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Effect of Technetium-99 Sources on Its Retention in Low Activity Waste Glass

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Abstract

Small-scale crucible melting tests on simulated waste glass were performed with technetium-99 (Tc-99) introduced as different species in a representative low activity waste simulant. The glass saw an increase in Tc-99 retention when $TcO_2 \cdot 2H_2O$ and various Tc-minerals containing reduced tetravalent Tc were used compared to tests in which pertechnetate with heptavalent Tc was used. We postulate that the increase of Tc retention is likely caused by different reaction paths for Tc incorporation into glass during early stages of melting, rather than the low volatility of reduced tetravalent Tc compounds, which has been a generally accepted idea. Additional studies are needed to clarify the exact mechanisms relevant to the effect of reduced Tc compounds on Tc incorporation into or volatilization from the glass melt.

1 Introduction

Radioactive wastes present at the U.S. Department of Energy's Hanford Site will be vitrified at the Hanford Tank Waste Treatment and Immobilization Plant (WTP). Tank wastes

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21 will be combined with glass-making additives in a slurry mixture called the feed, which is fed
22 into melters, and cooled into glass. Technetium-99 (Tc-99) is one of the more challenging
23 radionuclides present in Hanford low activity waste (LAW) because of its long half-life of $2.13 \times$
24 10^5 year and its penchant to become water-soluble pertechnetate. The pertechnetate ion
25 (TcO_4^-), a stable form of oxidized Tc, is highly mobile in oxidized aqueous conditions and volatile
26 at the temperatures of waste processing in glass melters [1, 2], thus inhibiting Tc incorporation
27 into the product glass [3-5].

28 As currently planned, volatilized Tc will be captured in an off-gas system, recycled back
29 to pretreatment, and eventually re-added to the glass melter [6]. This recycling also returns
30 sulfur and halides to the glass melt, which can limit the waste-loading of the glass [7]. Methods
31 of increasing the fraction of Tc incorporated into and retained in the glass (referred to as
32 “retention”) to avoid recycling are preferred, and several avenues of research are addressing
33 this area [5, 7, 8].

34 A possible solution is the capture of Tc either from liquid waste streams or from off-gas
35 condensates by incorporation into a durable mineral phase. For example, a mineral-forming
36 precursor could be added directly into waste streams before being fed to the melter, or to the
37 off-gas condensate. If the thermal stability and chemical durability of the selected mineral are
38 sufficient, incorporated Tc may remain within the mineral structure through melting of the
39 glass, thus inhibiting Tc volatility [9]. If used in the off-gas system, the resulting Tc mineral (not
40 containing sulfur or halides) could be recycled back to pretreatment, serve as a standalone
41 waste form, or be incorporated into a low-temperature waste form that is being considered for
42 immobilizing secondary wastes from the WTP [10, 11].

43 Minerals such as perovskite [12], pyrochlore [12, 13], spinel [14], and sodalite [15-17]
44 have been shown to incorporate Tc, and are therefore potentially suitable for this use [18].
45 Rhenium (Re) is used as a Tc surrogate due to the similarities of the pertechnetate and
46 perrhenate species, and Re-containing sodalite (with Re^{7+}) has demonstrated the utility of using
47 a durable mineral phase to increase Re retention in glass [9, 15]. However, attempts to
48 synthesize minerals, such as spinel that can incorporate tetravalent Tc, with tetravalent Re
49 were not successful, presumably because of differences in ionic size and redox potential. While
50 Re is a widely used chemical surrogate for Tc [2] that behaves similarly in heptavalent oxidation
51 states, the redox potentials and mechanisms of Tc and Re are not similar.

52 The retention, partitioning, and oxidation of Tc in feeds prepared with different Tc-
53 bearing minerals as well as TcO_2 were compared against KTcO_4 -spiked feed. Two standard
54 solutions— KTcO_4 and $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ —and four Tc-doped iron minerals—Tc-trevorite from $\text{Fe}(\text{OH})_2$,
55 Tc-magnetite from $\text{Fe}(\text{OH})_2$, Tc-goethite, and Tc-trevorite from co-precipitation—were prepared
56 and tested in melts of LAW simulant glasses formed at a series of temperatures. Both
57 inductively coupled plasma mass spectrometry (ICP-MS) and liquid scintillation counting (LSC)
58 were performed to measure Tc retention of all feeds and heat-treated samples. Leach tests
59 were performed to characterize the fraction of Tc in the soluble and insoluble phases of the
60 feed and glass-forming melt. X-ray absorption near edge spectrum (XANES) analysis was
61 performed to characterize the oxidation state of the Tc in the samples. The effects on Tc during
62 melting are discussed, and mechanistic explanations for these observations are offered.

