ORNL/TM-2022/2355

The Recovery of Medical Isotope ^{188}W from Irradiated W Metal Target – A New Approach

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February 2023

OAK RIDGE National Laboratory

ORNL IS MANAGED BY UT-BATTELLE LLC FOR THE US DEPARTMENT OF ENERGY

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Radioisotope Science and Technology Division

THE RECOVERY OF MEDICAL ISOTOPE 188W RECOVERY FROM IRRADIATED TUNSTEN METAL TARGET – A NEW APPROACH

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ACRONYMS

DI	deionized
ID	inner diameter
NPH	normal paraffin hydrocarbon
OD	outer diameter
ORNL	Oak Ridge National Laboratory

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ABSTRACT

There is widespread use of tungsten-188 in $^{188}W(t_{1/2} = 69\ d)/^{188}Re(t_{1/2} = 16.9\ h)$ biomedical generators. The Oak Ridge National Laboratory (ORNL) has been providing this product to the world since 1999. In ORNL's High Flux Isotope Reactor ^{188}W is produced via irradiation. Enriched ^{186}W targets in the form of sintered metallic rings achieve a compact loading in the irradiation vessel, providing a high yield per unit target. The enrichment of the target is >90% ^{186}W, and this isotope undergoes double-neutron capture to produce the desired ^{188}W product. While ^{188}W is produced by neutron bombardment, $^{191}Os(t_{1/2} = 15.4\ d)$ is simultaneously produced as a by-product and should be separated from ^{188}W by post irradiation treatment.

In the current processing pathway, the irradiated W metal rings are first converted into an oxide form, WO_3, by heating the rings at 750°C in a quartz reaction vessel inside a vertical furnace under a constant airflow. During heating, tungsten metal reacts with oxygen in the air to form tungsten oxides (WO_3) that are soluble in the follow up dissolution in 6 *M* NaOH. This oxidation process also converts ^{188}Os (the decay daughter of ^{188}W) and ^{191}Os (15.4 *d*, the irradiation produced by-product) into OsO_4, a highly volatile and toxic gas. The gaseous effluents driven from the quartz reaction vessel are passed through a scrubbing array to remove OsO_4 before the air is discharged from the process.

With this heterogeneous oxidation method, the metal target is simultaneously transformed into a soluble oxide form and volatile OsO_4 is removed from the solid WO_3 product by airflow and absorbed by the scrubbing array.

There are two major disadvantages of the method. First, oxygen reacts with only tungsten metal and not if tungsten alloys with other elements at high temperatures. The O_2–W reaction is retarded by WRe or WC formation or by non-W layers forming on the surface of the irradiated W rings and second, since OsO_4 of high yield (>90%) must be absorbed completely from the reaction of ($Os + O_2$), the NaOH scrubbers had to be made redundant size (2 × 1.5 L) for safety reasons.

To resolve both potential problems, direct dissolution of the irradiated W metal target with a selected reagent is preferred because it avoids the heating step that generates a large amount of volatile OsO_4. Hydrogen peroxide (H_2O_2) is a possible candidate for dissolving tungsten metal and alloys as well, although there is little information available regarding reactivity of Re or Os in H_2O_2.

The experimental results of dissolving nonradioactive W, Re and Os in H_2O_2 under various conditions provided in this report illustrates a method of H_2O_2 dissolution for irradiated W targets, with a complete dissolution of W and Re, but ≤10% dissolution of Os (converted into gaseous OsO_4 and carried out into a scrubber for absorption) during processing of irradiated W target. The portion of undissolved Os can be separated from W solution by a follow-up filtration step. Solubilities of W, Re, and Os in H_2O_2 at a temperature range of 14°–50°C are presented. A dissolution rate of W metal per surface area of W metal in H_2O_2 is calculated based on results of dissolving a W metal cylinder of known surface area in H_2O_2 at room temperature without stirring.

1. INTRODUCTION

Oak Ridge National Laboratory (ORNL) has produced ^{188}W since 1999 [1] via irradiation of an enriched ^{186}W target in the High Flux Isotope Reactor, which undergoes a double-neutron capture reaction to produce the desired ^{188}W product. In order to obtain the required specific activity of ^{188}W, two cycles (~45 days) of irradiation are typically required. However, this lengthy irradiation process produces Re and Os impurities (figure 1).

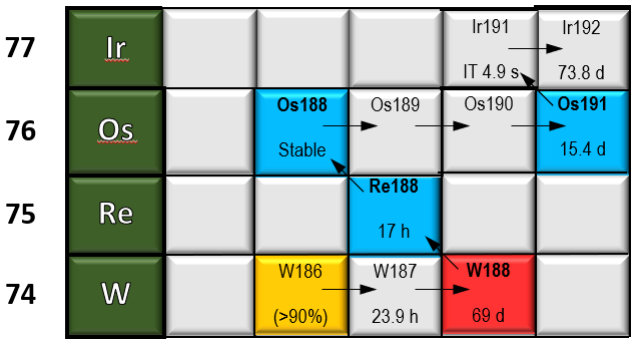


Figure 1. Production pathway for W-188 and its by-products by neutron irradiation.

The pressed and sintered ^{186}W metal rings were chosen as the target form for neutron irradiation because of their high density (19.3 g/cm^3) and high thermal conductivity [0.4 (cal/s)/(cm^3 °C/cm)]. Tungsten's good thermal conductivity is comparable to metals of aluminum (0.5) and copper (0.99). These properties allow for high target loading per rabbit, increasing the amount of W target per irradiation cycle. The sintered, irradiated targets are not readily dissolved for product preparation, requiring the conversion of the irradiated W metal target to a soluble oxide form, WO_3, through gas–solid oxidation. The conversion of W to WO_3 has the secondary purpose of separating Os impurities from the ^{188}W product via an array of processing equipment.

1.1 ORNL'S ^{188}W PROCESS AND PROCESSING SYSTEM EVOLUTION SINCE 1999

The processing equipment for treating irradiated W metal targets consists primarily of two parts: a quartz reaction vessel inside a vertical furnace and an OsO_4 scrubbing array. As shown in figures 2–4, the equipment design has evolved from 1999 to 2006 to 2020.

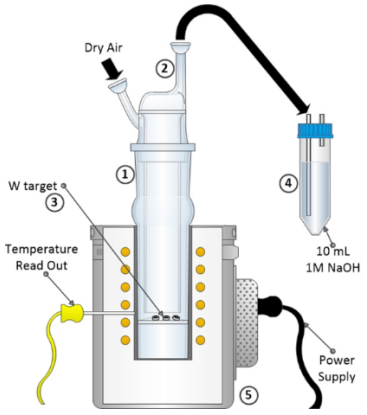


Figure 2. Apparatus design (1999) for one-step W → WO_3 conversion: (1) tube A, containing W pellets; (2) tube B, where Re deposits on the cooler end; (3) W pellets; (4) NaOH trap for OsO_4; (5) vertical furnace.

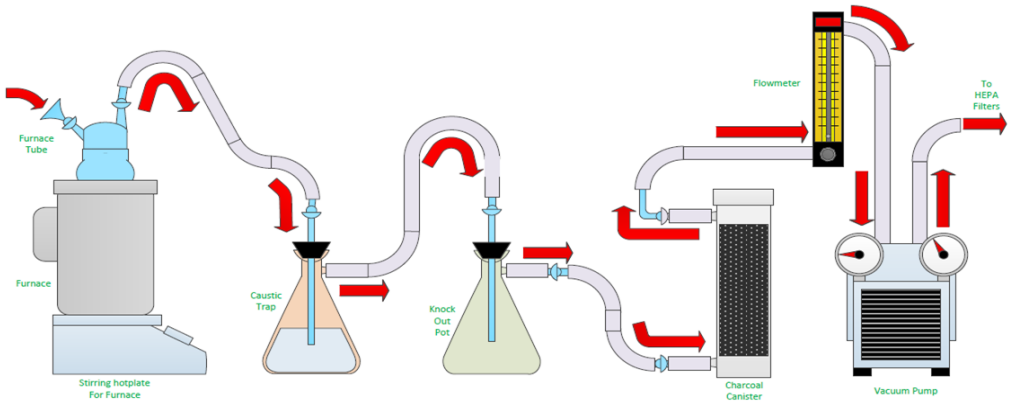


Figure 3. The furnace and OsO_4 scrubbing array implemented in ^{188}W process since 2006.

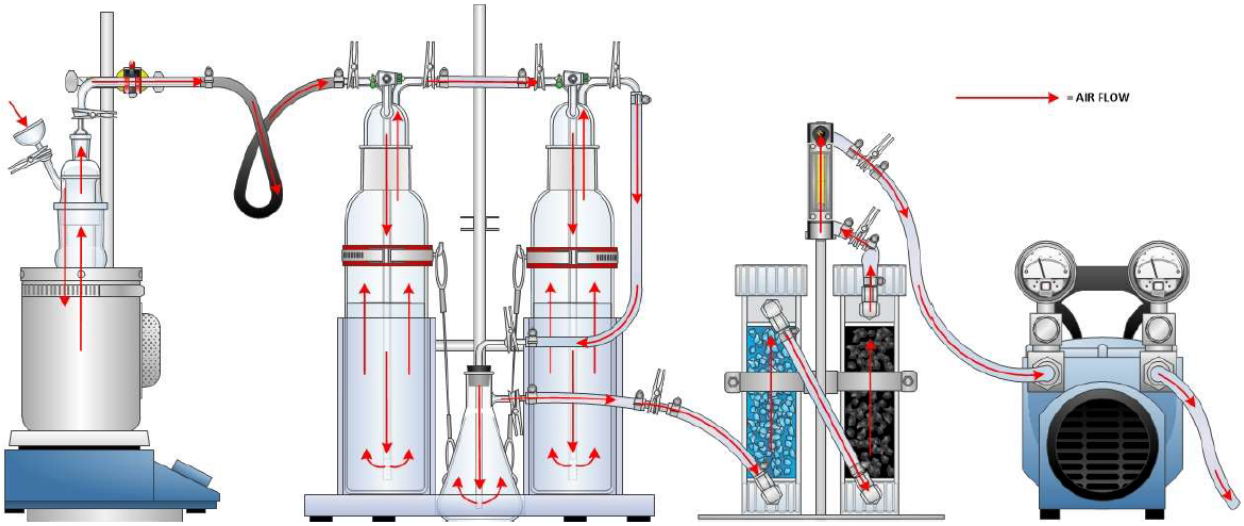


Figure 4. The furnace and OsO4 scrubbing array of the 2020 design for ^{188}W process.

