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Scandium Separation from Tungsten Crucibles

Preliminary Investigation into Separation of Scandium Metal from Tungsten Metal Crucibles Using an Acid Soak Process

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Abstract

The first step in an attempt to isolate Sc⁰ from a W⁰ crucible was explored by soaking the samples in a series of organic (HOAc) and inorganic (HCl, H₂SO₄, H₃PO₄, HNO₃) acids. All samples, except the HOAc, yielded a powder. The weight loss suggests that HNO₃ is the most efficient solvent; however, the powders were tentatively identified by PXRD and found to contain both W and Sc by-products. The higher weight loss may also indicate dissolution of the W⁰ crucible, which was further evidenced upon visual inspection of the crucible. The H₃PO₄ acid soak yielded the cleanest removal of Sc from the crucible. More work to understand the separation of the Sc⁰ from the W⁰ crucible is necessary but the acid routes appear to hold promise under not as of yet established criteria.

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INTRODUCTION

The goal of this project is to successfully remove the scandium (Sc^0) metal from a tungsten (W^0) crucible and recover the Sc^0 . The initial attempts to accomplish this goal involved soaking these crucibles in a variety of acids. The general chemical approach was to selectively dissolve one of the metals and then recover it through an oxidation-reduction (redox) reaction.

1.1. RESULTS AND DISCUSSION

Results. Those acids which were on hand were selected and are listed in Table 1. The general setup was to fill a beaker part way with the desired acid and to place the crucible into the acid. Half of the sample was dipped in order to track the progress of the reaction. The various results are detailed in Table 1, shown in Figure 1 and discussed individually below.

(a) Hydrochloric Acid. Upon introduction of the crucible into the HCl solution, the initial pale yellow solution smoked slightly. As time progressed (see Figure 2), the Sc^0 appeared to darken and began to dissolve. Also noted was the dissolution of the W^0 crucible along the edges. Overall a 10 % weight loss was recorded along with the formation of a black precipitate. This was separated from the solution, washed with water, and dried in an oven at 125 °C. PXRD patterns obtained on the dried powder indicated that W^0 (PDF 00-004-0806) was the main component and a minor phase of ScCl_3 (PDF 00-0420975) was also available. The changes wrought over time in the crucible soaked in HCl are shown in Figure 3. The mother liquor was also evaluated after it was dried to a red/yellow powder. The

	ACID	Visual	Wt Δ 4 d	PXRD
(a)	HCl	<ul style="list-style-type: none"> • smokes • darkens over time • Black ppt 	2.365 9.8 %	W^0 ScCl_3
(b)	H_2SO_4	<ul style="list-style-type: none"> • Cloudy white ppt 	0.47 2.12%	$\text{WO}_3 \cdot 0.5 \text{H}_2\text{O}$ $\text{H}_{0.2}\text{WO}_3$ $\text{Sc}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$
(c)	H_3PO_4	<ul style="list-style-type: none"> • Grey ppt • Clear ML 	1.197 5.47%	H_3PO_3 WO_3 W_5O_{14}
(d)	HOAc	<ul style="list-style-type: none"> • No Δ 	0.000 0.00%	No analysis
(e)	HNO_3	<ul style="list-style-type: none"> • Green ppt • Clear ML 	6.075 (26.0 %)	$\text{WO}_3 \cdot \text{H}_2\text{O}$ ScN

Table 1. Compiled results from the ‘soak’ of the Sc^0/W^0 crucible in a series of acids.



Figure 1. Experimental setup for Sc^0/W^0 crucible using (a) HCl, (b) H_2SO_4 , (c) H_3PO_4 , and HOAc.

small peaks present are in line with ScCl_3 (PDF 00-042-0975).

Figure 2. Pictures of crucible in HCl after (a) 0, (b) 15, (c) 48, and 96 h.