63 2 Preparation of Tc-99 source materials

64 2.1 *KTcO₄ standard solution*

65 The KTcO₄ standard solution was prepared as described by Soderquist et al. [19] for
66 doping glass with a control Tc source. Ammonium pertechnetate was dissolved and
67 recrystallized to ensure purity, and then dissolved in K₂CO₃ solution and slowly evaporated,
68 driving off ammonium carbonate was driven off during evaporation, leaving KTcO₄. The KTcO₄
69 was weighed and dissolved in water to create a spike solution of known Tc concentration.
70 Aliquots of this spike solution were added to feeds as necessary using a pipette.

71 2.2 *TcO₂·2H₂O standard solution*

72 The TcO₂·2H₂O was prepared by hydrolysis of (NH₄)₂TcCl₆ in water, as described in Rard
73 et al 1999 [20]. Dry (NH₄)₂TcCl₆ was dissolved in water and then warmed to near boiling with
74 dry N₂ (g) blown over the surface. The solution was evaporated nearly dry to expel HCl
75 produced by hydrolysis. The mixture was re-suspended in water and re-evaporated several
76 times to eliminate residual HCl. Hydrolysis was judged to be complete when the hydrous TcO₂
77 settled under gravity and left clear supernatant. The hydrous TcO₂ product was centrifuged,
78 washed with water to remove ammonium chloride, and finally dried at ~120°C under N₂ (g).

79 2.3 *Tc-trevorite from Fe(OH)₂*

80 Tc-trevorite was prepared as described by Lee et al. 2016 [21]. Five milliliters of a 0.5 M
81 NiCl₂ solution and 0.09 g of Fe(OH)₂ powder were added to a vial and shaken for 24 hours, after
82 which 15 mL of a solution of 0.001 M NaTcO₄ and 1 M NaOH was added. The combined
83 solutions were heated at 75°C for 72 hours. All solutions were anoxic, and work was performed
84 in an anoxic glove box. After the heat treatment, the reacted material was removed from the

85 hood and rinsed over a 0.45 μm filter. A scanning electron microscopy (SEM) micrograph of the
86 Tc-trevorite is shown in Figure 1. Based on SEM micrographs of the particles, particle sizes were
87 estimated to be 400 to 600 nm.

88 **2.4 Tc-magnetite from $\text{Fe}(\text{OH})_2$**

89 Tc-magnetite was prepared as described by Um et al. [22] in a manner similar to the Tc-
90 trevorite from $\text{Fe}(\text{OH})_2$. To synthesize the magnetite, NiCl_2 was excluded, and the $\text{Fe}(\text{OH})_2$ was
91 reacted with the NaTcO_4 and NaOH for 72 hours, without the initial 24 hour reaction with NiCl_2 .
92 Results from XRD analysis showed impurities of goethite (see **Error! Reference source not**
93 **found.**).

94 **2.5 Tc-goethite**

95 Tc-goethite was prepared as described by Um et al. [23]. Powdered goethite was
96 suspended in a $\text{pH} < 2$ HNO_3 solution. Powdered $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (3.48 g) was directly added to the
97 goethite slurry as a $\text{Fe}(\text{II})$ source, and the mixture was reacted for 1 day in an anoxic chamber.
98 Then, NaTcO_4 solution was added in 0.1M of NaOH solution and homogenized by shaking for 1
99 to 2 days before mixing with goethite slurry. After mixing, additional $\text{Fe}(\text{NO}_3)_3$ was added to
100 “armor” (i.e., precipitate an additional goethite layer upon) the goethite and continuously
101 reacted at 80°C for 7 days. The final Tc-goethite was rinsed, filtered, and dried in air before use.
102 A micrograph of the Tc-goethite is provided in Figure 2. Based on the image, the goethite
103 particles are approximately $1 \mu\text{m}$ by 200 nm .

104 **2.6 Tc-trevorite from coprecipitation**

105 Tc-trevorite particles were prepared using an aqueous mineralization of FeSO_4 , NiCl_2 ,
106 and pertechnetate as described by Lukens et al. [24]. The compounds were dissolved in

107 deionized water that was first sparged with N₂ (g) and then added to a 2 M NaOH/NaNO₃
108 solution that was finally heated to 95°C for 90 minutes. Several rinses and centrifuging steps
109 made the sample ready to use. XRD analysis presented in supplemental information of [24]
110 indicate crystallite size of 28 nm.

