Investigation of Molybdate Melts as an Alternative Method of Reprocessing Used Nuclear Fuel

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1. PDF: Powder Diffraction File

Abstract

An investigation of molybdate melts containing sodium molybdate (Na_2MoO_4) and molybdenum trioxide (MoO_3) to achieve the separation of uranium from fission products by crystallization has been performed. The separation is based on the difference in solubility of the fission product metal oxides compared to the uranium oxide or molybdate in the molybdate melt. The molybdate melt dissolves uranium dioxide at high temperatures, and upon cooling, uranium precipitates as uranium dioxide or molybdate, whereas the fission product metals remain soluble in the melt. Small-scale experiments using gram quantities of uranium dioxide have been performed to investigate the feasibility of UO_2 purification from the fission products. The composition of the uranium precipitate as well as data for partitioning of several fission product surrogates between the uranium precipitate and molybdate melt for various melt compositions are presented and discussed. The fission products Cs, Sr, Ru and Rh all displayed very large distribution ratios. The fission products Zr, Pd, and the lanthanides also displayed good distribution ratios ($D > 10$). A melt consisting of 20 wt% MoO_3 - 50 wt% Na_2MoO_4 -30 wt% UO_2 heated to 1313 K and cooled to 1123 K for the physical separation of the UO_2 product from the melt, and washed once with Na_2MoO_4 displays optimum conditions for separation of the UO_2 from the fission products.

Keywords

Used nuclear fuel recycle; Modified open fuel cycle; Uranium behavior in molybdate melts; Uranium separation; Recrystallization

1. Introduction

Pyrochemical processes are very attractive for recycling short-cooled used nuclear fuel due to the use of inorganic salts since they are more resilient against radiolytic processes than the aqueous or organic solvents, which are used in solvent extraction processes. [1-3] In addition, the use of inorganic salts has the potential to significantly reduce the volume of waste produced during the processing compared to solvent extraction processes.[1-3] Generally, halide-based molten salts have been used as electrolytes in electrorefining used nuclear fuel; [1-3]however, Ustinov *et al.* have explored molybdate melts for an alternative pyrochemical processing technique, specifically for oxide fuel treatment. [4-9] We explored this alternative approach in developing a so-called modified open fuel cycle in which the actinides are recovered for recycle to an advanced reactor without extensive processing.

In this approach, recrystallization methods are used to achieve the desired separations in which the used nuclear fuel is dissolved in the molybdate melt containing a mixture of sodium molybdate (Na_2MoO_4) and molybdenum trioxide (MoO_3) at temperatures between 1273-1473 K, and UO_2 (or transuranic oxides) recrystallize upon cooling, separating it from the fission products. [4-12] The process is based on the difference in solubility of the fission product metal oxides compared to the uranium (or transuranic) oxides in the molybdate melt.[4-12] The advantage of this process is that the fission products are more soluble in molybdate melt than the UO_2 . The fission product metals are oxidized in MoO_3 and form molybdates, or other oxides, and the resulting products are soluble in Na_2MoO_4 . [5] As the temperature of the system increases, the solubility of UO_2 in MoO_3 increases. At temperatures exceeding 1273 K, any UO_2 that dissolves in MoO_3 forms $\text{U}(\text{MoO}_4)_2$. [7] In addition, most of the fission product oxides are also very

soluble in Na_2MoO_4 , while UO_2 has very limited solubility, a property of the system that can be used for its separation from fission products. [4-11] Upon cooling to 973-1073 K, the fission products remain soluble in the melt, the mother liquor, whereas uranium precipitates as uranium dioxide or uranium molybdate, depending on the initial composition of the salt. [10-12] A wash of Na_2MoO_4 is then used to remove any remaining fission product oxides or molybdates from the uranium-bearing precipitate. [4-12]

Ustinov reported that recrystallization of $\text{U}(\text{MoO}_4)_2$ from a $\text{UO}_2\text{-MoO}_3$ melt containing fission products yielded a 98-99% purification from Cs, Ce, Pr, Zr, and Nb; however only a 60% purification from Ru and Rh was achieved [1]. For the recrystallization of UO_2 from a $\text{UO}_2\text{-MoO}_3\text{-Na}_2\text{MoO}_4$ melt, the purification from Cs, La, Zr and Nb was 98.5-99.9% efficient. [4] There is no change in the oxidation state of uranium (or transuranics); therefore, no electrochemical methods or additional oxidants or reductants are required, and the actinide oxide product can be filtered from the fission products that remain in the melt.[10-12]