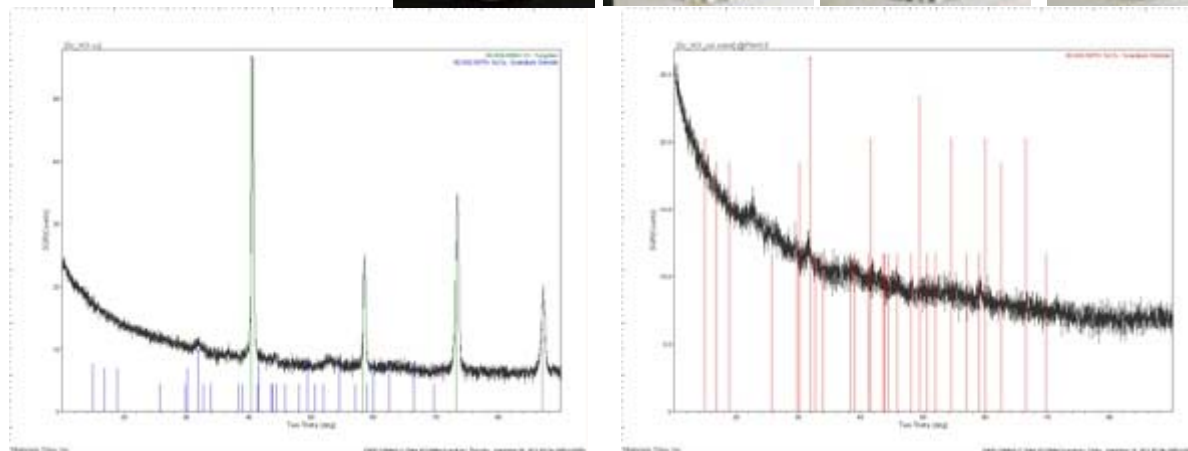
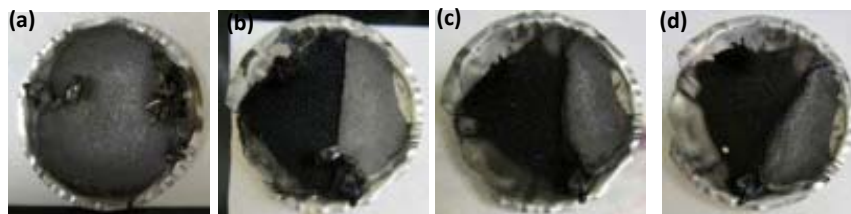
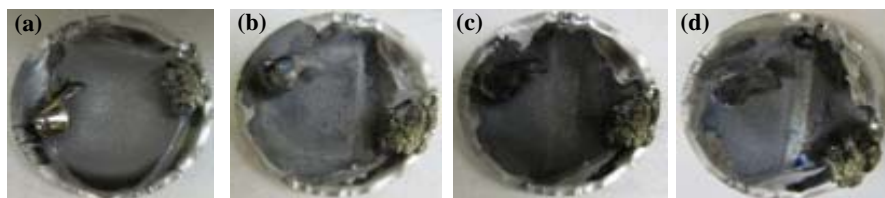


Figure 3. XRD patterns of (a) black powder precipitate and (b) dried mother liquor powder.

(b) **Sulfuric Acid.** Upon placement of the crucible into the H_2SO_4 solution, the surface of the Sc° began to bubble. The surface of the crucible did not significantly change; however, a white precipitate formed very quickly and grew over time. The crucible showed some etching of the Sc° but did not appear to attack the W° . Figure 4 shows the changes that occurred over time. The weight change was less dramatic than that noted for the HCl system and it is no surprise that the surface did not appear significantly altered.

Figure 4. Pictures of crucible in H_2SO_4 after (a) 0, (b) 15, (c) 48, and 96 h.



Separating the insoluble portion from the acid and ambient humidity proved to be difficult. The mother liquor solution could be dried to a white powder at 125°C but would readily hydrate upon cooling to room temperature. The XRD pattern of the wet sample is shown in Figure 5. The XRD pattern obtained was complicated but the compounds isolated were tentatively identified as tungsten oxide hydrate ($\text{WO}_3 \cdot 0.5 \text{H}_2\text{O}$; PDF 00-036-1143), tungsten hydrogen oxide ($\text{H}_{0.2}\text{WO}_3$; PDF 00-020-0483), and scandium sulfate hydrate ($\text{Sc}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$; PDF 00-031-1226).