111 **3 Glass feed preparation**

112 Low activity waste glass AN-102 was used as a test glass in continuity of research by Jin
113 et al. 2015, following the recipe prepared by Matlack et al. 2011 [5, 25]. The composition of AN-
114 102 glass feed to make 1 L of slurry is shown in Table 1. [25]. The feed slurry was batched in
115 17.5 g amounts which were used for three 5-gram heat treatments, leach test, and XANES
116 analysis. Table 1 shows the batching followed for tests used. The agate-milled powder
117 components and the dissolved simulant portion were mixed together and sub-divided into
118 Teflon[®]™ beakers. Various Tc sources were added to each beaker and the mixture (i.e., the
119 feed) was stirred briefly. The beakers were then placed in a drying oven (usually overnight) at
120 105°C. The dried feeds then were milled for 5 minutes in an Al₂O₃ ball mill to ensure
121 homogeneity of the final feed.

122 The Tc concentrations of the trevorite and magnetite sources were ascertained by
123 measuring the Tc concentration of the solutions in which they were synthesized. The Tc
124 concentrations of the solutions were measured after synthesis by ICP-MS and LSC, with Tc lost
125 from solution assumed to be in the mineral product. In the case of the goethite, measurement
126 of the Tc concentrations of both the synthesis solution and the goethite after acid digestion
127 were made by ICP-MS [26]. Finally, the Tc concentrations of the TcO₂ and K₂TcO₄ solutions were
128 estimated gravimetrically from the dry weight of K₂TcO₄ used to prepare the sources.

129 KTcO₄ was added to approximate a concentration of 100 ppm Tc in glass, while other
130 test materials were added to the extent they were available. The Tc content of each dried feed
131 was directly measured by LSC, which was used as the baseline to calculate Tc retention for each
132 sample. To measure experimental uncertainty, a duplicate batch of KTcO₄ feed was prepared
133 from raw materials, heat-treated, and analyzed in triplicate.

134 **4 Experimental Procedure**

135 **4.1 Heat treatments**

136 Once a dried, powdered feed was prepared, 5.0 g samples were placed in Pt-Rd crucible
137 and into a Deltech furnace at ~20 °C. The furnace was powered on and heated to ~150°C. After
138 reaching 150°C, the temperature was programmed to increase at a rate of 5°C min⁻¹ to target
139 temperatures of 600, 800, or 1000°C. When the furnace reached the target temperature, it was
140 powered off and allowed to cool to room temperature. This treatment is different than heat
141 treatment carried out on Re-containing AN-102 glass by Jin et al. 2015 [5], where samples were
142 air quenched. As a consequence, samples in the present test underwent heating slightly longer,
143 taking perhaps an hour to cool below 400°C. Once cool, the samples were removed from the
144 furnace, weighed, and removed from the crucible. Whole samples were then pulverized in the
145 alumina ball mill for 5 minutes to ensure homogeneity.

146 To evaluate the uncertainties of the experiments in this study, duplicate or triplicate
147 tests or analyses were performed for selected conditions and samples. Two batches of AN-102
148 feeds spiked with 100 ppm KTcO₄ were prepared separately. The original KTcO₄ feed batch was
149 used for the full of heat treatment series while a duplicate feed batch was heat-treated to

150 1000°C in triplicate by placing all three samples contained in separate Pt-Rd crucibles into one
151 furnace.

152 **4.2 Weight Loss Correction**

153 Weight loss from evolved gases occurs as feed is heated and transitions into
154 glass. The results of chemical analyses for Tc concentration in heat-treated samples were
155 corrected for this weight loss in order to account for Tc concentrations in all samples. The
156 weight-loss factor is the ratio of the mass of heat-treated sample to the mass of dried feed used
157 for heat treatment. The weight-corrected Tc concentration normalized to the starting
158 concentration in dried feed is calculated by multiplying the as-measured Tc concentration in
159 heat-treated sample by the weight-loss factor. Then, Tc retention is the ratio of weight-
160 corrected Tc concentration in a heat-treated sample to the Tc concentration in the dried feed.

161 **4.3 Chemical analyses**

162 NaOH fusion of the dried feed and heat-treated samples was performed to prepare the
163 samples for LSC determination of the Tc concentration. Preparation involved placing ~50 mg of
164 each sample into Ni crucibles, adding 2.5 mL of 20 wt% NaOH solution, and mixing the contents.
165 The crucibles were heated on a hot plate to ~450°C at which point the water had evaporated
166 and the NaOH had become a liquid flux and dissolved much of the solid sample. After cooling,
167 the NaOH and remaining solids were transferred into a 50 mL centrifuge tube and washed with
168 water. After centrifuging, the supernatant was set aside. The Ni crucibles were rinsed into the
169 centrifuge tube containing the remaining solids with 1 mL of concentrated HNO₃ and several
170 milliliters of water rinses after which only a residue presumed to be undissolved ZrSiO₄
171 remained in the centrifuge tubes. This undissolved ZrSiO₄ was present in the dried feeds and

172 samples heated to 600°C, but not present in samples heated to higher temperatures. The HNO₃
173 solution and previous supernatant were combined, adjusted to pH 1-3 with dilute HNO₃, and
174 diluted to 45 mL final volumes with deionized water.