Small scale experiments using gram quantities of uranium have been performed to test the feasibility of using the molybdate melts to purify UO_2 from fission products. In addition to looking at the feasibility of the molybdate melts, the method of contamination of the UO_2 product by the fission products, and the optimum conditions for dissolution and precipitation of uranium oxide or molybdate and its separation from selected simulated fission product oxides were investigated. Our study explored UO_2 recovery as a function of the composition of the molybdate melt, temperature, and precipitate washing with sodium molybdate.

2. Experimental

2.1. Materials

Nickel based alloys were suggested to be suitable containers for studies conducted in these salt compositions [4, 5, 9], but, severe corrosion was observed when Inconel (Sigma Aldrich) was used as a crucible and basket material in the presence of MoO_3 . A glassy carbon crucible was also experimented with in preliminary tests; however, the crucible corroded after prolonged use in molybdate melts. Platinum was selected for the crucible and basket construction based on its good corrosion resistance to molybdate melts. The platinum crucible, and mesh for the basket were both in-house materials. The crucible was 1.5” in diameter by 1.5” in height. In-house depleted uranium oxide pellets, UO_2 , were used as the source of uranium for the tests. Before processing, the pellets were crushed into smaller pieces to achieve faster dissolution.

Fission product oxide simulants and Na_2MoO_4 were purchased from Sigma Aldrich. The MoO_3 was purchased from MP Biomedicals. The oxides and molybdates were homogenized by grinding with a mortar and pestle. The fission product oxide composition used in the study is given in Table 1. This composition is based on a calculated composition of fission products in the used fuel, with an initial enrichment of 3.2%, after 33 MWd/kg burnup at a mean flux of $3.24 \times 10^{18} \text{ n m}^{-2} \text{ s}^{-1}$ in a typical pressurized water reactor after 10 years of cooling. [13] Select fission product oxides (Tb, Dy, and Er) are in a much higher concentration in the composition than what was calculated due to the difficulty in measuring such small quantities of the oxides in a glovebox.

2.2. Experimental Setup of the Melt

Small-scale experiments containing six to seven grams of UO_2 and approximately fifteen grams of MoO_3 and Na_2MoO_4 in varying $\text{MoO}_3:\text{Na}_2\text{MoO}_4$ ratios were performed in a vertical tube furnace inside an argon atmosphere glovebox with oxygen levels less than 10 ppm, and the moisture level between 3 and 50 ppm. Figure 1 displays a flowchart of the basic separations process. A diagram of the tube furnace and experimental setup is shown in Figure 2. The crucible was situated in the furnace and surrounded by Inconel heat shields. For uranium phase formation experiments, UO_2 , Na_2MoO_4 , and MoO_3 were loaded into the crucible without the basket, heated in the furnace at rate of about 573 K hr^{-1} until the temperature reached 1473 K, and held for about 8 hours to allow for the dissolution of UO_2 in the melt. The temperature was monitored by a type K thermocouple. For fission product partitioning experiments, UO_2 , Na_2MoO_4 , MoO_3 , and the fission product mixture were loaded into the basket and placed in the crucible. The mixture was heated at the same rate and to the same temperatures for the same amount of time, as the phase formation experiments. Because the melt was in a closed furnace, the possible release of gaseous fission products upon the dissolution of the simulated UO_2 fuel into the melt could not be monitored. The melt was then cooled to a pre-determined temperature in the range of 973-1073 K, at which point the uranium precipitated as an oxide or molybdate. The platinum basket was lifted out of the crucible to allow for the physical separation of the uranium product from the fission products, which remained in the salt phase. The temperature was held at 973-1073 K for about 10 hours to give ample separation time. When the system was cooled to room temperature, the precipitate was recovered. After the precipitate was recovered from the basket, the product was washed with approximately thirty grams of liquid Na_2MoO_4 .