It is important to note the differences between these equipment system designs.

1. The equipment array designed in 1999 was for the initial stage with 0.54 g of irradiated W target, and the air supply was delivered by a gas cylinder, referred to as positive pressure mode (+P). The equipment arrays of 2006 and 2020 are for mass production of ^{188}W with 4.83 g irradiated W target, and the air supply was delivered by a vacuum pump in negative pressure mode (-P).

2. A 1999 design of OsO_4 scrubber operated with 10 mL of 1 *M* NaOH without a charcoal canister (at 20 mL/min airflow). In the 2006 design, the scrubbing array consisted of a scrubber containing 250 mL of 0.1*M* NaOH, a pot of knockout, and a can of charcoal (being operated at an air flow of 3-9 L/min). In 2020, a scrubbing array includes two scrubbers in series, each containing 1.5 L of 1 *M* NaOH, a knockout pot, and a charcoal canister (which is used with an air flow of ≤2 L per minute).

3. There are differences between the 2006 and 2020 NaOH scrubbers not only in their sizes, geometric shapes, and amounts of NaOH used, but also in the gas inlet tubes. As compared with the straight open inlet tube of the 2006 scrubber, the two caustic scrubbers of 2020 with dispersion frits improved OsO_4 absorption by interaction of tiny gas bubbles of increased interfacial area with liquid NaOH (Figure 5).

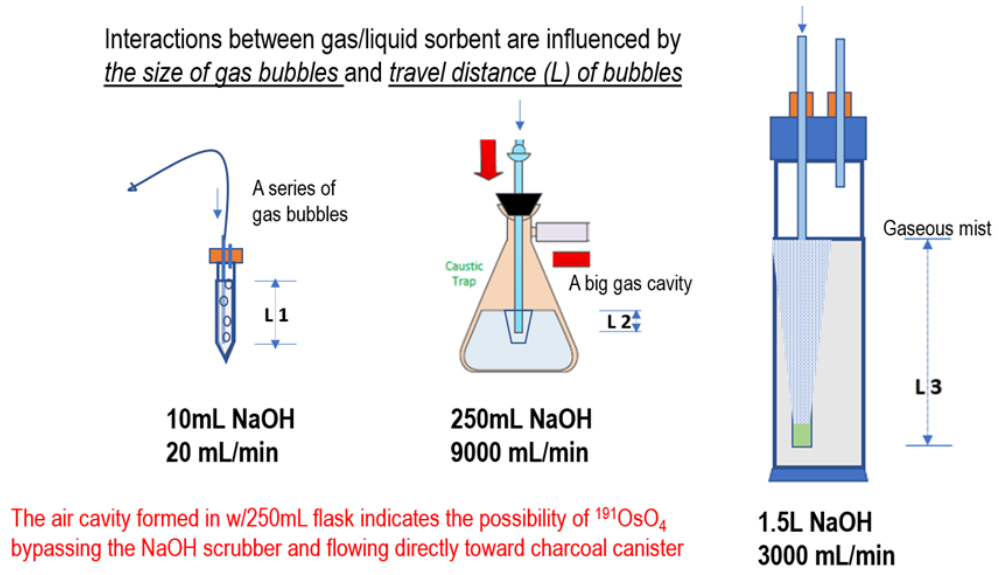
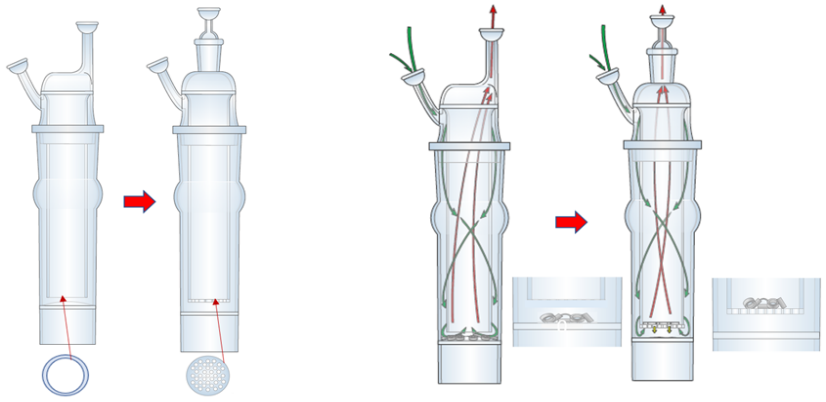


Figure 5. Comparison of scrubbers in 1999, 2006, and 2020 designs.

4. The quartz reaction vessel used in the 1999 and 2006 systems was identical, as the two quartz tubes (A & B in Fig.2) joint-connected to allow airflow along the jacket from top to bottom, where oxidation reaction with W pellets at 750°C, then out of the assembly from the chimney (in tube B) into the caustic scrubber. The design of the vessel was revised in 2020. As shown in Figure 6, tube B was changed from straight open to one with a perforated stage for W rings to sit on.



Open tube vs. perforated stage W rings on vessel bottom vs. on the stage

Figure 6. Vessel chimney structure change in 2020 design with W rings on perforated stage.

The change in the vessel structure ensures that interaction of O_2 and W rings with minimum amount of surface coverage by converted WO_3 powder (the rings were buried with bulky WO_3 when they rested on the bottom of the reaction vessel).

The purpose of the design change is to improve the efficiency of the heterogeneous chemical reaction of gaseous O_2 with the solid W metal rings during the heating of the W metal target at 750°C with an air flow (21% O_2) passing through the quartz vessel and then to the scrubbing array. When W metal is heated in air, metallic W is converted to WO_3 powder (Eq. 1), which remains in the vessel while Re and Os are oxidized into semi volatile or volatile oxide forms (Eqs. 2 and 3), allowing airflow to carry them out of the heating zone.

$$2W_{(s)} + 3O_{2(g)} \rightarrow 2WO_{3(s)} \quad (1)$$

$$Os_{(s)} + 2O_{2(g)} \rightarrow OsO_{4(g)} \quad (2)$$

$$2Re_{(s)} + 3O_{2(g)} \rightarrow 2ReO_{3(g)} \quad \text{or} \quad 2Re_{(s)} + 7O_{2(g)} \rightarrow 2Re_2O_{7(g)} \quad (3)$$

The toxic and volatile OsO_4 (both ^{191}Os and ^{188}Os) from the airflow is then absorbed by a sodium hydroxide (NaOH) scrubber downstream (Eq. 4), whereas ReO_3 and Re_2O_7 sublimate and deposited on top of the quartz reaction vessel outside the heating zone. The reactions 1–4 are all heterogeneous reactions whose reaction efficiency heavily depends on optimal engineering parameter control and equipment design.

$$2OsO_{4(g)} + 4NaOH_{(aq)} \rightarrow 2Na_2OsO_{4(aq)} + 2H_2O + O_{2(g)} \quad (4)$$

The efficiency of the reaction shown in Eq. 1 determines the percentage of W to WO_3 conversion (i.e., the ^{188}W recovery rate of the campaign), while The efficiency of the reaction shown in Eq. 4 determines the facility's radiological safety because $^{191}OsO_4$ penetrates high efficiency particulate air filters if it escapes from the scrubbing array **[2]**.

1.2 OTHER PATHWAYS TO DISSOLVE W TARGET WITH LESS $^{191}OSO_4$ FORMATION

The generation of OsO_4 by heating a W(Os) metal target in an airflow is a highly efficient process with 90~100% of Os/OsO_4 conversion rate. It requires a redundant OsO_4 scrubbing array to ensure the absorption of 100% of the harmful volatile OsO_4 generated during the heating process. This is the reason why NaOH scrubbers increased from 10 mL of 1 *M* NaOH to two 1.5 L of 1 *M* NaOH from 1999 to 2020. The OsO_4 scrubbing array of the 2020 design has successfully reduced the chances of $^{191}OsO_4$ being released during ^{188}W campaigns. It is important to note, however, that while the volatile $^{191}OsO_4$ is produced in the ^{188}W process, there is a possibility of OsO_4 release in the event that the scrubbing array malfunctions or errors are made in the arrangement of the arrays.

The formation of volatile OsO_4 is a prerequisite reason why ^{191}Os release might occur into the environment. The coproduction of ^{191}Os with ^{188}W product is inevitable during the reactor irradiation of the ^{186}W target. As long as the formation of volatile $^{191}OsO_4$ is constrained, it may be possible to minimize ^{191}Os release. An ideal method would be to use a suitable reagent to dissolve the irradiated W metal target directly without heating it (Eq. 2). However, dissolving W metal selectively, while leaving Os, Re, and other impurities undissolved, would be the best option.

When ORNL started designing the ^{188}W process 20 years ago, this option was considered, but didn't materialize due to the lack of such dissolving reagent candidates. All dissolving agents in the literature

appear to dissolve both W and Os simultaneously. As an example, the dissolution of W metal in H_2O_2 has been discussed by numerous sources since the 1930s. Murau, 1961 published comparative data on the dissolution of metallic W and Mo in H_2O_2 **[3]**, confirming that W metal can be dissolved in hydrogen peroxide. Due to the many similarities between W and Os, chemists inferred that Os can be dissolved in H_2O_2 as well. The occurrence of gas bubbles when Os comes into contact with H_2O_2 has been considered positive evidence supporting this hypothesis.

As part of the 2020 campaign to mitigate OsO_4, efforts were made to dissolve Os metal residue using several reagents. Since H_2O_2 failed to dissolve Os metal residue, the author explored the questionable conclusion that "Os metal is soluble in H_2O_2 at room temperature". This led to a series of dissolution tests, including sintered W rings, chunks of W metal, Os and Re metal powder, with and without stirring at 14°C to 50°C

As only a small portion of Os metal powder had been dissolved by H_2O_2, a second round of tests was conducted using an organic normal paraffin hydrocarbon (NPH, an OsO_4 sorbent) phase on top of the aqueous phase to determine if (1) the disappeared small portion of Os solids was dissolved in liquid phase or converted into gaseous Os species and (2) OsO_4 is the chemical form of the gaseous Os species or not, since only gaseous OsO_4 can react with inert NPH to form solid OsO_2 being trapped in the organic phase. This second round of Os dissolution tests was carried out in H_2O_2 with NPH at a temperature range of 14°C to 50°C.

After two rounds of experiments, a selective dissolution method using 30% H_2O_2 has been proposed for treating irradiated W metal targets in the future. The dissolution rate of W metal is dependent on its surface area. Based on dissolution data of a W metal cylinder of known surface area, we calculated a rough dissolution rate in 30% H_2O_2 per unit area of W metal.