175 For LSC analyses, a 0.5-mL aliquot of each sample was transferred to a LSC vial and
176 combined with 15 mL of LSC cocktail. ZrSiO₄, when present, was transferred to a separate LSC
177 vial, suspended in 15 mL of LSC cocktail, and counted as well (all counts from ZrSiO₄ residue
178 were less than 1% of the total for analyzed samples). A Packard Instruments TriCarb® 3100TR
179 was used for LSC for Tc analyses. Counts were recorded from the 0 to 300 keV regions, which
180 captures ⁹⁹Tc 294 MeV β energies. Total counts then were normalized by the exact weight of
181 the sample fused, and the concentrations of the dilution and 0.5 mL added to the LSC vial to
182 give concentration of Tc in each sample.

183 For selected samples, ICP-MS was used to determine Tc concentration in solid samples
184 after microwave-assisted digestion as described by Lee et al. [21]. A set of the same selected
185 samples also was submitted to Southwest Research Institute (SwRI) for Tc concentration
186 determination by ICP-MS after KOH fusion similar to Re analyses described in previous studies
187 [5, 27].

188 **4.4 Leach tests**

189 Leach tests were performed to determine the fraction of water-soluble Tc in the dried
190 feed and the samples heat-treated to 600 and 800°C. Based on the results of previous leach
191 tests by Jin et al. [5], It was assumed that there was a negligible soluble phase, and therefore no
192 water-soluble Tc, remaining after heat treatment to 1000°C. For the samples tested, 0.3 g of
193 each was added to a 15 mL centrifuge tube, and 14 mL of room-temperature deionized water

194 was added. The centrifuge tubes were inverted and shaken manually for 50 minutes, and then
195 centrifuged at 3000 RPM for 6 minutes. This procedure provided approximately an hour of
196 contact between the solids and water. This extended leaching period was chosen because the
197 10 minutes of leaching with room temperature water used by Jin et al. [5] was not aggressive
198 enough for some samples. After leaching, the supernatant was pipetted off the compacted
199 solids and saved as the “leach” supernatant. The centrifuged solids were rinsed with 14 mL of
200 deionized water, and then the tubes were vigorously shaken to combine the water and solids.
201 The tubes were then centrifuged a second time, and the second supernatant was pipetted off
202 and saved as the “rinse” supernatant. Dilute HNO₃ was added to each supernatant to reduce
203 the pH to within the 1 to 3 range. A 0.5 mL aliquot of each pH-adjusted supernatant was
204 transferred to a LSC vial, combined with 15 mL of LSC cocktail, and counted on the LSC
205 instrument as described above. The sum of the activities for the supernatants is the total
206 soluble fraction of Tc in each sample. Residual solids remaining after the leaching steps were
207 dried in the drying oven at approximately 100°C and weighed to determine the mass fraction of
208 the sample that was water soluble.

209 **4.5 XANES analysis**

210 XANES analysis was carried out using the Stanford Synchrotron Radiation Light source to
211 collect the data at room temperature, as in Lukens et al [24]. Approximately 0.5 g portions were
212 taken from each feed and selected heat-treated sample and taped inside Teflon®TM sampled
213 holders using Kapton tape. X-rays were mono-chromatized using a double crystal
214 monochromator with Si 220 crystals. The second crystal was detuned by 70% to reduce the
215 harmonic content of the beam. Intensities of the incident and transmitted x-ray beam were

216 measured using N₂ (g)-filled ion chambers. Fluorescence data was obtained using a Canberra
217 100 element Ge detector; for the magnetite samples, two layers of aluminum foil were placed
218 in front of the detector to reduce the intensities of the Fe fluorescence lines. The data were
219 corrected for dead time effects. Data were averaged using the software package SixPack as
220 described by Lukens et al. [28].