2.3. Composition of Uranium Product

Experiments varying the composition of the initial melt of MoO_3 , Na_2MoO_4 , and UO_2 allowed for the determination of the composition of the main uranium-bearing precipitate upon cooling. Compositions of the melts studied are given in Table 2. To determine the composition of the uranium product from different compositions of the molybdate melts, samples of the uranium precipitate were analyzed using X-ray diffraction analysis (XRD). After cooling, samples of the uranium precipitate were transferred to a hood. The samples were ground and washed several times with de-ionized (DI) water to remove excess molybdate melt, and then air dried. A thin layer of powder was placed on a glass plate covered with double sided tape to allow the precipitate to adhere to the slide. The precipitate was then covered with a thin Mylar film. To identify the uranium-bearing phases obtained, the experimental XRD spectra were compared to the PDF¹ database.[14]

2.4. Dissolution of Uranium Product for ICP-MS Analysis

After cooling, a portion of the uranium-bearing precipitate was removed from the basket and transferred for dissolution. Samples were first washed with NaOH to remove any residual molybdenum salts, and then washed with 0.1M HNO_3 , which removes any remaining fission products that could be present on the surface of the precipitate. Due to the high solubility of sodium molybdate, 65 g/100 g H_2O , [15], deionized water with a resistivity $\geq 18 \text{ M}\Omega \text{ cm}$ was used to remove a significant portion of the molybdate salt present in the precipitate after the sodium molybdate wash. After several washes and decanting of the UO_2 precipitate with water, the resulting precipitate was green/brown. The precipitate was initially suspended in the water wash, forming a green/brown solution. The precipitate eventually settled, leaving a yellow solution indicating the presence sodium molybdate in the wash, and the water wash was decanted away. This wash was performed several times. If sodium hydroxide was used instead of water,

a clear solution formed. Sodium hydroxide was very effective for removal of molybdenum salts (>99.9% of all Mo present in the precipitate). Both water and sodium hydroxide washes were also effective for the removal of any remaining cesium. When Cs_2O was dissolved in MoO_3 at temperatures exceeding 673 K, Cs_2MoO_4 formed, which is very soluble in water. For precipitates containing uranium molybdates, a combination of NaOH and H_2O_2 was the most effective way for dissolution of the uranium molybdates (UMo_2O_8 , $\text{UMo}_7\text{O}_{22}$, and $\text{UMo}_{11}\text{O}_{35}$). On the other hand, precipitates obtained from mixtures with higher Na_2MoO_4 content were mostly UO_2 and they dissolved in $\text{HNO}_3/\text{H}_2\text{O}_2$ solutions. The product of mostly UO_2 and possibly $\text{Na}_4\text{U}(\text{MoO}_4)_4$, was then dissolved in HNO_3 with the addition of H_2O_2 to accelerate dissolution of the UO_2 . Elemental analysis of uranium containing precipitates was performed using ICP-MS (PerkinElmer SCIEX ELAN DRC II) with a reported uncertainty of $\pm 10\%$.

3. Results

3.1. Uranium Speciation

Figure 3 shows photographs of the precipitated products after they were recovered from the Pt mesh basket. Information regarding the composition of each melt, the color of the samples after rinsing with water, the major and minor uranium species identified, as well as the solubility of the product is provided in Table 2.

3.2. Fission Product Partitioning

After dissolving the uranium product using the procedure discussed in Section 2.4, samples were analyzed using ICP-MS to determine the distribution ratio of the fission products remaining in the sample. To determine the effectiveness of the separation, the distribution ratio was calculated

from ratio of the mass of fission product in the melt and the mass of fission product remaining in the uranium product:

$$D = \frac{Fission\ Product_{melt}}{Fission\ Product_{U\ Product}}$$

Distribution ratios for the fission products studied are provided in Figures 5-7.