2. EXPERIMENTAL METHODS

2.1 REAGENTS AND MATERIALS

Osmium metal powder (841 µm or 20 mesh, 99.95%) was purchased from Sigma-Aldrich. Tungsten metal powder (10 µm, 99.99%) and Re metal powder (788 µm or 22 mesh, 99.999%) were purchased from Alfa Aesar by Thermo Fisher Scientific. A cast cylinder of W metal (99.97%, OD3.175 × L6.35 mm) was purchased from VWR/Summus (Part no. 44250-09). Thirty percent H_2O_2 was purchased from Sigma-Aldrich. A broken piece (~¼) of enriched ^{186}W ring was pressed and sintered (1,400°C for 4 h) by ORNL's Stable Isotopes Group. NPH was purchased from Exxon Mobil Chemical Co.

2.2 PROCEDURES

Operations: Load a known amount of solid metal into a vial, then add H_2O_2 in room temperature and begin to record the time taken for the metal to dissolve. The dissolution can be stopped by replacing the H_2O_2 in the vial with deionized (DI) water, followed by filtering, drying, and weighing the remaining solids (figure 7).

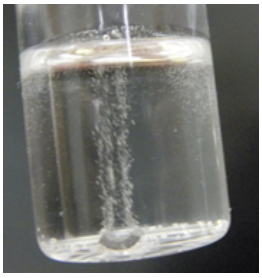


Figure 7. Dissolution of solid material in 30% H_2O_2 without heating and stirring (soak in a vial of H_2O_2 directly).

Operations: Set up a water bath with stirring at the designated temperature (°C), monitored with a Digi-Thermo Meter. A vial containing a known amount of solid metal was placed in a water bath pre-adjusted to the designated temperature (°C) and monitored with a Digi-Thermo Meter. To begin the dissolution process, add H_2O_2 to the vial and start recording the dissolution time. To stop dissolution, replace H_2O_2 in a vial with DI water, then filter and dry the solids (Figure 8).

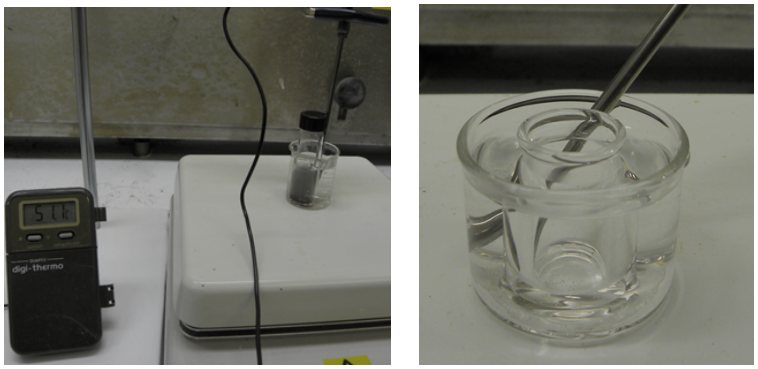


Figure 8. Dissolution of solid material in 30% H_2O_2 with heating and stirring.

Operations: In a vial, place a known amount of Os powder and pre-wet the powder with DI water of known volume. Add organic NPH to form a liquid organic phase above the aqueous phase. Set up the water bath at the designated temperature (°C) with stirring, then add a known volume of H_2O_2 and record the time. To stop the dissolution, add DI water to replace the H_2O_2 in the vial. To measure the weight of undissolved solids in aqueous phase, pipet the solid with water onto filter paper, then dry and weigh it. Transfer organic NPH with imbedded solid onto separated filter paper, dry, and weigh (Figure 9).

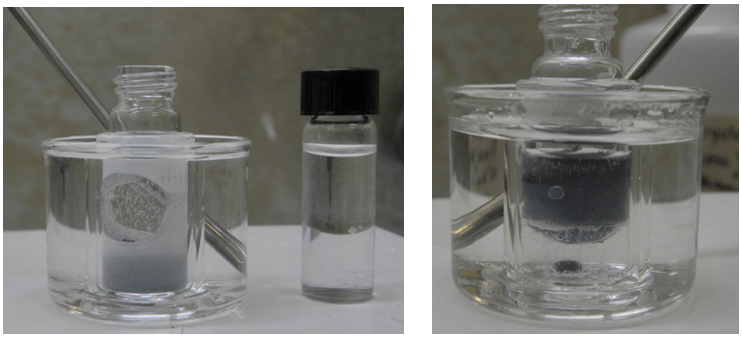


Figure 9. Dissolution of Os powder in 30% H_2O_2 at designated t°C with stirring and a NPH phase in vial.

Operations: Pre-weigh a Whatman 542 paper with a pore size of 2.7 microns prior to using it. Filter the contents of the vial by using filter paper and a Thermo-Scientific pump (Part no. 420-1901). After washing with ethanol, unpack the paper and allow it to air dry. Air drying takes 5–7 days for each (paper+solid). Weighing begins on the third day and continues until the readings stabilize. Weigh the air-dried filter paper with a Mettler-Toledo electronic balance, then calculate the difference between pre- and post-filtration (Figure 10).

Figure 10. Filtration setup (left) and equipment (middle) of undissolved solids and equipment for measurements of solid weights (right).

3. RESULTS AND DISCUSSION

3.1 FIRST ROUND OF DISSOLUTION EXPERIMENTS

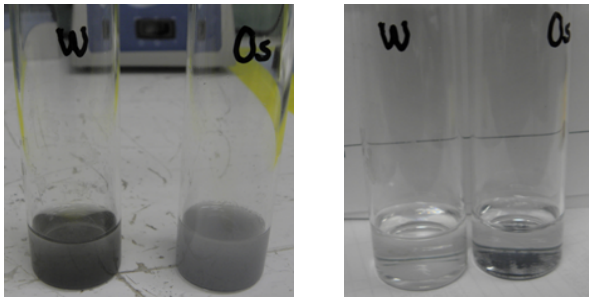
From October 2020 to July 2021, a series of dissolution tests in 30% H_2O_2 was performed with W and Os metal powders, as well as with sintered W metal rings. The experimental conditions for these tests are listed in Table 1.

Table 1. Experimental conditions of dissolving W, Os metals and the mixture in 30% H_2O_2, respectively.

Date	Metals (mg)	H_2O_2 (mL)	Stir	Heating	Bubbling	Clear after	t° C $_{dissolution}$	In vial as
12/11/2020	W (54.1)	5	N	N	Mild	1 h 56 min	Ambient	Clear
	Os (23.3)	5	N	N	Aggressive		> Ambient	Solid
12/17/2020	W Ring (158.1)	8	N	N	Mild	3 h	Ambient	Clear
	W (78.9)	8	N	N	Mild	1 h 30 min	Ambient	Clear
	Os (83.2)	8	N	N	Aggressive		> Ambient	Solid
12/21/2020	W + Os (70.1+73.3)	5	N	N	Aggressive		> Ambient	Reduced solid
12/29/2020	W (67.4)	4	Y	≤50	Aggressive	12 min	Ambient	Clear

** "Mild" = tiny bubble streams. "Aggressive" = lots of bubbles. Os remained undissolved.

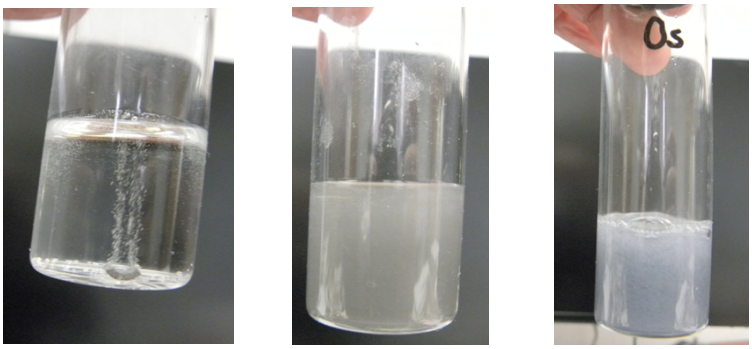
During the experiment on 12/11/2020, both vials containing metal powders W and Os, respectively, emitted gas bubbles after 30% H_2O_2 was added (more bubbles in the vial of Os). This gave the impression that both W and Os metal powders would dissolve in H_2O_2, which makes dissolution time the determining factor. The vials were left on a benchtop without stirring or heating for 1 h 56 minutes. There was no visible W powder left in one vial, while Os metal powder continued to bubble in another. After sitting overnight, the Os vial stopped bubbling with solid Os powder sitting in the vial (Figure 11).



During After

Figure 11. W and Os metal powders in H_2O_2 during and after dissolution.

In the experiment on 12/17/2020, the previous test was repeated using a third vial containing one-fourth piece of enriched ^{186}W ring to dissolve with H_2O_2. Testing with sintered W ring provides information about the dissolution of solid W metal with a low surface area. A steady stream of gas bubbles was observed to be generated without any heating or stirring for the W ring, while more bubbles were observed for the W powder, and even more bubbles were observed for the Os powder (but no Os was dissolved) (Figure 12).



(1) **(2)** **(3)**

Figure 12. W ring (1) , W powder (2) and Os powder (3) in H_2O_2 during dissolution (no heating/stirring).

With more W powder (Vial W-2), a complete dissolution was achieved in 1 h 30 min. W ring (Vial W-1), with much less surface area, took 3 h to achieve the condition of no visible W residue, whereas Os metal powder (Vial Os) generated gas bubbles that stopped overnight and showed no dissolution of Os powder by observation prior to weighing (Figure 13).

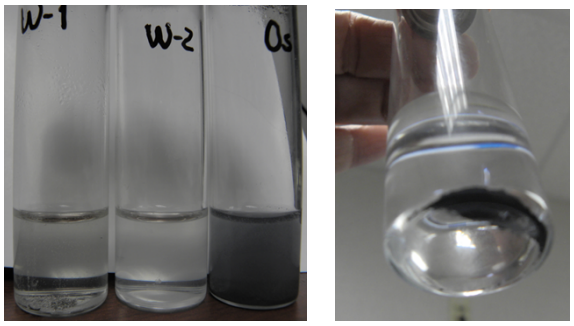


Figure 13. No visible undissolved W solid in vials of W-1 & W-2; Os powder showed no dissolution.

On 12/21/2020, dissolution of a known amount of mixture of W and Os metal powders was tested to determine the mutual influence of the reactions to W and Os, instead of each one separately (Figure 14). The dissolution of W-Os seemed more aggressive than in individual vials, with enormous gas bubbles generated. As gas bubbling will continue in the reaction between Os and H_2O_2, filtration began after 2 hours 9 minutes of dissolution (longer than the dissolution time for W in previous experiments). Mixture dissolution results (Figure 14) are comparable to those of individual metal dissolution according to the data on filtration/drying/weighing. In this stage, the fact that H_2O_2 does not dissolve Os metal has been accepted by experimenters.