The powder had flecks of black which may be the tungsten. $\text{Sc}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ is reported to be a

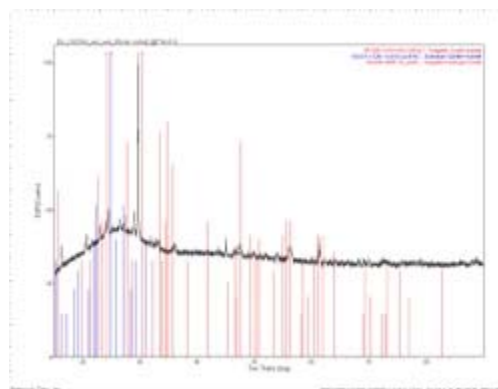
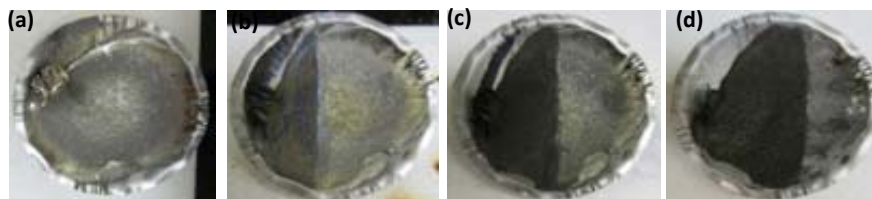


Figure 5. XRD pattern of mother liquor of the H_2SO_4 sample dried at 125°C .

hygroscopic white powder which is consistent with the bulk of the material isolated here.

(c) **Phosphoric Acid.** There was no noticeable reaction upon placing the crucible into the H_3PO_4 solution. Over time, small bubbles were noted. As can be seen in Figure 6, the surface is substantially darkened which indicates a reaction had occurred, which is

Figure 6. Pictures of crucible in H_3PO_4 after (a) 0, (b) 15, (c) 48, and 96 h.



further evidenced by the 5.46% weight loss. This would account for the grey precipitate formed over the 4 d period. PXRD analysis indicated that this powder was tungsten (W^0 , 00-004-0608) but an amorphous phase was also evident (Figure 7). Again, the mother liquor was centrifuged, dried ($550\text{ }^\circ\text{C}$ for 24 h), and the resulting white powder was analyzed by PXRD. The resulting spectrum was complex and difficult to match with existing PXRD patterns; however, the pattern appears to fit H_3PO_3 (PDF 01-072-0518) with minor phases of WO_3 (PDF 01-085-2460) and W_5O_{14} (PDF 01-041-0745). These are shown in Figure 8.

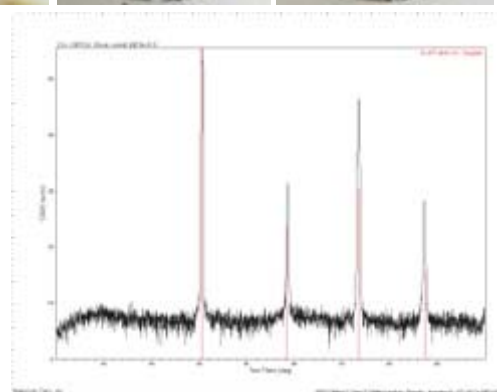


Figure 7. PXRD pattern of mother liquor of the H_2SO_4 sample dried at $125\text{ }^\circ\text{C}$.

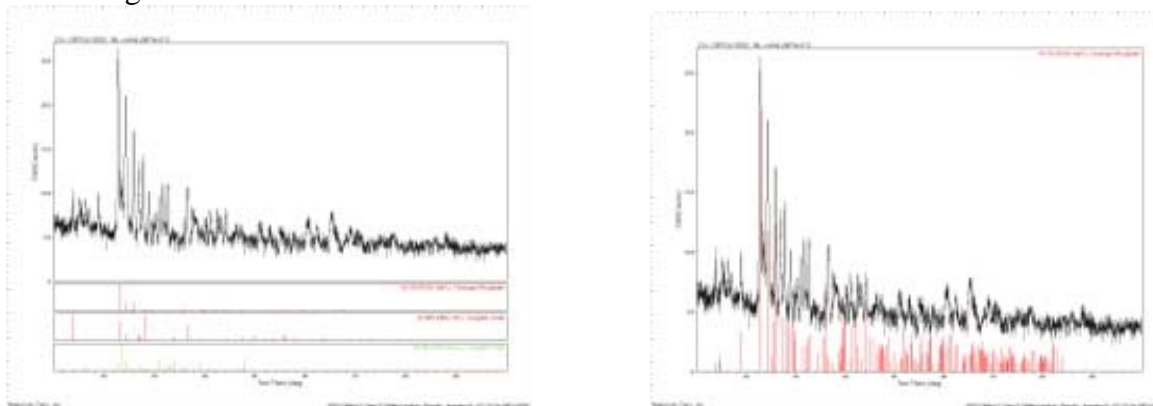
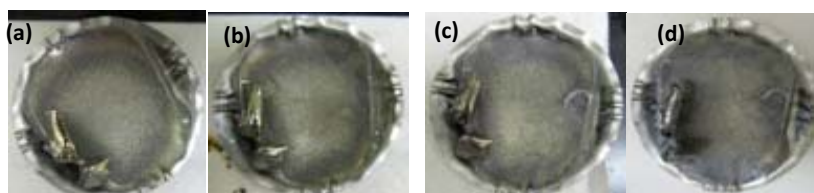