4. Discussion

4.1. Uranium Composition

The composition of MoO_3 and Na_2MoO_4 in the initial melts directly affected the uranium phase formed during precipitation. It was observed that melts consisting of a MoO_3 mass fraction smaller than UO_2 resulted in a UO_2 precipitate as the major product. These results are consistent with the phase diagram produced by Ustinov *et al.* [5]. The phase diagram reveals that compositions consisting of much higher mass fractions of MoO_3 result in $\text{U}(\text{MoO}_4)_2$. Results reported here confirm that MoO_3 -rich salt compositions ($\text{MoO}_3 > \text{UO}_2$) usually lead to the formation of the purple uranium molybdate precipitate ($\text{U}(\text{MoO}_4)_2$).

Samples resulting in UO_2 displayed good separation between UO_2 and the excess molybdate salt. As seen in Figure 3, the product of Sample 1 formed from the composition 20% MoO_3 -50% Na_2MoO_4 -30% UO_2 showed two separate layers. The bottom dark layer is the UO_2 , which settled to the bottom of the crucible upon cooling, while the top yellow layer is the less dense excess MoO_3 and Na_2MoO_4 . After this sample was washed with water to remove the molybdate salt layer, it was analyzed by XRD. The XRD spectrum of this sample, Figure 4, confirmed the

effective separation, as no molybdate salt remained in the sample. Based on XRD analysis, the product was identified as UO_2 .

To determine the effect of Na_2MoO_4 washes on the product's composition, two samples of the same composition (60% MoO_3 -30 % UO_2 - 10% Na_2MoO_4) were analyzed, one with a Na_2MoO_4 wash (sample 6) and one without the wash (sample 5). Sample 5 resulted in a $\text{U}(\text{MoO}_4)_2$ product, which was to be expected with such a high concentration of MoO_3 . Sample 6 resulted in a UO_2 product. According to Ustinov, the Na_2MoO_4 wash forms two incongruently melting compounds with the $\text{U}(\text{MoO}_4)_2$ left in the melt, and, upon cooling, these compounds decompose to a UO_2 product in the temperature range between 973 and 1073 K. [4] Our products from samples 5 and 6 confirmed Ustinov's findings. The ability of the Na_2MoO_4 wash to form the UO_2 product from the $\text{U}(\text{MoO}_4)_2$ product demonstrated the necessity of the Na_2MoO_4 wash. Ustinov *et al.* explained that the limited solubility of the UO_2 in the Na_2MoO_4 is important because the MoO_3 serves as the solvent, while the Na_2MoO_4 serves to precipitate the UO_2 . This explains the reason that melts consisting of UO_2 - MoO_3 recrystallize $\text{U}(\text{MoO}_4)_2$, while melts consisting of UO_2 - Na_2MoO_4 - MoO_3 recrystallize UO_2 . [4]

4.2. Fission Product Partitioning

Figures 5-7 display the distribution ratios of the fission products in melts as a function of sample composition, temperature of the melt, and number of Na_2MoO_4 washes. In all of the melts, Cs, Sr, Ru, and Rh displayed very large distribution ratios ($D > 100$), indicating good purification of the uranium product. Other fission products, including Zr, Pd and the lanthanides (Ln) displayed smaller distribution ratios, ($D > 10$), however, this purification is an adequate separation from the uranium product. In order to determine optimum conditions for the removal of the fission

products with small distribution ratios ($D > 10$) and to increase purification of the uranium product, the methods by which the fission products contaminate the uranium product was examined.

According to Tul'skii *et al.*, the fission products have four methods by which they could contaminate the UO_2 product[7]:

1. The fission product oxide could be dissolved in the mother liquor and entered the UO_2 product via adsorption or trapping of the mother liquor onto the surface of the product.
2. The fission product oxide can interact with the uranium mixed molybdate $3\text{Na}_2\text{MoO}_4 \cdot 2\text{U}(\text{MoO}_4)_2$, replacing the Na ion in the mixed molybdate.
3. The fission product oxide or molybdate could crystallize parallel to the UO_2 , but not be washed out during elutriation because the specific gravity of the fission product oxide is too close to the specific gravity of the UO_2 product.
4. The fission product oxide could form a solid solution with the UO_2 , which would incorporate the fission product into the UO_2 lattice during crystallization.