221 Initially, XANES analyses were performed for all dried feed and heat-treated samples for
222 the KTCO₄, Tc-goethite, and Tc-magnetite feeds. Subsequently for the remaining samples,
223 XANES was performed for the dried feed and 600°C samples only because the samples that
224 were measured indicated that Tc⁴⁺ oxidized rapidly after 600 °C. All Tc retained in the 800 and
225 1000 °C samples was assumed to be Tc⁷⁺. Sharply decreasing amount of Tc⁴⁺ from feed to 600
226 °C samples demonstrate this trend. .

227 **5 Results**

228 Table 2 summarizes Tc concentrations before and after heat treatment to 1000°C,
229 weight-loss factor, and Tc retention in all four 1000°C KTCO₄-spiked samples. The relative
230 standard deviation (RSD) was calculated from the four measurements as an estimate of
231 reproducibility for Tc concentrations in the feeds and heat-treated samples and given in Table
232 2.

233 Table 3 and **Figure 3** compare the Tc concentrations in two dried feed samples (goethite
234 and KTCO₄ feeds) and one heat-treated sample (KTCO₄ heated to 1000°C) obtained by three
235 different analytical techniques: LSC after NaOH fusion, the primary technique used in this study;
236 ICP-MS after microwave-assisted digestion; and ICP-MS after KOH fusion (performed at SwRI).
237 The RSD values given in Table 2 were used to calculate the standard deviations of LSC results for

238 the KTcO_4 feed and 1000°C heat-treated samples as given in Table 3. The standard deviations
239 are generally slightly smaller than the differences between LSC and two set of ICP-MS results
240 (see Figure 3), which suggests that there may be minor analytical biases. The discussion in this
241 study is based only on the LSC measurements.

242 Table 4 summarizes the Tc concentrations in dried feed and heat-treated samples
243 (weight corrected for heat-treated samples), weight-corrected Tc concentrations in leach
244 solutions of dried feed and heat-treated samples, weight-loss factors, and calculated Tc
245 retentions in heat-treated samples. Table 4 also includes the results of XANES analysis showing
246 the fractions of Tc^{7+} and Tc^{4+} found in each sample.

247 Figure 4 shows the fraction of total Tc added to the feed retained in soluble and
248 insoluble phases of the dried feed and heat-treated samples (in short, “fraction of
249 soluble/insoluble Tc”) as a function of temperature. The fraction of soluble Tc was calculated by
250 dividing the weight-corrected Tc concentration in leach solution by the Tc concentration in
251 dried feed, which represents the fraction of total Tc that was present in dried feed and then
252 remained in soluble phase of each sample after heat treatment. The fraction of insoluble Tc was
253 obtained by dividing the difference between weight-corrected Tc concentrations in whole
254 sample and leach solution by the Tc concentration in dried feed. The Tc retention in heat-
255 treated samples is given as the sum of soluble and insoluble Tc fractions, and was measured
256 directly with NaOH fusion and LSC counting. The balance (100% minus Tc retention) represents
257 the fraction of Tc volatilized. Figure 5 shows the fractions of Tc^{7+} and Tc^{4+} in each sample
258 normalized to the Tc concentration in the dried feed, which was calculated by multiplying the

259 weight-corrected Tc concentration in the whole sample with the as-measured fraction of Tc^{7+}
260 and Tc^{4+} in each sample determined by XANES analysis.

261 **6 Discussion**

262 Slow-cooling the heat-treated samples in the furnace presents a variation from previous
263 studies with AN-102 simulated LAW with Re. The cooling rate of the furnace in question has not
264 been quantitatively measured, but observation reveals that the temperature drops several
265 hundred degrees in several minutes, and takes several hours to cool the final several hundred
266 degrees to room temperature. Comparisons of pertechnetate and perrhenate retentions at
267 1000 °C show good agreement, suggesting that the additional time spent at the highest
268 temperatures is limited enough to be immaterial. Future work with Tc crucible tests quenched
269 in air are planned and will shine additional light on the effect of slow-cooling compared to air-
270 quenching.

271 As shown in Table 4 and Figure 4, the final Tc retention after heat treatment to 1000°C
272 can be improved by using reduced Tc sources— $TcO_2 \cdot 2H_2O$ or Tc-doped minerals—compared to
273 the baseline $KTcO_4$. Although there were no practical differences in final Tc retention at 1000°C
274 between the feeds with $TcO_2 \cdot 2H_2O$ (52.7% retention) or Tc-doped minerals (53.1 to 57.9%
275 retention), there were differences in the temperature dependencies of Tc valence and Tc
276 partitioning into soluble and insoluble phases. This section discusses these differences in Tc
277 behavior as a function of temperature to help understand the mechanism on how different Tc
278 sources affect Tc volatilization/incorporation during early stages of feed melting processes.