Figure 8. PXRD pattern of dried mother liquor of the H_3PO_4 sample (a) common solution, (b) H_3PO_3 specific.

(d) **Acetic Acid.** There was no noticeable change in the acetic acid/acetic anhydride sample both in visual properties (Figure 9) or weight analysis. Additional characterization was not pursued.

Figure 9. Pictures of crucible in HOAc after (a) 0, (b) 15, (c) 48, and 96 h.



(d) Nitric Acid. Upon placement of the crucible in the 7M HNO₃ solution the solution immediately turned a pale yellow-green color and bubbles formed on the Sc⁰ surface. Within minutes a black precipitate began to form and settle on the bottom of the beaker. After sitting for 3 h. no more bubbles were generated and the crucible was weighed. A mass loss of 18.5 wt% was recorded. The crucible was returned to a beaker with a fresh solution of 7 M HNO₃. No

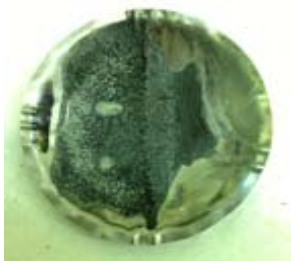


Figure 10. Picture of crucible after 72 h in HNO₃.

bubbles were noted likely due to surface passivation. The crucible was removed from the 7 M HNO₃ solution and placed in contact with 15.8 M HNO₃. Immediately upon contact with concentrated HNO₃ an intense reaction was observed with rapid bubble formation and emission of red-orange colored fumes (likely nitrous oxides). After a few minutes the solution was diluted with the addition of 7 M HNO₃ solution to slow down the reaction rate. After 24 h there was no evidence of further dissolution taking place and the total mass loss was recorded at 21.4%. Visually it was apparent that at least some of the mass loss was directly due to Sc⁰ dissolution

though clearly some W⁰ was lost as well as evidenced by a small hole in the crucible. The final (72 h) sample from a conc HNO₃ sample is shown in Figure 10.

The precipitate from the HNO₃ solution was separated by centrifugation. The PXRD analysis of the resultant green powder soak was identified as WO₃H₂O (PDF 00-043-0679), see Figure 11.

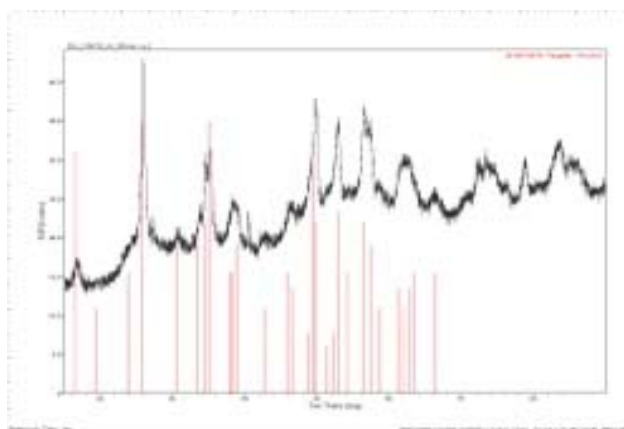


Figure 11. PXRD patterns of green precipitate.

After removing the insoluble portion by centrifugation, the mother-liquor was heated (~70-100°C) in an evaporating dish to dry the solution to a white powder.