The first two methods of contamination could be reduced by washing the product with multiple Na_2MoO_4 washes. The Na_2MoO_4 wash would dissolve the fission product oxide on the surface of the product, removing the contaminant from the product. The Na_2MoO_4 wash would also react with the mixed molybdate contaminated with fission products, and decompose the uranium-bearing phase to the UO_2 product. The third method of contamination is expected to be compensated for by physically lifting the Pt mesh basket with the UO_2 product out of the mother liquor, thus separating the UO_2 product from the mother liquor upon cooling. For example, in the case of Ru, Tul'skii was able to conclude that the Ru crystallizes parallel with UO_2 but can be

separated if there are separate zones for crystallization.[7] These separate zones are achieved during the physical separation of the UO_2 contained in the Pt basket upon cooling to temperatures low enough for the UO_2 to precipitate, but higher than the crystallization temperatures of the fission product oxides. At these temperatures, while the UO_2 is precipitating in the Pt basket, the liquid fission product oxides remain in the Pt crucible. The final method of contamination is considered the most common method of contamination for the fission product oxides, as most of the fission product oxides, especially the lanthanides, are known to form solid solutions with UO_2 . [16, 17]

4.2.1. Effect of Melt Composition

Figure 5 shows data from samples with varying $\text{MoO}_3\text{:Na}_2\text{MoO}_4$ ratios at a constant concentration of UO_2 . The compositions containing 20, 30, and 50% MoO_3 were of interest because uranium phase composition experiments indicated that these $\text{MoO}_3\text{:Na}_2\text{MoO}_4$ ratios produce the desired UO_2 product. To investigate the effect of the melt composition on fission product partitioning, partitioning experiments heated to 1413 K were conducted because initial uranium phase composition experiments were performed at this temperature. When the same experiment was performed at 1313 K, similar trends were seen for the partitioning of fission products from the UO_2 product. The composition that displayed the best partitioning at 1413 K for the lanthanides and Zr is the 20% MoO_3 -50% Na_2MoO_4 -30% UO_2 composition. From the uranium product composition experiments, this composition resulted in UO_2 as the final product. The UO_2 can be contaminated by the lanthanides and zirconium oxides during the crystallization process because of the formation of fission product oxide - uranium oxide solid solutions[16-18]. For example, as zirconium dissolves in the molybdate melt, the compound ZrMo_2O_8 forms, which incongruently melts and decomposes to ZrO_2 [4]. Fission product contamination was

lessened in the 20% MoO_3 -50% Na_2MoO_4 -30% UO_2 melt because the high concentration of Na_2MoO_4 allowed for the increased solubility of the lanthanides and zirconium in the melt, forming molybdates, and the low concentration of MoO_3 decreased the solubility of UO_2 in the melt, decreasing the fission product oxide's opportunity to form solid solution with the UO_2 .

When the Na_2MoO_4 concentration was decreased below 50% and the MoO_3 concentration was increased to the same level as UO_2 (30% MoO_3 -40% Na_2MoO_4 -30% UO_2), the distribution ratios for the lanthanides and zirconium decreased. This result suggests that the solubility of the zirconium and lanthanide fission product oxides is directly proportional to the amount of the Na_2MoO_4 in the melt, which is consistent with the finding above. However, this trend was not seen in the composition 50% MoO_3 -20% Na_2MoO_4 -30% UO_2 , at 1413 K, where the distribution ratios for zirconium and the lanthanides are greater than the 30% MoO_3 -40% Na_2MoO_4 -30% UO_2 composition. From the uranium product composition experiments, it was seen that the samples containing 30% MoO_3 -40% Na_2MoO_4 -30% UO_2 formed a UO_2 product, while the 50% MoO_3 -20% Na_2MoO_4 -30% UO_2 composition formed UO_2 and $\text{U}(\text{MoO}_4)_2$ products. The increased solubility of the UO_2 in the melt due to larger MoO_3 : Na_2MoO_4 ratios allowed for more $\text{U}(\text{MoO}_4)_2$ production, which possibly resulted in lower fission product oxides contamination.

The high distribution ratios of Sr and Cs appear almost independent (in log scale) of the weight fractions of MoO_3 and Na_2MoO_4 . As SrO-UO_2 is known to form solid solutions [16, 17], the trace amount of Sr left in the product could be attributed to a solid solution of SrO_2 formed with UO_2 , however, this trace amount of Sr is more likely present due to the interaction SrMoO_4 with the mixed molybdate, $3\text{Na}_2\text{MoO}_4 \cdot 2 \text{U}(\text{MoO}_4)_2$. The removal of this type of contamination is discussed in a later section.