279 For the dried feeds, Figure 4 and Figure 5 show that the $KTcO_4$ feed had ~100% Tc in the
280 soluble phase as Tc^{7+} while the feeds with Tc-goethite and Tc-magnetite had 100% Tc in the

281 insoluble phase as Tc^{4+} , which would be expected. However, the two feeds with Tc-trevorite
282 had ~20% of Tc in the soluble phase (18.2 to 22.8%) and ~10% of the total Tc as Tc^{7+} . The
283 soluble Tc^{7+} found in the trevorite feeds is likely a result of partial oxidation of the trevorite
284 particles during slurry preparation and drying. The feed with $TcO_2 \cdot 2H_2O$ had 14.3% Tc in the
285 soluble phase and 23% as Tc^{7+} , suggesting that $TcO_2 \cdot 2H_2O$ oxidizes only partially to form soluble
286 Tc^{7+} during slurry preparation and drying. This observation is different from the results reported
287 by Kim et al. [29] who observed full oxidation of $TcO_2 \cdot nH_2O$ immediately after contact with
288 simulated waste. It is likely that the difference was caused by different composition of
289 simulated waste. In summary, more than 80% Tc for $TcO_2 \cdot 2H_2O$ and Tc-trevorite feeds and
290 100% Tc for Tc-goethite and Tc-magnetite feeds stayed as insoluble Tc^{4+} through slurry
291 preparation and drying. The better oxidation resistance of Tc-goethite during slurry preparation
292 and drying is likely a result of the armoring mentioned in Section 2.5. The better resistance to
293 oxidation of Tc-magnetite compared to Tc-trevorite is possibly due to the magnetite containing
294 Fe^{2+} which may act as a sacrificial anode, delaying the oxidation of Tc^{4+} .

295 Only a small fraction of Tc (2.8 to 11.4%) was in the soluble phase for all samples heat
296 treated to 800°C (Figure 4). As mentioned in Section 4.3, soluble Tc is not expected to be in the
297 samples heat treated to 1000°C; therefore, leach tests were not performed for those samples.
298 As shown in Figure 5, the samples heated to 800 and 1000°C contain ~100% Tc as Tc^{7+} by
299 XANES, presumably in insoluble (glassy) phase for $KTcO_4$, Tc-goethite, and Tc-magnetite.

300 As mentioned earlier, the important differences between feeds lie in the temperature
301 dependencies of Tc valence and Tc partitioning into the soluble or insoluble phases especially in
302 the samples heat treated to 600°C. We will first compares the results of the $KTcO_4$ feed with

303 $KReO_4$ feed in Jin et al. [5], and then discuss the effects of $TcO_2 \cdot 2H_2O$ and Tc-minerals on Tc
304 behavior observed in the 600°C samples.

305 **6.1 $KTcO_4$ versus $KReO_4$**

306 Figure 6 compares the fractions of total un-volatilized Re and Tc as a function of heat
307 treatment temperature for AN-102 feeds spiked with $KReO_4$ [5] and $KTcO_4$ (present study). In
308 general, Re and Tc show similar trends for both insoluble and soluble phases. This result agrees
309 with Matlack and Kim [25, 29] that Re is a good surrogate for Tc. One exception to this was the
310 lower solubility of Tc at 800°C than for Re (Figure 6 bottom plot). It is possible that Tc
311 experienced excess volatilization from the sulfate-rich salt phase at 800°C (see Darab and Smith
312 [4]) during slow cooling in a hot furnace compared to air quenching used by Jin et al. [5].

313 **6.2 Effect of $TcO_2 \cdot 2H_2O$**

314 As shown in Table 4 and Figure 4 for both feeds spiked with $KTcO_4$ and $TcO_2 \cdot 2H_2O$, the
315 samples heat treated to 600°C had the same normalized Tc concentration as the dried feeds--
316 that is, there was no volatile loss of Tc during heating to 600°C. Figure 7 shows the fractions of
317 Tc added to the feed remaining in the insoluble and soluble phases as a function of heat
318 treatment temperature for the two feeds. At 600°C, the $TcO_2 \cdot 2H_2O$ feed had slightly higher
319 fraction of Tc in the insoluble phase (incorporated into the glass-forming melt) than the $KTcO_4$
320 feed. As shown in Figure 5, the $TcO_2 \cdot 2H_2O$ feed initially had 77% Tc as Tc^{4+} in the dried feed
321 compared to 6% for the $KTcO_4$ feed, which may suggest that the difference in Tc valence states
322 in the dried feeds affected how much Tc incorporated into the glassy phase at 600°C. However,
323 the effect of Tc valence state on Tc volatilization could not be determined because there was no
324 volatile loss of Tc up to 600°C for both feeds.