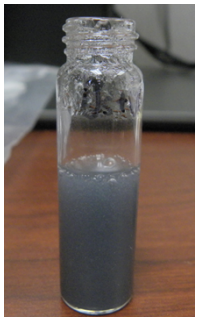


Figure 14. Dissolution of a W–Os powder mixture in H_2O_2 with no heating or stirring.

An experiment on 12/29/20 was performed with W powder and H_2O_2 with a stirrer bar inside the vial to assess the effects of heating or stirring (Figure 15). Vials were placed in a water bath heated by an HP-3000 hot/stirring plate. At water temperature of ≤50°C and stirring, the W metal powder in the vial was dissolved completely within 12 minutes, compared to 1.5 hours without stirring at ambient temperature.

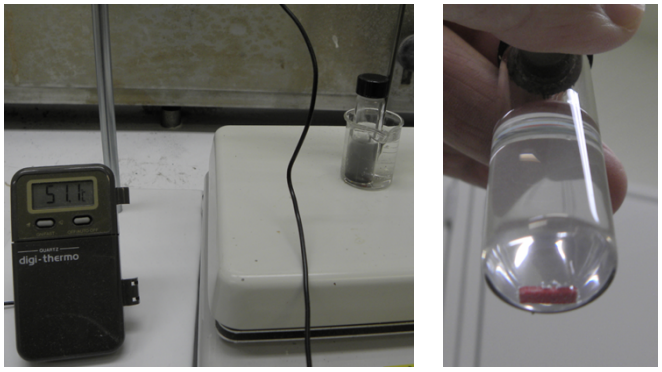


Figure 15. Dissolving with stirring at ≤50°C (left) and after completely dissolved in 12 min (right).

For the above experiments, the contents in vials, whether they were clear solution or solid, were filtered with pre-weighed filter paper (2.7 μm), washed with ethanol, and then air-dried. Based on the weight difference in the dried filter papers, the undissolved solids were calculated (Table 2).

Table 2. Metal content in dissolving vials and relevant weight measurement data.

Date	Metals in vials (mg)	Paper (mg)	Paper + undissolved solids (mg)	Undissolved solids on paper (mg)	Undissolved vs. original	Note
12/11/2020	**W** (54.1)	160.7	162.9	2.2	4.07%	
	Os (23.3)	161	183.2	23.3	**95.29%**	
12/17/2020	**W** Ring (158.1)		No filtration	To keep enriched ^{186}W		Vial content is stored
	W (78.9)	157.9	161	3.1	3.93%	
	Os (83.2)	160	240.7	80.7	**97.0%**	
12/21/2020	**W** + **Os** (70.1+73.3)	154.7	227.7	73	**99.59%** (Os)	Assume W 100% dissolved
12/29/2020	**W** (67.4)	160.9	163.7	2.8	4.15%	

Note: Percentage calculations are based on the assumption of undissolved solids remain in metal forms.

Except for the dissolved solution of the ^{186}Os ring piece (12/17/2020), all other vial contents were filtered, dried, and weighed to compare with filter paper weights prior to use .

The vials containing the W metal powder were clear and had a faint residue of a white cotton-like material that was barely visible. The undissolved residue from W dissolution was weighed at ~4% of the initial weight of W powder. Undissolved W from white cotton–type residue was obviously no longer in W metal form. There were many more gas bubbles observed in vials containing Os metal powder during dissolution in H_2O_2 (seemingly dissolving), but Os metal powder remained the same after bubbling stopped with time. The behavior of Os in H_2O_2 gives a tentative conclusion that aggressive bubbling in vials containing (Os + H_2O_2) was not the result of Os dissolution in H_2O_2, but more likely was a catalytic reaction of the conversion of H_2O_2 to water, which stopped when the concentration of H_2O_2 was reduced.

These experiments have demonstrated that H_2O_2 can dissolve powdered W metal or sintered rings into a water-soluble form, although ~4% of the original W metal turns into a solid compound of unknown chemical composition (white cottons residue).

Under ambient temperature, approximately 3% weight loss was observed in the original Os powder when it was interacted with H_2O_2. The knowledge of the reaction pathway leading to this loss of 3% solid Os in H_2O_2 deserves further studies.

While the vials after W dissolution in H_2O_2 showed no temperature increase, those after Os dissolution showed an increase in temperature (exothermic reaction).

3.1.1 Summary of the First Round of Dissolution Tests

The dissolution of W metal powder/chunk in H_2O_2 is extremely efficient, with a dissolution rate of at least 96% (The 4% weight percentage of the undissolved white cotton residue vs. original W weight was based on an assumption of the white cotton residue in W metal form), a higher conversion rate than the result of 90% obtained using the heating method in a non-radioactive test [2]. The exact equation for W dissolution in H_2O_2 was not found in literature. The author proposes an equation as follows, and the reasons for choosing H_2WO_4 as the reaction product are discussed in Section 4.2.3:

$$W_{(s)} + 3\ H_2O_{2(l)} \rightarrow H_2WO_{4(l)}\ (\text{i.e., } WO_3.H_2O) + 2\ H_2O \qquad (5)$$

The minimum amount of H_2O_2 required for the dissolution of W metal can be calculated as 1.828 mL of 30% H_2O_2 per gram of W metal (i.e., **1.828 mL/g W metal**). As per Eq. (5), 30% H_2O_2 used in this study is always in excessive amounts toward W metal.

Dissolution of Os metal powder in H_2O_2 at ambient temperature (higher than ambient due to exothermic reaction) is obviously low, with a “dissolution rate” of only 3%–4%. At this stage, it is unknown where the "dissolved Os” went, either to liquid phase or to gaseous species such as OsO_4 that escaped from the vials .

The results of the first round of experiments prompted the following questions:

- Can higher temperatures result in more dissolution of Os metal?
- Is the "dissolved Os” converted into volatile OsO_4 that needs to be scrubbed further?
- What is the behavior of Re metal in H_2O_2?
- What is the dissolution speed of W metal in H_2O_2 if it is in chunks rather than powder form?

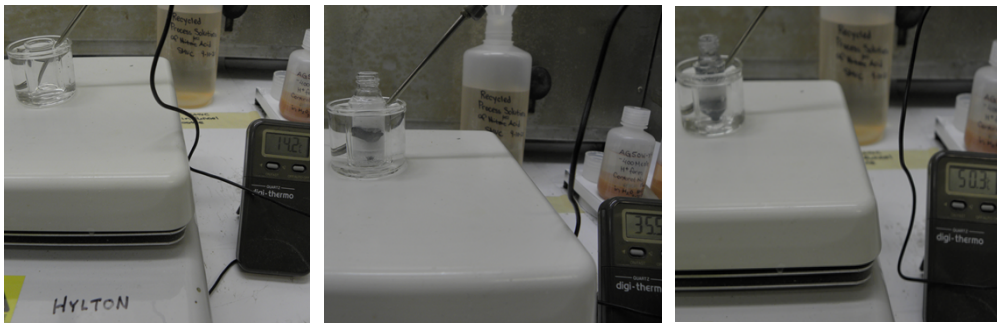
3.2 SECOND ROUND OF DISSOLUTION TESTS

The experiment on 12/29/2021 demonstrated that Os metal could be dissolved at higher temperatures by using a controlled temperature water bath. By using the NPH organic phase on top of the aqueous H_2O_2 phase of the Os dissolver vial, the OsO_4 (if it is produced during Os dissolution in H_2O_2) can be absorbed and reduced to visible black $OsO_2.xH_2O$ trapped in organic phase [2]. After filtering, drying and weighing the remaining Os in the aqueous phase and the black $OsO_2.xH_2O$ in the organic phase, the mass distribution in both phases can be determined. Additionally, the formation of visible black $OsO_2.xH_2O$ would confirm that OsO_4 is generated during the dissolution of Os in H_2O_2.

3.2.1 Dissolution of Os Metal Powder in H_2O_2 at Elevated Temperature with Organic NPH as OsO_4 Sorbent

Following a few trials using NPH as OsO_4 sorbent in the dissolver vial, a series of experiments were conducted on 9/28/2021 with three batches of Os metal powder of known amounts in vials, prewetted with 0.1 ml DI H_2O, then with 2 mL of organic NPH added into the vials, respectively. The three vials were adjusted to the desired temperature in the water bath with stirring, then 1.0 mL of 30% H_2O_2 was added dropwise into vials with time recorded.

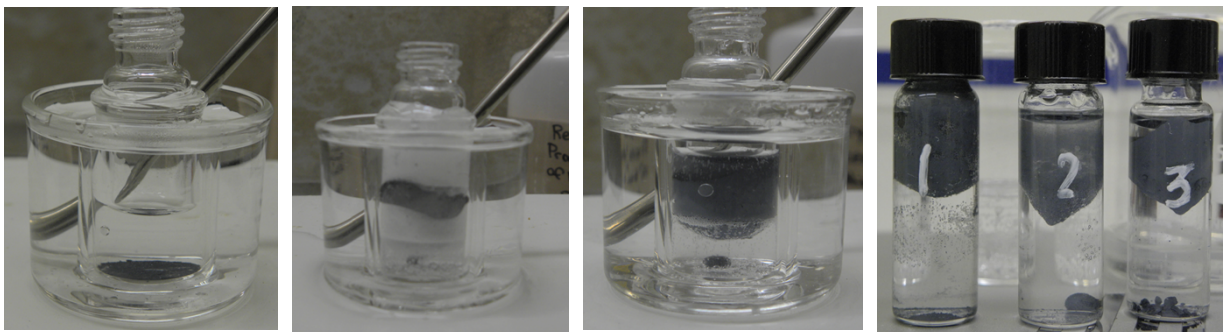
The purpose of this experiment was to investigate (1) whether Os metal powder will dissolve further in H_2O_2 at elevated temperatures and (2) whether "dissolved" Os will turn into volatile OsO_4. The temperatures selected were ambient (14.6°C), 35°C, and 50°C. We set the maximum temperature for the proposed dissolution process of irradiated W metal target in H_2O_2 to < 60°C because H_2O_2 decomposition ($2\ H_2O_2 \rightarrow 2\ H_2O + O_2$) increases with temperature **[4]**. Each experiment was controlled by a different temperature as shown in figure 16.