4.2.2. Temperature Effects

Figure 6 displays the fission product partitioning that result from varying the temperature to which the melt was heated. The distribution ratio for the heavier lanthanides, and Zr, appeared to be nearly constant at the two temperatures studied for the concentration of 30% MoO_3 , while the lighter lanthanides, displayed better partitioning at the lower temperatures, especially for the 50% MoO_3 composition. As previously discussed, the lanthanides form solid solutions with UO_2 . [16-19] Increasing the temperature of the system increased the solubility of the UO_2 in the MoO_3 . This increased solubility of the UO_2 potentially allows for increased formation of the fission product oxide- UO_2 solid solutions. This observation explains the greater purification of the lanthanides at the lower temperatures.

Another fission product that exhibited temperature dependence was Ru, which had better partitioning at the higher temperatures. Unlike the rest of the fission product oxides, RuO_2 is not soluble in MoO_3 . [4] RuO_2 is also very volatile at temperatures exceeding 1173 K, therefore, the higher temperature could lead to volatilization of Ru from the melt; however, our experiments were not designed to detect fission product vaporization.

4.2.3. Effects of the Na_2MoO_4 Washes

As seen in the uranium product composition experiments, the Na_2MoO_4 wash breaks down the $\text{U}(\text{MoO}_4)_2$ product to form a UO_2 product. This approach is not the only application of the Na_2MoO_4 wash. One method for the fission product oxides to contaminate the uranium product is by dissolving in the mother liquor and adsorption or trapping of the mother liquor onto the surface of the UO_2 product. Due to the slight solubility of the UO_2 in Na_2MoO_4 and the large

solubility of the fission product oxides in the Na_2MoO_4 , washes using Na_2MoO_4 can remove this form of contamination by forming the fission product molybdates.

Fission product oxides can also interact with the mixed molybdate $3\text{Na}_2\text{MoO}_4 \cdot 2\text{U}(\text{MoO}_4)_2$ by replacing the sodium ion[7]. Fission product molybdates and uranium molybdate are very soluble in Na_2MoO_4 , therefore, multiple washes using Na_2MoO_4 decompose the mixed molybdate, removing the fission product contamination and purifying the UO_2 product.

Figure 7 shows the distribution ratios of all the fission products after one or three Na_2MoO_4 washes performed for a composition of 30 % MoO_3 -40% Na_2MoO_4 - 30% UO_2 . The distribution ratio for Cs, Sr, Rh and Pd clearly indicated that surface or substitutional contamination occurred because the purification of the fission products increased by increasing the number of Na_2MoO_4 washes. When Tul'skii *et al.* performed experiments to remove trace amounts of Cs from UO_2 , they speculated that the Cs was incorporated into the mixed molybdate lattice of $3\text{Na}_2\text{MoO}_4 \cdot 2\text{U}(\text{MoO}_4)_2$ by replacing the Na ion .[7] The high distribution ratio achieved for the Cs after multiple washes of Na_2MoO_4 suggest that nearly all of the Cs was removed from the UO_2 product. The results of the Na_2MoO_4 washes indicate that the Cs is likely incorporated in the of $3\text{Na}_2\text{MoO}_4 \cdot 2\text{U}(\text{MoO}_4)_2$ lattice (or surface contamination). Sr and Rh also exhibited reasonable purification from the final product with multiple washes of Na_2MoO_4 . SrO is known to form Sr_2MoO_4 with MoO_3 , and Rh_2O_3 is very soluble in the Na_2MoO_4 and MoO_3 , which would result in their increased removal from the product with multiple washings. Little information is known of how Pd interacts with the MoO_3 and Na_2MoO_4 . Due to the increased purification that Pd displays with multiple washes of Na_2MoO_4 , it is speculated that Pd contaminates UO_2 either by

dissolution in the mother liquor followed by adsorption or trapping of the mother liquor onto the surface of the UO_2 , or by an interaction with the mixed molybdate.