325 Figure 7 shows that the fraction of insoluble Tc increased more for the $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ feed
326 than for the KTcO_4 feed from 600 to 800°C. There were only 3.4 and 2.8% of soluble Tc
327 remaining at 800°C for $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and KTcO_4 , respectively. This indicates that during heating
328 from 600 to 800°C, almost all Tc that did not become incorporated into the glass-forming melt
329 volatilized. The fraction of total Tc volatilized during heating from 600 to 800°C was 48.9% for
330 the KTcO_4 feed and 36.6% for the $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ feed while the fraction of Tc incorporated into
331 glassy insoluble phase was 27.4% (bringing the total insoluble Tc to 48.3%) for the KTcO_4 feed
332 and 34.7% (total insoluble Tc of 58.7%) for the $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ feed. Considering that 100% of the Tc
333 was present as Tc^{7+} at 600°C for both feeds as shown in Figure 5, the valence state of Tc at 600
334 °C is not wholly responsible for the difference between the fractions of Tc that volatilized or
335 incorporated into the glass melt during heating from 600 to 800°C in these feeds.

336 **6.3 Effect of Tc-minerals**

337 Figure 8 shows the fraction of total Tc added to the feed remaining in the insoluble
338 phase as a function of heat treatment temperature for the feeds spiked with various Tc-
339 minerals compared to the feed with KTcO_4 . Similar to feeds with KTcO_4 and $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$, all the
340 feeds with Tc-minerals had no noticeable volatile loss of Tc during heating to 600°C (Figure 4),
341 but there were differences in the fractions in the insoluble phase (Figure 8) and the degrees of
342 oxidation (fraction of Tc^{7+} , Figure 5).

343 As shown in Figure 4 and Figure 5, the Tc-goethite sample had 92.8% of its initial Tc
344 remaining at 600°C, with all of it as Tc^{4+} and 95.2% of it insoluble. Considering that the melting
345 point of a typical goethite mineral is 350°C, the survival of 100% Tc^{4+} up to 600°C in the Tc-
346 goethite feed is not understood although it could be a result of either the armoring process

347 discussed previously in Section 2.5 or transformation into hematite that occurs above about
348 230°C [30], which is shown to be energetically favorable [31]. According to Jin et al. [3-5],
349 various fractions of mineral additives had already reacted by 600°C including ~50% of the
350 quartz to form an early glass-forming melt. The glass formed at 600°C contained 22.9 % of the
351 total Re in the $KReO_4$ feed [9] and 20.6 % of the total Tc in the $KTcO_4$ feed (see Figure 6 top
352 plot). Although it is likely that a similar fraction of glass-forming melt was formed at 600°C in
353 the Tc-goethite feed, the experimental and characterization methods used in the present study
354 could not determine the split factors of insoluble Tc into Tc-minerals and the glassy phase. Two
355 cases can be considered for the Tc-goethite feed at 600°C: 1) all Tc was still in Tc-goethite (i.e.,
356 there is no Tc incorporated into the glassy phase) or 2) a fraction of the Tc incorporated into the
357 glassy phase, which implies the existence of Tc^{4+} in glassy phase. During heating from 600 to
358 800°C for the Tc-goethite feed, Tc retention decreased from 92.8% to 66.9%, and 95% of the Tc
359 was Tc^{7+} at 800°C, with only 6% of Tc in the soluble phase; that is, almost all Tc remaining in the
360 glassy phase was Tc^{7+} .

361 As shown in Figure 8, the feeds with Tc-magnetite and both Tc-trevorite had lower
362 fractions of insoluble Tc (35.6 to 59.9%) compared to the feed with Tc-goethite (88.1%) in
363 samples heat treated to 600°C. This trend agrees with the fraction of Tc^{4+} in the condensed
364 phase; that is, 15 to 46% of the total Tc remaining as Tc^{4+} for the feeds with Tc-magnetite and
365 both Tc-trevorite compared to 100% for the Tc-goethite feed heat treated to 600°C. Although
366 the magnetite and trevorite phases with higher melting points should be more thermally stable
367 than the goethite, the feed with Tc-goethite showed superior resistance to oxidation or melting
368 reaction likely because of the armoring mentioned in Section 2.5. However, the different

369 temperature dependencies of the fractions of insoluble Tc and oxidized Tc^{7+} among three Tc-
370 minerals is difficult to explain without detailed information on incorporation and distribution of
371 Tc into mineral structure, especially on the mineral surface. Full characterization of the Tc-
372 mineral phases was not pursued in the present study but is planned for selected Tc-minerals to
373 better understand the mechanism that governs the effect of Tc-minerals on Tc incorporation
374 into glass melt.