Ambient t°C (14.6°C) **Set for 35°C** **Set for 50°C**

Figure 16. Temperature control in experiments of Os metal dissolution in H_2O_2 with NPH sorbent.

During each dissolution run, the water bath temperature was set and maintained. The Os metal powder was weighed into the vial and prewetted with 0.1 mL DI water (Trials have shown that the Os powder would be wrapped into the organic NPH phase after direct contact with NPH, and would remain in the organic phase even after 30% H_2O_2 had been added to the mixture, which interfered with the separation of the undissolved solid Os from $OsO_2.4H_2O$ derived from the solution. After adding NPH to the vial, the vial was placed in a water bath to reach the desired temperature. The dissolution time of the 30% H_2O_2 was recorded as soon as 1.0 mL of H_2O_2 was added. Three experiments were planned each lasting 60 minutes. However, the experiment at 35°C was interrupted after 45 minutes. To stop the dissolution experiment, DI water was added to the vials to replace or dilute the aqueous phase. These operations are depicted in figure 17.



Before H_2O_2 added **H_2O_2 added** **Close to 60 min** **After replaced with H_2O**

Figure 17. Observation of the Os powder dissolution in H_2O_2 with NPH as volatile OsO_4 sorbent.

In addition to the general description of the post-dissolution operations in Section 2.2, pipetting undissolved Os metal powder out with addition of more DI water to the vial was the first step with the NPH phase (which impregnates black $OsO_2.xH_2O$) above the aqueous phase. The solids in H_2O_2/H_2O were transferred directly from the vial to the filter paper in the filter set up. The vacuum-filtration of the filter paper contents was performed with the addition of ethanol washes until no visible solids remained in the aqueous phase in the vial. The filter paper + solid were then removed from the filtration setup and placed in an air-drying tray. A new filter paper was placed on the filtration setup, and the remaining vial

contents (H_2O + NPH + $OsO_2.xH_2O$) were transferred onto the new filter paper before being washed with ethanol. The pre-weighed filter paper was identified as 1 and 2 (for vial 1), 3 and 4 (for vial 2), and 5 and 6 (for vial 3). In a cabinet, a tray containing six pieces (paper and solids) was air dried for 12 days. Upon completion of the eleventh and twelfth days of drying, each piece was weighed and confirmed to be dry. In Table 3, the experimental conditions and weighing data for each test are provided.

Table 3. Experimental data for tests dissolving Os in 30% H_2O_2 at elevated t°C with NPH sorbent.

Vial	Os (mg)	H_2O (mL)	NPH (mL)	Stir	t°C	H_2O_2 (mL)	Min		Paper (mg)	Paper +dry solid	Dry solid	%, if as Os	Os (mg) if from $OsO_2.4H_2O$
1 14.6°C	77.5	0.1	2.0	Y	14.6	1.0	60	A	165.2	241.1	75.9	97.98	
								O	163.4	173.4	10.0		6.465
2 35°C	77.1	0.1	2.0	Y	35	1.0	45	A	166.6	237.9	71.5	92.74	
								O	163.2	173.3	10.1		6.530
3 50°C	77.8	0.1	2.0	Y	50	1.0	60	A	162.2	232.5	70.3	90.36	
								O	172.2	182.5	10.3		6.659

Note: Percentage calculations are based on the assumption of undissolved solid in aqueous as in Os metal form.

Table 3 shows that, under similar conditions, higher temperatures result in a faster dissolution of Os metal in H_2O_2. Although the dissolution time for the 35°C run was less than 60 min, more Os was dissolved than for the 14.6°C run for 60 minutes. The maximum dissolution rate of Os metal in H_2O_2. at 50°C was < 10% in 60 minutes, which represents a much lower Os/OsO_4 conversion than the current heating process. As reported in **[2]** heating at 750°C in air resulted in a conversion of over >90% of Os/OsO_4 within 74 minutes.

As an inert alkane, NPH does not react with most chemicals, except with transition metal tetroxides (e.g., OsO_4 or RuO_4), which reduce to solid hydrous dioxides when reacting with NPH. Based on the visible black solid trapped in the NPH phase, it was concluded that dissolved Os converted to volatile OsO_4 by reaction with H_2O_2, resulting in a loss of weight of Os metal in aqueous phase. It is still not known exactly how (Os + H_2O_2) forms volatile OsO_4. However, the formation of visible black Os dioxide supports the existence of OsO_4 before it interacted with NPH. The author proposed the following reaction equation for the formation of OsO_4:

$$Os_{(s)} + 4\ H_2O_{2(l)} \rightarrow OsO_{4(g)} + 4\ H_2O \qquad (6)$$

This proposed Eq-6 indicates a reaction route for Os → OsO_4 in H_2O_2, however volatile OsO_4 formation is obviously not as favorable as H_2WO_4 formation proposed in Eq-5. The calculated minimum amount of 30% H_2O_2 for each gram of Os metal is 2.41 mL/g Os according to Eq.6.

Table 4. Calculated total Os in two phases vs. input Os metal powder.

Vial	Os (mg)	Os (mg) in aq.	x =	Os (mg) in $OsO_2.xH_2O$	Total Os (mg) in (aq. + org.)	Total Os cal. vs. Os input
1	77.5	75.9	2	7.367	83.27	107.4 %
2	77.1	71.5	2	7.440	78.94	102.4 %
3	77.8	70.3	2	7.588	77.89	100.1 %
1	77.5	75.9	4	6.465	82.37	106.3 %
2	77.1	71.5	4	6.530	78.03	101.2 %
3	77.8	70.3	4	6.659	76.96	98.92 %

The follow up formation of $OsO_2.xH_2O$ per OsO_4 interaction with NPH is a known fact in chemistry, however, it is unclear whether x = 2 or x = 4. Whatever the composition of the solid black in NPH, whether it is $OsO_2.2H_2O$, or $OsO_2.4H_2O$, it is possible to calculate the amount of Os in the oxides from the weights of the dried solid black (Table 4).

Despite uncertain hydration number (x) for the hydrous Os dioxide in NPH phase, $OsO_2.xH_2O$ should be consistent with either x = 2 or x = 4. It was found, however, that when adding the calculated Os amount from weighed $OsO_2.xH_2O$ to the weight of the undissolved solid in the aqueous phase, the sum is higher than the total (assuming that the solid in aqueous is pure Os metal). This seems to indicate that (1) part of the undissolved solid in the aqueous phase could be in a chemical form of Os with other elements (for example, low-degree Os oxide, which is a precursor to gaseous OsO_4), and (2) the amount of Os oxide decreases as the temperature of Os dissolution in H_2O_2 increases (i.e., temperature plays a significant role in the formation of lower-degree Os oxides before volatile OsO_4 is formed).

It has been reported in the literature [5] that solid OsO_2 is produced when Os metal is in contact with OsO_4 or an oxidizing agent (e.g., H_2O_2) at high temperatures, although 50 degrees Celsius cannot be defined as a "high temperature". A very small percentage of OsO_2 will influence the Os mass balance calculations in the 9/29/2021 test, making the total recovery of Os higher than 100%.

Based on our calculations, it can be concluded that at the allowed high temperature, the formation of harmful gaseous OsO_4 from Os metal in H_2O_2 is less than 10%, which is much lower than that of the current heating method (>90%) used in the ^{188}W process. Consequently, the generated volatile $^{191}OsO_4$ from the same amount of irradiated W target would be one-tenth of the amount generated during the heating process, resulting in a lower requirement for NaOH scrubbing and a lower disposal of caustic liquid waste.

3.2.2 Dissolution of Re Metal Powder in H_2O_2

In irradiated W metal targets, ^{188}Re (a decay daughter of ^{188}W) is present in quantities comparable to Os impurities. The heating method for ^{188}W processing converts Re into semivolatile forms (Eq. 3) during reaction with O_2 at 750°C and partially carries it out of the hot zone of the quartz vessel away from the solid product ^{188}W. The ^{188}W process does not require completely separating Re from W, as Re and Os will not absorb onto the alumina column when loading ^{188}W feed on alumina to fabricate $^{188}W/^{188}Re$ biomedical generators [6]. Despite this, the behavior of Re metal in H_2O_2 is a big concern due to its possible influence on the dissolution of W metal. The International Atomic Energy Agency's Mallinckrodt procedure operation manual [7] recommended dissolving 1–10 mg of ^{186}Re metal in 0.2 ml of 30% H_2O_2. As a result, the author accurately predicted that Re metal would dissolve in H_2O_2.

As part of the experiment on 7/7/2021, 148.7 mg of Re metal powder (99.999% purity, 22 mesh) were weighed in a glass vial, then 8.0 mL of 30% H_2O_2 were added without stirring in the vial at ambient temperature. Table 5 provides the experimental conditions and results of the dissolution experiment.

Table 5. Experiment conditions of Re metal dissolution and results.

Metals (mg)	H_2O_2 (mL)	Stir	Heating	Bubbling	Clear after	t° $C_{dissolution}$	In vial as
Re (148.7)	8	N	N	Vigorous	2 min	Warm	Clear

An intense reaction started with a puff of white vapor when the 30% H_2O_2 was added and contacted the Re metal powder in the vial. Within two to three minutes, the vapor dissipated and the Re powder disappeared, leaving a clear, yellowish gray solution. Figure 18 shows the solution of dissolved Re metal (left), while on the right is the crystal-clear solution of dissolved W metal. The temperature of the vial with the Re dissolution felt warm to the touch, well above ambient temperature.

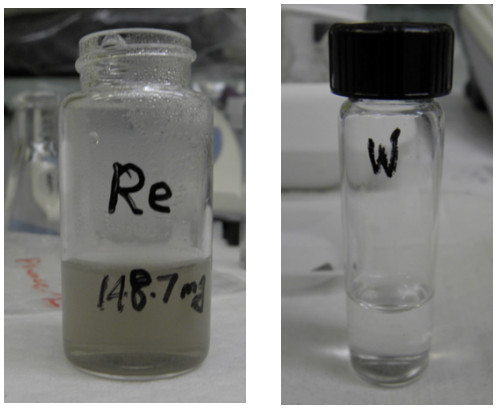


Figure 18. Dissolution of Re metal powder in H_2O_2 and its resulting color vs. that of dissolved W.

The reaction between Re metal and H_2O_2 is clearly exothermic, fierce, and rapid. Heat released from the dissolution of Re in H_2O_2 will raise the temperature of the aqueous solution and must be considered during the procedure design for irradiated W metal target dissolution in H_2O_2.