None of the lanthanides exhibited a change in distribution ratio with additional Na_2MoO_4 washes, suggesting that the lanthanides did not contaminate the UO_2 product by forming a mixed molybdate, and that the oxides does not dissolve in the mother liquor, and crystallize on the UO_2 through trapping or adsorption. Tul'skii *et al.*, claimed that Ce entered the UO_2 lattice by forming a solid solution of $\text{UO}_2\text{-Ce}_2(\text{MoO}_4)_3$ during crystallization. Tul'skii also claimed that the $\text{Ce}_2(\text{MoO}_4)_3$ dissolves in the mother liquor, and penetrates the UO_2 by adsorption. [7] Figure 7 does not support this second claim, as the distribution ratio for Ce did not increase as the number of Na_2MoO_4 washes increase.

5. Conclusion

Molybdate melts demonstrated the ability to separate fission products from a uranium product for potential application of a modified open fuel cycle for used fuel treatment. Overall, the conditions we identified to achieve the purest uranium oxide product were:

1. A melt consisting of 20 wt% MoO_3 - 50 wt% Na_2MoO_4 -30 wt% UO_2
2. Heating the melt to 1313 K and performing the physical separation of the UO_2 from the mother liquor.
3. Washing the uranium product once with Na_2MoO_4 .

It was determined that melt compositions containing more MoO_3 than UO_2 yield uranium molybdates as a major species, such as UMo_2O_8 , while melts containing less MoO_3 lead to the formation of UO_2 precipitate as a major species.

The fission products investigated in the mock fuel displayed adequate partitioning from the uranium precipitate product. Certain fission products such as Cs, Sr, Ru and Rh displayed particularly good separations ($D=100-55000$), while Zr, and the lanthanides, had lower distribution ratios ($D=5-100$). Distribution ratios greater than 10 are adequate for purification of the UO_2 . Zirconium and the lanthanides displayed the best partitioning in melts consisting of 20% MoO_3 -50% Na_2MoO_4 -30% UO_2 .

The fission product oxides exhibited better partitioning when the system was only heated to 1313 K as compared to 1413 K. The UO_2 and fission products were more soluble in the MoO_3 at 1413 K, which increased the opportunity to form solid solutions with the fission product oxides as the solution was cooled to precipitate the UO_2 .

A number of washes of Na_2MoO_4 allowed for greater removal of Cs, Sr, Rh and Pd contaminants from the UO_2 by dissolving them into the wash solution. These contaminants were likely present in the UO_2 from adsorption or trapping of the mother liquor onto the surface of the product, or interacting with the mixed molybdate $3\text{Na}_2\text{MoO}_4 \cdot 2\text{U}(\text{MoO}_4)_2$ by replacing the Na ion. However, no obvious benefit in repeated washing steps was observed for Zr and lanthanides, and thus was not deemed necessary for purification of the UO_2 product.

This study demonstrated the feasibility of using the molybdate process for the recovery of UO_2 and provided insight into fission product partitioning during the process. However, a significant

amount of work remains to be completed before the process can be used in the treatment of used nuclear fuel.

6. References

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5. Acknowledgements

The submitted manuscript has been created by U Chicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government. Argonne National Laboratory's work was supported by the U.S. Department of Energy, Office of Nuclear Energy, under contract DE-AC02-06CH11357.

6. Figures

Figure 1. Flowchart diagramming UO_2 partitioning in the molybdate melt.

Fission Product Composition, mg of FP Metal/g-U									
Metal	Sr (SrO)	Zr (ZrMoO ₅)	Ru (RuO ₂)	Rh (Rh ₂ O ₃)	Pd (PdO)	Cs (Cs ₂ MoO ₄)	La (La ₂ O ₃)	Ce (CeO ₂)	Nd (Nd ₂ O ₃)
mg/g-U	0.805	3.79	2.28	0.492	1.433	2.49	1.28	2.48	4.22
Metal	Sm (Sm ₂ O ₃)	Eu (Eu ₂ O ₃)	Gd (Gd ₂ O ₃)	Tb (Tb ₂ O ₃)	Dy (Dy ₂ O ₃)	Er (Er ₂ O ₃)	Lu (Lu ₂ O ₃)	Pr (Pr ₂ O ₃)	total FP metals
mg/g-U	0.9	0.136	0.126	0.003*	0.001* (0.138)	0.001* (0.151)	0.001* (0.127)	1.17	21.6 (~2.2%)

*larger quantities than expected for this mock fuel composition were actually used; the actual quantities are given in parenthesis below the calculated quantity.