The PXRD pattern (see Figure 12) was extremely complex and a direct match could not be readily elucidated. The pattern on the left has three possible products and the one on the right matched the ScN pattern (directly overlaid for easier viewing).

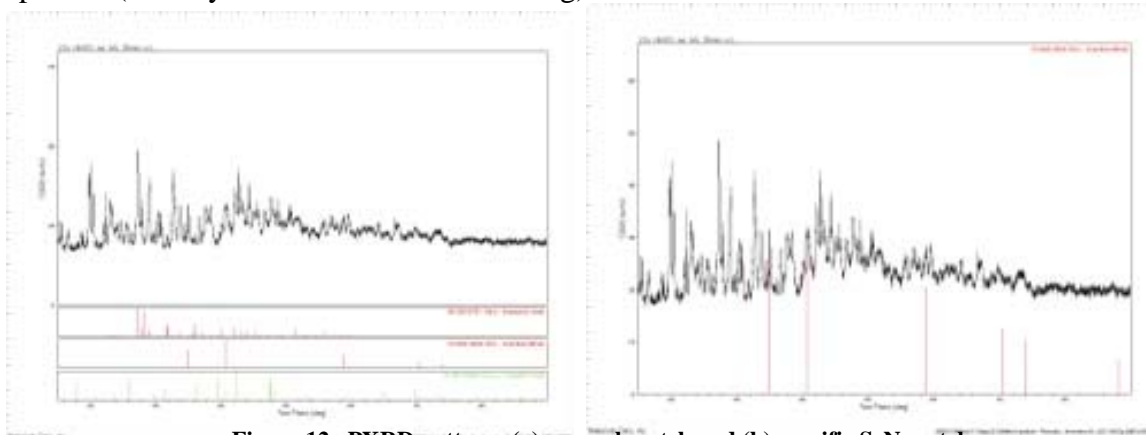


Figure 12. PXRD patterns (a) general match and (b) specific ScN match.

(e) Oxalate information. In an attempt to measure the amount of Sc in the HNO₃ solution an oxalate precipitation was attempted. A 10 mL aliquot of the pale yellow-green scandium-tungsten nitric acid solution was placed in a glass scintillation vial. 10 mL of 0.3M oxalic acid aqueous solution was slowly added to the vial and a white precipitate formed and eventually settled out. This precipitate was recovered by vacuum filtration and a PXRD pattern was obtained. The PXRD pattern for the oxalate precipitate proved to be WO_{2.90} (PDF 00-036-0102 and 00-018-1417) and tungsten carbide (CW₃; 00-042-0853) of the resultant powder from the HNO₃ soak was identified as WO₃H₂O (PDF 00-043-0679).

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Summary and Conclusion

All of the inorganic acids were found to readily etch the samples studied. The weaker organic acid did not appear to impact the bound metals. It is tempting to just look at the largest weight loss and use that acid as the best method for removing the Sc⁰ from the W⁰; however, this may include the dissolution of both or the least desired metal. This is confirmed when the PXRD is analyzed where each sample investigated showed W products were present. Typically, these products were identified as either the oxide or hydrate species, independent of the acid used. The high Z of the W may dominate the smaller Z of Sc in the final spectra, so determination of quantity should be limited as well. For those Sc materials identified, they were, not unexpectedly, identified as the anion derivative of the acid. The nitrate reaction is an exception where it may have been reduced all the way to the nitride. The most efficient and cleanest acid wash appears to be the H₃PO₄ soak which preferentially removed Sc while minimally impacting the W crucible. Additional work to clarify and determine the optimal conditions are necessary to verify the above efforts.

FUTURE DIRECTIONS

The standard reduction potential [$\text{Sc}^{+3} + 3\text{e} \rightarrow \text{Sc}^0$] is $E^\circ = -2.077$ V. Therefore the conversion of the $-\text{Cl}$, $-\text{SO}_4$, $-\text{NO}_3$ (or $-\text{N}$) derivatives to the metal is assumed to be accomplished by electrolysis methodologies. In particular, Sc^0 is formed from the electrolysis of the eutectic melt of ScCl_3 and other salts at $700\text{-}800$ °C. Further exploration of reducing agents to chemically generate the Sc^0 should also be available.

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