3.2.3 Dissolution of Cast Cylinder of W Metal in H_2O_2 for an Estimate of W Dissolution Speed

W dissolution in H_2O_2 appears mild compared to Re dissolution in H_2O_2. Knowing the W powder of 10 μm of high surface area can be completely dissolved in 12 min with stirring at ≤50°C (Table 1), the time to dissolve sintered W rings of low surface area would be longer. In the dissolution test on 12/27/2020, a broken piece of sintered ^{186}W ring (**158.1 mg**) took 3 h to dissolve in 8 mL of H_2O_2 at ambient temperature without stirring (Table 1). Because of its rough metal surface, this sintered ^{186}W ring piece has more surface area than a cast tungsten metal piece. Therefore, a cast natural W metal cylinder (**OD 3.177 x L 6.35 mm**, 99.97% purity) with a smooth finish was used for the dissolution test with H_2O_2, in order to determine its dissolution rate per unit surface area of the W metal cylinder (Figure 19).

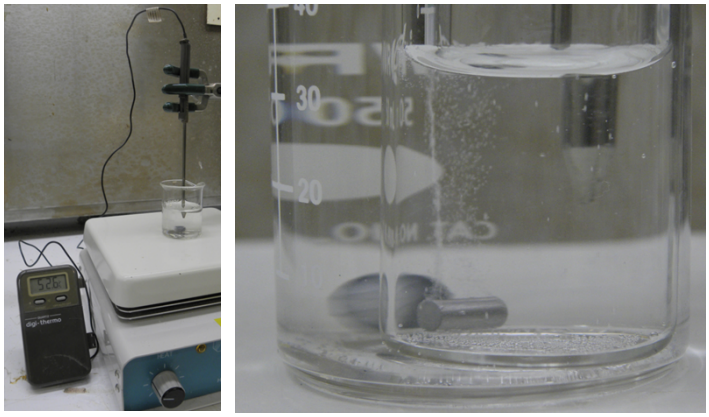


Figure 19. Dissolve a W metal cylinder in H_2O_2 at ≤50°C for the dissolution rate per surface area.

In this case, a W metal cylinder weighed **970.8 mg**, and its surface area was calculated to be **0.79173 cm²**. The vial containing 10 mL of 30% H_2O_2 was placed in a water bath with stirring (i.e., stirring in the bath beaker, but outside the vial with the W cylinder). Upon the placement of the cast W cylinder into the vial, the dissolution process begins. A hot/stirring plate maintained the temperature of the water bath. As shown in Table 6, the temperature of the water bath was controlled and recorded during the experiment on 2/17/2021 along with the dissolution time.

Table 6. Temperature variation during dissolution of the W metal cylinder in H_2O_2.

Time	**15:14**	**15:17**	**15:20**	**15:22**	**15:24**	**15:26**	**15:28**	**15:30**	**15:32**
t °C	45.0	47.4	49.5	48.4	49.9	51.4	49.7	50.0	49.8
Time	**15:34**	**15:37**	**15:40**	**15:45**	**16:16**	**16:41**	**16:45**	**17:40**	**18:00**
t °C	48.2	47.8	47.0	46.2	46.5	49.7	49.8	49.3	49.2

The dissolution time for the W cylinder in H_2O_2 at 45°C to 51.4°C was 2 h 46 min.
The W cylinder weighed **880.1 mg** after air drying. Table 7 provides the experimental conditions .

Table 7. Dissolving a W cast cylinder of known surface area in H_2O_2 in controlled t°C.

Size (mm) $_{start}$ W(mg)	**H_2O_2 (mL)**	**Stir**	t° C	**Min**	**Bubbling**	Size (mm) $_{after}$ **W (mg)**	Dissolved W (mg)
Φ3.175 × 6.35 (970.8)	10	N	50°C	166	Mild	Φ3.13 × 6.24 (880.1)	41.9

The W dissolved from this cylinder within 2h 46 min in H_2O_2 is (970.8 - 880.1 =) 90.7 mg. Ignoring the surface area change of the cylinder, the surface area-dependent dissolution rate can be calculated as:

(90.7×60/166/0.79173 =) **41.407 mg W/(h.cm²)**.

The total surface area of eight W rings can be calculated based on following average dimensions of eight natural W rings: height of 2.33 mm, outer diameter (OD) of 6.146 mm, and inner diameter (ID) of 3.92 mm. The apparent surface area (S) = outer side (S_o) + inner side (S_i) + 2× ring flat = 0.44988 + 0.28694 + 2 × 0.175984 = 1.08879 (cm^2) /ring. If all eight rings are counted, total surface area is (8× 1.08878 =) 8.71030 cm^2. Per the above calculated dissolution rate, it would be (41.407 × 8.71030 =) **360.667 (mg/h).** Results showed that **13.39 hours** are needed to dissolve the eight W rings (total 4.83 g) at ≤50°C.

While thirteen hours constitutes a long dissolution period for 8 sintered W rings, the following factors should speed the process:

1. The dissolution of irradiated W rings in 30% H_2O_2 would be achieved by stirring. (There was no stirring involved in the above dissolution test for dissolution speed measurement.)

2. As a result of the rough surface of the pressed/sintered W rings, the real surface area of W metal rings should be greater than the calculated "apparent" surface area (as compared to a cast W cylinder with a smooth finish).

3. The rapid dissolution of ^{188}Re metal, the decay daughter of ^{188}W distributed within the W rings, will result in structural defects and increased surface area with the rings to react with 30% H_2O_2.

Additional factors will influence the dissolution period. It is important to note that a single experiment determining the dissolution rate of W metal may be inaccurate. The assumption of the W metal cylinder's surface area is not accurate because dissolution with H_2O_2 for 166 min changed the dimensions of cylinder from OD 3.175 × L 6.35 mm to OD 3.130 × L 6.24 mm, resulting in a 3% decrease of the cylinder's apparent surface area (0.79173 cm^2 → 0.76748 cm^2) in 166 min of dissolution (assuming no dimple formation). As a result of W dissolution at the two ends of the cylinder, dimples formed in the center of the round surface. This is likely due to the relatively low density, found in the cylinder's core (figure 20).

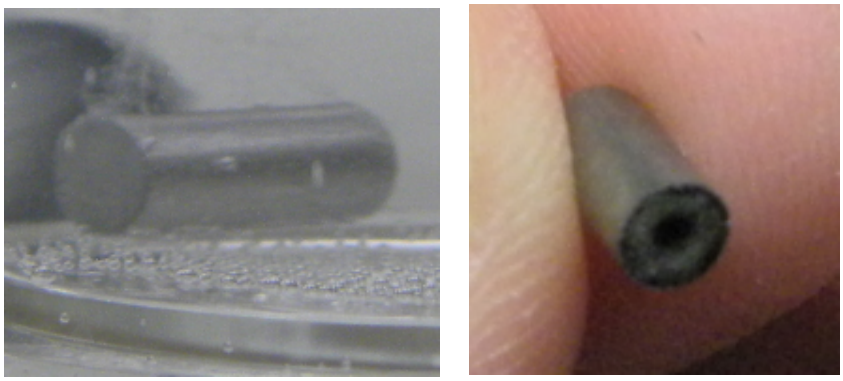


Figure 20. Surface changes of the cast cylinder of W metal after dissolution in H_2O_2.

Furthermore, the dissolution was not evenly distributed along the surface of the cylinder. The low-density area of the cylinder dissolved faster than the other zones, resulting in a larger surface area than that calculated apparent one using direct dimension measurements.

Thus, the W dissolution rate of **41.407 mg W/(h.cm^2)** is only a very conservative reference parameter when estimating dissolution hours under the given conditions.

4. OPERATIONS OF DISSOLVING IRRADIATED W TARGET IN H_2O_2 AND THREE CONCERNED CHEMISTRY ISSUES

4.1 OUTLINE OF DISSOLUTION OF IRRADIATED W TARGET IN H_2O_2 IN ^{188}W PROCESS

The proposed selective dissolution method should be performed in a device with the following functions: (1) An original quartz vessel with a modified Tube B, and a two-port cap, with one port allowing hot cell air to enter the vessel, the other port is connected to the OsO_4 scrubbing system, and a vacuum pump to remove the atmosphere (2) a furnace for controlling the rate of dissolution in H_2O_2 at desired temperatures; and (3) a stirring capability (Figure 21).

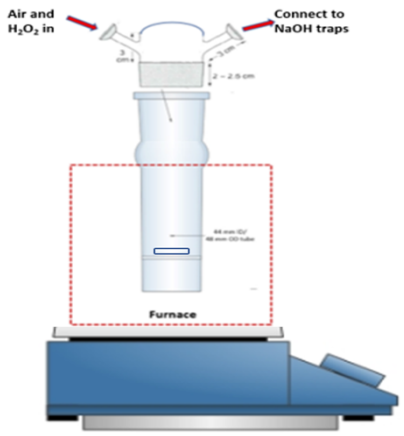


Figure 21. Dissolution assembly for dissolving irradiated W metal rings in H_2O_2.

An assembly design can be modified (e.g., use a shorter dissolver instead of Tube A) or the top cap may have a tube connected to one of the ports for inserting into the H_2O_2 solution for stirring by air bubbling instead of a stirring machine.

Upon loading irradiated W metal rings and a stir bar into the tube A of the quartz vessel, a two-port cap is joint-connected to secure the assembly. It is recommended that before the operator adds 30% H_2O_2 in batches, the assembly should be connected to NaOH/charcoal traps, and airflow should be delivered by a pump at a low rate, so that any gas generated from dissolution is carried out of the vessel and interacts with the NaOH scrubber.

As soon as H_2O_2 is added to the quartz vessel and stirring is turned on, the reaction between H_2O_2 and the irradiated W rings will start to generate aggressive bubbling (indicating dissolution of W metal and Os catalytic reaction with H_2O_2) as well as a puff of white vapor (indicating dissolution of Re metal). Rapid dissolution of Re impurities will produce tremendous heat and raise the vessel's temperature. During this time, the vessel does not require heating by the tube furnace. When the temperature of the vessel drop to <40°C (indicating the surface Re of W rings has been consumed), the furnace should be turned on, and the quartz vessel temperature should be controlled at ≤50°C.

The addition of H_2O_2 should be done batchwise, and bubbling should be taken as an indication of dissolution. Nonradioactive experiments showed that H_2O_2 dissolves metals of W and Re but only small portion of Os.

Based on preliminary calculations in Section 3.2.3, eight irradiated W targets (4.83 g) will require 13.4 h to completely dissolve in H_2O_2. If the W target is irradiated, the dissolution time may be shortened because explosive dissolution of Re in the rings will result in a larger surface area for the reaction of H_2O_2 with W. Compared with the heating method used in ^{188}W campaigns, the process of dissolving H_2O_2 is clearly more efficient and easier to control. One-tenth of the harmful $^{191}OsO_4$ generation reduces the size requirement of NaOH traps and liquid waste disposal.

