1 ± 1.7 mg (96% enriched ¹⁸⁶W). Pellets were sintered at 1400 °C. Targets were irradiated for 24 days at a neutron flux of 1 × 10¹⁵ neutrons·s⁻¹·cm⁻². ^b See Figure 1. ND: not detected.

The much smaller oxidation rate of the W bead relative to that of sintered pellets is due to a near-perfect-crystal lattice of the bead (with a density of ~19 g·cm⁻²), and hence its much smaller surface area for reaction with O₂. The effect of temperature on the degree of oxidation at a constant heating period is shown in Figure 4. In these experiments, the W pellets all had a mass of 300–310 mg and were sintered at 1200 °C. Within 30 min, the oxide conversion was 82% at 350 °C and 98% at 550 °C.

In preliminary test runs, the three neutron-irradiated ¹⁸⁶W pellets were allowed to cool for ~100 days and then processed in the apparatus shown in Figure 1 in a glovebox. Target pellets were heated at 730–750 °C under a 15–20 mL/min flow of air for ~15 h. The freshly produced WO₃ was readily dissolved in a 3-fold molar excess of 1 M NaOH directly added to tube A. Gentle heating increased the dissolution rate without requiring the addition of peroxide. Clear solutions were obtained in the three test runs which were performed. The ability to completely and rapidly dissolve the freshly produced WO₃ is an important advantage of this approach. In three test runs, using the apparatus shown in Figure 1, the dark band formed on the cooler part of tube B was dissolved in water and analyzed for radioactivity. The mass assignments of the Re fraction remain to be performed once the radioactivity has decayed to an acceptable level. A summary of the radioactive contents found in each fraction, tubes A and B and trap C (Figure 1), is given in Table 1. The average experimental yield of ¹⁸⁸W produced in the three test targets, at the end of irradiation, was 1.4 ± 0.1 mCi/mg of ¹⁸⁶W, with an experimental-to-theoretical ratio of 0.62.¹²

As stated earlier, the dissolution of neutron-irradiated WO₃ targets typically contains a black residue of

Scheme 1. Pathway for the Nucleosynthesis of Stable ¹⁸⁷Re from ¹⁸⁶W^a



^a Values in parentheses are the natural abundances of ¹⁸⁷Re and ¹⁸⁶W.

unknown chemical composition which resists dissolution in alkaline media and must be filtered out. In an attempt to understand the possible origin of the residue, a W target was irradiated for 2713 h and then allowed to cool for ~4 years. Prior to processing, the target contained 3.1 μCi of ¹⁸⁸W, 0.06 μCi of ¹⁹²Ir, 20.2 μCi of ¹⁹⁴Os, and 5.1 μCi of ⁶⁰Co. After the processing, 77% of the ¹⁹⁴Os, 72% of the ⁶⁰Co, and <0.03% of the ¹⁸⁸W activity (or <0.001 μCi) were detected in the black residue. A portion (~10%) of residue was subjected to ICP-MS analysis, and the preliminary results indicated the composition of the residue as 39% ¹⁸⁶W, 58% ¹⁸⁷Re, 0.07% ¹⁹¹Ir, and 0.05% ¹⁹³Ir. NAA of another portion of the residue gave a similar mass distribution: 43% ¹⁸⁶W, 53% ¹⁸⁷Re, 0.08% ¹⁹¹Ir, and 4% ¹⁹⁰Os. The absence of an Os signal in ICP-MS is due to the loss of Os during sample preparation (see the Experimental Section). From NAA, the ¹⁸⁷Re content of the total residue was estimated at 58.6 mg or ~11% of the original mass of the target. This value is in fair agreement with the theoretical calculations, indicating that >10% of the ¹⁸⁶W target is transmuted to stable ¹⁸⁷Re under our experimental conditions by the pathway shown in Scheme 1 (thermal neutron cross sections for ¹⁸⁶W and ¹⁸⁷Re were taken from ref 13; the cross-section for ¹⁸⁷W is our measurement, which is unpublished).

¹⁹²Ir and ¹⁹⁴Os are most likely produced from further nuclear transmutation of ¹⁸⁷Re involving a number of neutron capture and β⁻ decay processes. The theoretical treatment of such a complex case is beyond the scope of the present work, but it has been discussed in some detail in ref 12. Cobalt-60 is produced from ⁵⁹Co impurity, which existed in the target.

The origin of the black residue is related to the long irradiation of the W target in the reactor.³ The chemical form(s) of the insoluble W in the residue is not known; both insoluble polytungsten anions and binary compounds with Re are possible. Furthermore, our preliminary results indicate that the specific activity of insoluble ¹⁸⁸W in the residue (2.1 × 10⁻⁵ μCi/mg) is ~200 times smaller than that of the soluble ¹⁸⁸W (5.8 × 10⁻³ μCi/mg). Most likely, this phenomenon is a consequence of the hot atom effect, but the mechanism is unclear at this time. Note that, in our typical production run involving WO₃, the gross radiation field of the residue, 1 week of postprocessing (to allow for short-lived ¹⁸⁸Re and ¹⁸⁷W to decay), is always negligible relative to that of the dissolved target solution.

In conclusion, the fabrication and evaluation of the self-supporting tungsten metal powder target in the form of vacuum-annealed pellets has been reported for routine production of ¹⁸⁸W for use in the ¹⁸⁸W/¹⁸⁸Re biomedical generators. The applicability of heterogeneous oxidation techniques for one-step conversion of

metallic W to WO_3 at $\sim 750^\circ\text{C}$ in a stream of air, with simultaneous separation of W from Re and Os impurities, has been demonstrated. It was shown that the freshly produced WO_3 was readily dissolved in a 3-fold molar excess of 1 M NaOH without requiring the addition of peroxides. Highly enriched ^{187}Re and number of neutron-rich isotopes of Os are coproduced during the long neutron irradiation of the W target. It was shown that the valuable ^{187}Re fraction can readily be recovered. Because of its simplicity, the technique has been proven suitable for hot cell and remote operations. In addition, our preliminary analysis of the black residue, which is typically encountered in the dissolution of neutron-irradiated WO_3 targets, indicating that ^{186}W and ^{187}Re are the main constituents of the residue. Unexpectedly, the specific activity of insoluble ^{188}W in the residue is ~ 200 times smaller than that of soluble ^{188}W .

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