Table 1. Fission product composition based on a calculated composition of 3.2% enriched used fuel with 33 MWd/kg burnup at a mean flux of $3.24 \times 10^{18} \text{ n m}^{-2} \text{ s}^{-1}$ in a typical PWR after 10 years of cooling.[13] Fission product partitioning experiments contained about 2.2 % of this composition in each melt.

Figure 2. Experimental setup inside the tube furnace

Figure 3. Photographs of uranium precipitates obtained from the melts of varying MoO₃, Na₂MoO₄, and UO₂ compositions.

Sample #	Initial Composition (weight %)			Color after H ₂ O wash	Species		Soluble in
	MoO ₃	Na ₂ MoO ₄	UO ₂		Major	Minor	
1	20%	50%	30%	gray-black	UO ₂		Hot HNO ₃ /H ₂ O ₂
2	30%	40%	30%	gray, yellow-green	UO ₂	Na ₄ U(MoO ₄) ₄	Hot NaOH/H ₂ O ₂ partially hot HNO ₃ /H ₂ O ₂
3	40%	30%	30%	brown-purple	U(MoO ₄) ₂	UMo ₇ O ₂₂	partially hot HNO ₃ partially hot NaOH/H ₂ O ₂
4	50%	20%	30%	brown-purple-gray	UO ₂ , U(MoO ₄) ₂	Na ₄ U(MoO ₄) ₄	partially hot HNO ₃ /H ₂ O ₂ partially hot NaOH/H ₂ O ₂
5	60%	10%	30%	dark blue-purple	U(MoO ₄) ₂		Hot NaOH/H ₂ O ₂ partially hot HNO ₃ /H ₂ O ₂
6	60% MoO ₃ , 10% Na ₂ MoO ₄ , 30 %UO ₂ washed with Na ₂ MoO ₄ heat to 1150 °C			green-gray	UO ₂	Na ₄ U(MoO ₄) ₄	Hot NaOH/H ₂ O ₂ partially hot HNO ₃ /H ₂ O ₂
7	50%	-	50%	purple	U(MoO ₄) ₂	UMo ₁₁ O ₃₅ UMo ₇ O ₂₂	Hot NaOH/H ₂ O ₂
8	70%	10%	20%	dark blue, purple	U(MoO ₄) ₂	UMo ₇ O ₂₂	Hot NaOH/H ₂ O ₂
9	30%	10%	60%	green-gray	UO ₂	Na ₄ U(MoO ₄) ₄	Hot HNO ₃ /H ₂ O ₂

Table 2. XRD results of uranium species precipitated from different compositions of MoO₃, Na₂MoO₄, and UO₂

Figure 4. XRD pattern of uranium precipitate obtained from the salt mixture containing 20% MoO₃-50% Na₂MoO₄- 30% UO₂ heated to 1313 K and cooled to room temperature. This spectrum is compared to a UO₂ powder and a standard pattern for UO₂.

Figure 5. Distribution ratios for selected fission products at varying concentrations of MoO_3 and Na_2MoO_4 , and constant 30% UO_2 . Samples were heated to 1413 K and cooled to 1223 K at a rate of 38 K min^{-1} , and then were washed once with Na_2MoO_4 .

Figure 6. Distribution ratios of fission products from tests conducted at two dissolution temperatures followed by cooling at a rate of 38 K min^{-1} . Samples contain 30% MoO_3 , 40% Na_2MoO_4 , and 30% UO_2 and were washed once with Na_2MoO_4 .

Figure 7. Distribution ratios of the fission products after uranium precipitate was treated with one or three Na₂MoO₄ washes. The precipitates were obtained from samples containing 30% MoO₃, 40% Na₂MoO₄, and 30% UO₂ that were heated to 1413 K and cooled to 1223 K at a rate of 38 K min⁻¹.