4.2 CONCERNED CHEMISTRY ISSUES

4.2.1 Where Does the Undissolved Os Metal in H_2O_2 Dissolution Go? Does Os Matter in ^{188}W Product?

In the above non-radioactive Os metal powder dissolution tests, the undissolved Os – the majority of which is Os metal and a small fraction of solid precursor of OsO_4 – remained as solids in the dissolver

and could be easily separated from the dissolved W product by filtration (A filtration with a 2 μm filter is already a routine operation step following NaOH dissolution in ^{188}W process.) This can be attributed to the large size (20 mesh) of the Os metal powder used in the tests.

Inside the irradiated W metal target, the irradiation-generated Os from a W nucleus in metal lattice should be in small size of dispersed state and may not be captured by a 2 μm filter in routine filtration after the target dissolution. This is why the shipped product of ^{188}W solution in previous campaigns contained an appreciable amount of Os (^{188}Os and ^{191}Os, only ^{191}Os is detectable as a weak β^- emitter), even though 90% of the Os had already been converted to volatile OsO_4 and away from ^{188}W solution.

As the shipped ^{188}W product solution was caustic (NaOH), with ^{191}Os in sodium osmate form trapped in solution with no chance of forming harmful $^{191}OsO_4$; therefore, the shipping of ^{188}W product with the impurity ^{191}Os is safe.

Based on conservative estimates, the amount of Os remaining in the ^{188}W product solution by the H_2O_2 dissolution method may be 10 times higher than that by the heating method. Although ^{191}Os has a short half-life of 15.4 days, the influence of Os content on ^{188}W/^{188}Re generators' clinical performance is still a concern by the users. Figure 22 shows a simplified process of a ^{188}W/^{188}Re generator's feed loading and follow-up multiple ^{188}Re milking.

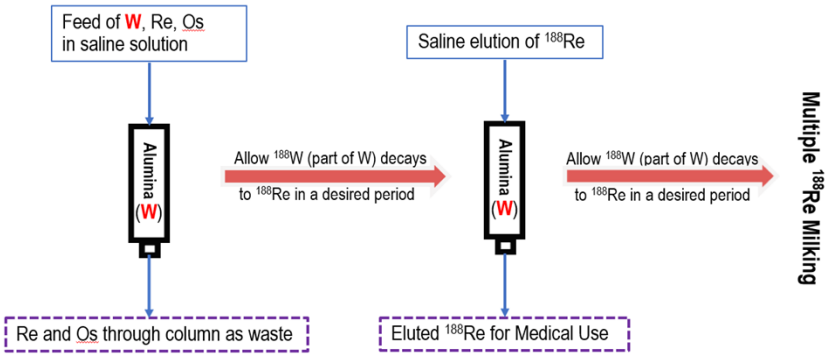


Figure 22. Simplified process layout for ^{188}W/^{188}Re generator loading and ^{188}Re milking.

According to **[6]** regarding the ^{188}W/^{188}Re generator's feed loading, WO_4^- (^{188}W and ^{186}W) in saline feed will be retained on the alumina column, while ReO_4^- and OsO_4^- in the feed passing through the column as waste. The absorbed ^{188}W on the column will be allowed for the ingrowth of its decay daughter ^{188}Re for a desired period and then eluted (milked) from the column with saline as pure ^{188}Re for medical use. The ^{188}W absorbed on the column will be kept for additional ^{188}Re ingrowth and will be harvested at the next milking.

There is no safety issue associated with shipping or a negative impact on the quality of ^{188}Re milking, and the presence of ^{191}Os in the ^{188}W product solution does not pose a quality concern for the ^{188}W campaign product. With the focus on campaign process safety, it would be preferable for the irradiated W target to be processed in a manner that does not generate harmful $^{191}OsO_4$. The H_2O_2 dissolution method at least produces much less volatile $^{191}OsO_4$, which has the advantage of utilizing fewer resources.

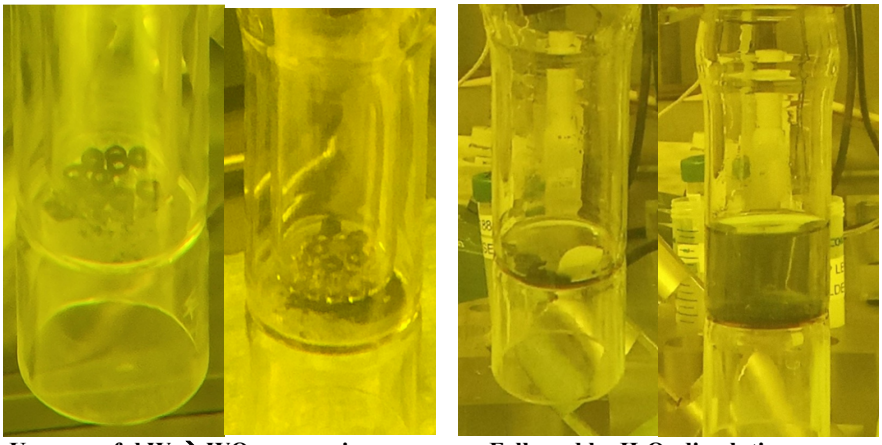
4.2.2 Does H_2O_2 Dissolve Irradiated Target of W Metal Alloys (Indirect Evidence by Campaign W-2106)?

The oxidation reaction retardance of W→ WO_3 has occasionally been observed during the treatment of irradiated W metal targets with air since 1999.This retardance was attributed to the possibility of (1)

formation of WRe (e.g., with ^{188}Re), (2) formation of WC (lubricate residue from ring fabrication), and (3) contaminant coating on the ring surface, but none of these have been proven by analytical data of the problematic target.

Due to the limited availability of non-radioactive WRe and WC, direct H_2O_2 dissolution of these two was not performed. However, experience indicates that if a liquid reagent dissolves a metal, it will dissolve an alloy of that metal. For instance, HCl dissolves both Pu metal and $PuBe_{13}$ alloy. In contrast, if a gas (e.g., O_2) reacts with a metal, it may not react if the metal is alloyed with another element.

In a recent ^{188}W production campaign (W-2106), eight irradiated W rings (4.83 g) were first heated in air at a rate of 1 L/min to convert W→WO_3. A total of 31 hours of heating were performed over the course of 4 days at 750°C, with an additional 5 hours of heating at 790°C on the fifth day with no conversion of W rings to the WO_3 powder (Figure 23). By shaking solids on the perforated stage, smaller flakes of solids fell through holes to the bottom of the vessel, with the ring solids remaining on the stage. Following the removal of Tube B (containing solids in the form of rings), the solid flakes in Tube A were soaked in 6 *M* NaOH for the dissolution of any WO_3 and then sampled and analyzed for ^{188}W yields per heating method (Table 8), showing only ~10 % of the normal ^{188}W yield **[8]**.



Unsuccessful W → WO_3 conversion **Followed by H_2O_2 dissolution**

Figure 23. Campaign W-2106: heating for 36 h in 5 days, followed with a 5h H_2O_2 dissolution.

The processing experience indicates that the W target material will not be converted to WO_3 by heating in air once it is contacted with NaOH. This batch of solid flakes (about one-fourth of the total target of 4.83 g) was decided to be tested for the dissolution of H_2O_2. It is the only time, to date, that ORNL has conducted a trial of irradiated W target treatment by H_2O_2 dissolution.

Following a DI H_2O rinse, a known amount of 30% H_2O_2 was added to Tube A and the tube was capped as shown in Figure 21, which was connected to 2 × 1.5 L NaOH scrubbers in series with an airflow of 1 L/min to assist with OsO_4 absorption (if any). As soon as H_2O_2 was added in batches, aggressive gas bubbles began to form with the generation of heat. The vessel's temperature raised from 33°C to 57°C, which demonstrated an exothermic reaction of Re metal in H_2O_2. Therefore, the heating by furnace was started after a period of four hours without furnace heating. After 4 hours of dissolution, heating was initiated and maintained for an additional hour at <50°C to complete a total of 5 hours of dissolution in H_2O_2.Table 8 summarizes the operation steps and radiological analysis of ^{188}W and ^{191}Os. (^{188}Os is not detectable by radiological analysis.)

Table 8. Campaign W-2106: Target treatment, ^{188}W recovery, and ^{191}Os release

	W Target (g)	@750°C (hour)	@790°C (hour)	Air (L/min)	In 6 M NaOH	In NaOH Traps*
By heating	**4.827**	25	6	1	^{188}W 2.3 Ci ^{188}Re 2.89 Ci ^{191}Os 15.5 mCi	^{191}Os 247.2 mCi*

	W Flakes (g)	No heating (hour)	@≤50° C (hour)	Air (L/min)	In H_2O_2	In NaOH Traps
By H_2O_2	**~1.2**	4	1	1	^{188}W 1.43 Ci ^{188}Re 1.77 Ci ^{191}Os ND	^{191}Os 260 mCi in Trap-1 ^{191}Os ND in Trap-2

*This is the sum of ^{191}Os in 5 Trap 1 in 5 days not including what in Trap 2

Due to daily working hour limitation, this H_2O_2 dissolution test was stopped and did not resume in the next day. Some visible flakes remained in the vessel undissolved. The resulting solution was filtered and sampled for radiological analysis. Additionally, NaOH in two traps was analyzed for absorbed ^{191}Os. Based on the analytical data for Campaign W-2106, it appears that 31 hours of heating did not achieve a successful conversion of W → WO_3 due to unknown changes to the features of W metal rings; however, H_2O_2 dissolved more W into solution over the course of 5 hours.

Unlike W→WO_3 conversion by heating would be terminated once the W rings touch NaOH. The rings being contacted with NaOH would be continued dissolving by H_2O_2 as shown in this dissolution test. Furkina et al **[9]** recently demonstrated a H_2O_2 dissolution of a cyclotron irradiated W metal target in caustic solution up to 3*M* NaOH. It proves that W dissolution by H_2O_2 can be conducted in caustic liquid. Therefore, when fail to achieve a complete conversion of W→ WO_3 by heating in campaigns, it would be OK to add NaOH to dissolve the partially converted WO_3 and then add H_2O_2 directly into the caustic solution, if preferred, for further dissolution of the retarded W target.

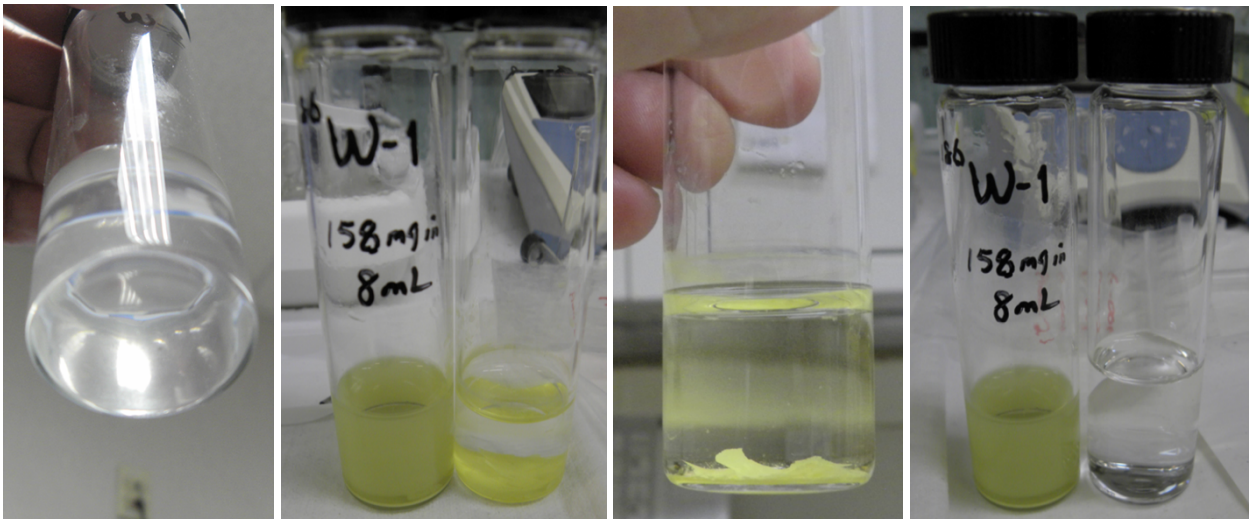
It would be expected that the retarded W target in Campaign W-2106 would be further dissolved if more hours of H_2O_2 dissolution were allowed in the processing. For the recovered total 3.73 Ci of ^{188}W, **61.7% was by 31 hours' heating, while 38.3% by 5 hours' H_2O_2 dissolution**. The detection of ^{191}Os in NaOH Trap 1 due to H_2O_2 dissolution confirmed that Os converts to volatile OsO_4 during H_2O_2 dissolution process and a NaOH scrubbing system is still required. The fact of no ^{191}Os absorbed/detected in NaOH Trap 2 indicates the redundancy of 1.5 L 1*M* NaOH trap size for H_2O_2 dissolution process. One argument may draw attention to the amount of ^{191}Os generated during this 5h H_2O_2 dissolution test: 260 mCi (1.43 Ci of ^{188}W) vs. 247.2 mCi (2.3 Ci of ^{188}W by 5d heating) that seems against the results of only 3% of Os → OsO_4 in non-rad H_2O_2 dissolution tests. Unlike pure Os metal powder being dissolved in non-rad tests by H_2O_2, the 1.2 g of retarded target residue in campaign 2106 is obviously no longer in W or Os metal form (because no further formation of WO_3 and OsO_4 by heating). The reason why other chemical forms of osmium (e.g., -W-Os- alloy) are easier to be oxidized to volatile OsO_4 by H_2O_2 is still unknown, but it is not hard to admit that the Os in a defect alloy lattice (after W in -W-Os- lattice is dissolved by H_2O_2) is easier oxidized in H_2O_2 solution than the Os in a perfect -Os-Os- metal lattice in similar H_2O_2 dissolution conditions.

Although lack of direct evidence of H_2O_2 dissolving WRe or WC alloys, the radioactive test involving H_2O_2 dissolution of a retarded W target clearly demonstrated H_2O_2's efficacy in further dissolving the

retarded W target (regardless of the W alloys). A recently published paper [10] describes the successful dissolution of irradiated $^{186}WS_2$ targets by H_2O_2. This provides further evidence that W compounds are dissolved by H_2O_2. If non-radioactive WRe and WC are available in the future, a direct dissolution test by H_2O_2 should be conducted to confirm their dissolution in H_2O_2 as well as the alloy formation to be the retarded target.

4.2.3 What Is the Chemical Form of the Dissolved W Target in H_2O_2?

Another question relating to the 188W process is the chemical form of W in H_2O after it is dissolved by H_2O_2. The dissolved W solution of H_2O–residual H_2O_2 (without NaOH) appears transparent. The dissolved W solution in glass vials did not show any changes until a greenish yellow gel coating was formed on the walls after six months. This greenish yellow W compounds formed in H_2O–H_2O_2 media can be easily dissolved by adding a few drops of 1 *M* NaOH and then turned back into transparent solutions (Figure 24).



W metal dissolved in H_2O_2 **Gel formed in H_2O in months** **Gel coating peeled off** **Before/after drops of NaOH added**

Figure 24. Dissolved W compound precipitates out in H_2O and redissolved at higher pH.

The greenish yellow gel cannot be sodium tungstate (Na_2WO_4) since there was little sodium (Na^+) in the solution before NaOH was added, and Na_2WO_4 appears as white precipitates. It is likely that the yellow gel coating was formed as a result of the formation of a solid tungstic acid which was present in hydrated forms of tungsten trioxide (WO_3) (e.g., monohydrated $WO_3.H_2O$ or H_2WO_4). The features of tungstic acid include its insoluble nature in water and soluble nature in ammonia [11]. As shown in Figure 25, commercial H_2WO_4 is available in various forms such as precipitates, microstructures, and dehydrated oxides.

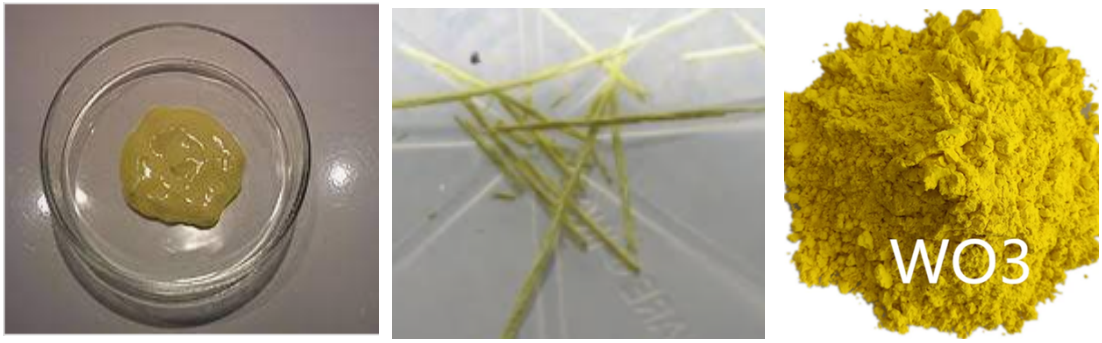


Figure 25. Commercial products of H_2WO_4, microstructure, and dehydrated WO_3.

It is open to discussion whether the gel is tungstic acid or another W compound. When processing ^{188}W, it is important to add NaOH to the H_2O-H_2O_2 solution after dissolution of the irradiated ^{188}W product has been completed in order to keep the product in sodium tungstate to prevent precipitation loss during transport or storage if the solution is not sufficiently basic.

5. CONCLUSIONS

During nonradioactive experiments, W and Re metal powders dissolved in H_2O_2 at rates of >95% and 100% respectively, while Os metal powder dissolved with a rate of <10% at ≤50°C. An aggressive bubbling phenomenon by Os + H_2O_2 was found to be caused by a catalytic reaction between H_2O_2 and water, while most of Os metal remains solid with a small portion of solid Os converted into volatile OsO_4. For ^{188}W processing safety, it is still necessary for the scrubber to absorb harmful OsO_4 that is released from the dissolved portion of Os metal.

A dissolution test of a W metal cast cylinder of known surface area produced a conservative dissolution rate of W in H_2O_2, which gave an estimate of 13.4 hours for each load of irradiated W rings (4.83 g of eight rings) to dissolve completely at ≤50°C. It should be noted that this parameter of W dissolution in H_2O_2 was obtained by using a W metal cylinder of smooth surface finish, no contact of NaOH and no formation of a retarded composition. This dissolution hour parameter should be used only as a reference for general dissolution of W metal in H_2O_2.

The less-hour-trial of H_2O_2 dissolution in Campaign W-2106 proved the effectiveness of H_2O_2 dissolution of the retarded W target after its contact with NaOH, giving additional 38.3% of ^{188}W yield in only 5 hours while the other 61.7% by heating in 31 hours (in 5 days).

As compared to the current method for irradiated W targets that involves two days or three days of heating at 750°C with a NaOH traps holding 2 × 1.5 L for scrubbing large amounts of volatile $^{191}OsO_4$ and disposal of waste NaOH, the new method of H_2O_2 dissolution provides ease of operation, energy efficiency, and less $^{191}OsO_4$ (if not retarded target) for scrubbing and disposal of waste NaOH. To simplify processing equipment array and operation controls, the author recommends using H_2O_2 dissolution rather than current heating methods for future ^{188}W campaigns. This will result in a reduction in manpower requirements and energy consumption. On the other hand, much lower $^{191}OsO_4$ generation reduces the long-term danger to the processing facility.

For future irradiated W target treatment, the ^{188}W processing team may wish to continue using existing heating equipment. The H_2O_2 dissolution method can thus be kept as a supplementary method in the event that retarded W targets are encountered and the heating method does not work well, as in the case of

Campaign W-2106. If this is the case, the supplementary H_2O_2 dissolution should be allowed to take longer than previously calculated hours (i.e., 13.4 h), because retarded targets take longer to dissolve than pure W metal targets.

The new H_2O_2 dissolution method may enable ^{188}W customers to switch their future orders from dissolved ^{188}W solution to irradiated W metal rings, because solid rings can be shipped more safely than liquid rings, and irradiated rings can be dissolved onsite by H_2O_2 with simple devices before feed adjustments are made on the $^{188}W/^{188}Re$ generators. The options for simple dissolvers include the one shown in Figure 18 of **[2]** with a connected OsO_4 sorbent trap or a simple vial dissolver with a top organic NPH phase as OsO_4 sorbent. It is recommended that ORNL keeps at least one ring in the rabbit for dissolution and radiological analysis to determine how much ^{188}W is in the other seven rings.

In general, the H_2O_2 dissolution method will improve the capabilities of ^{188}W process.

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