375 Based on current results, the effect of particle size is inconclusive. The Tc-trevorite
376 phase was created by two methods, but neither was fully characterized. SEM imaging shows
377 particle sizes apparently larger for the case of the Tc-trevorite from $Fe(OH)_2$.

378 Based on observations from tests with four Tc-mineral feeds that 1) there was no
379 noticeable Tc volatilization up to 600°C and 2) there was no soluble Tc remaining at 800°C, we
380 believe that the balance of Tc not incorporated into insoluble glassy phase volatilized during
381 heating from 600 to 800°C. This finding signifies that although there were large differences in
382 the fraction of total Tc remaining as Tc^{4+} at 600°C (15 to 100%), they did not lead to a
383 noticeable difference in the fraction of Tc volatilized during heating from 600 to 800°C.

384 **6.4 Summary on the effect of reduced Tc sources**

385 It is known that reducing conditions lead to lower volatile loss of Tc during vitrification
386 because lower-valence Tc^{4+} compounds are less volatile than Tc^{7+} species such as pertechnetate
387 [2, 4, 28]. The test results obtained during this study confirmed that the addition of Tc as Tc^{4+}
388 compounds or Tc^{4+} minerals decreases Tc volatilization during crucible melting compared to
389 Tc^{7+} pertechnetate. However, the results do not support the presumption that low volatility of
390 the Tc^{4+} compounds is responsible for reduced Tc volatilization. This claim is primarily based on

391 the following two observations: 1) the $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ feed showed lower Tc volatilization during
392 heating from 600 to 800°C than the KTcO_4 feed although both feeds had 100% Tc as Tc^{7+} at
393 600°C, and 2) the four feeds with Tc-minerals showed no noticeable difference in Tc
394 volatilization during heating from 600 to 800°C although they all had different fractions of Tc^{4+}
395 remaining at 600°C. In other words, Tc volatilization in the AN-102 feeds with various Tc sources
396 tested in this study seems to be affected by factors other than the valence state of the Tc. The
397 initial valence state of the Tc appears to cause some condition that effects volatility even after
398 all the Tc is oxidized.

399 Jin et al. [5] proposed that the composition of soluble salt phases and partitioning of Re
400 into these phases during melting play important roles in how Re becomes incorporated into the
401 glassy phase up to ~800°C, above which no additional incorporation of Re was observed. Based
402 on the results on Re partitioning as a function of temperature reported by Jin et al. [5], it can be
403 assumed that the Tc-containing salt phase in the KTcO_4 feed is predominantly nitrate up to
404 600°C but then becomes dominated by sulfate as temperature increases to 700°C and above.
405 The Tc in the KTcO_4 feed incorporates into the glass-forming melt or volatilizes while the Tc-
406 containing molten salts react with other feed components. However, a common difference for
407 the feeds with $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and Tc-mineral feeds compared to the KTcO_4 feed is that the Tc
408 would incorporate into glass or volatilize while Tc-containing solids ($\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and Tc-minerals)
409 react with either salt or early glass-forming melt that already formed at lower temperatures; in
410 other words, there was a difference in reaction or reaction paths that accompany Tc
411 incorporation or volatilization. Unlike the study by Jin et al. [5], the present study was not
412 designed to investigate detailed reaction paths during the feed melting process because a

413 larger temperature interval was used and chemical analyses were performed for Tc only instead
414 of all feed components.

415 **7 Conclusion**

416 The present crucible melting tests with a representative LAW feed spiked with KTcO_4
417 showed that Tc and Re have similar behaviors in terms of volatilization and incorporation into
418 glass phase during early stages of feed melting. This finding is consistent with previous results
419 showing that Re is a good Tc surrogate under oxidizing conditions. The test results of the feeds
420 spiked with reduced forms of Tc showed that the addition of Tc as $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ and various Tc^{4+} -
421 minerals decreased Tc volatilization during crucible melting compared to Tc^{7+} pertechnetate.
422 However, results from the present do not support the presumption that low volatility of the
423 Tc^{4+} compounds is responsible for reduced Tc volatilization. We postulate that other factors not
424 related to Tc valence state, such as different reaction paths that accompany Tc incorporation or
425 volatilization, are likely important. Additional studies are needed to investigate the effect Tc-
426 minerals on partitioning and distribution of Tc during melting of simulated LAW glass feeds and
427 their effect on Tc incorporation into and volatilization from glass melt.

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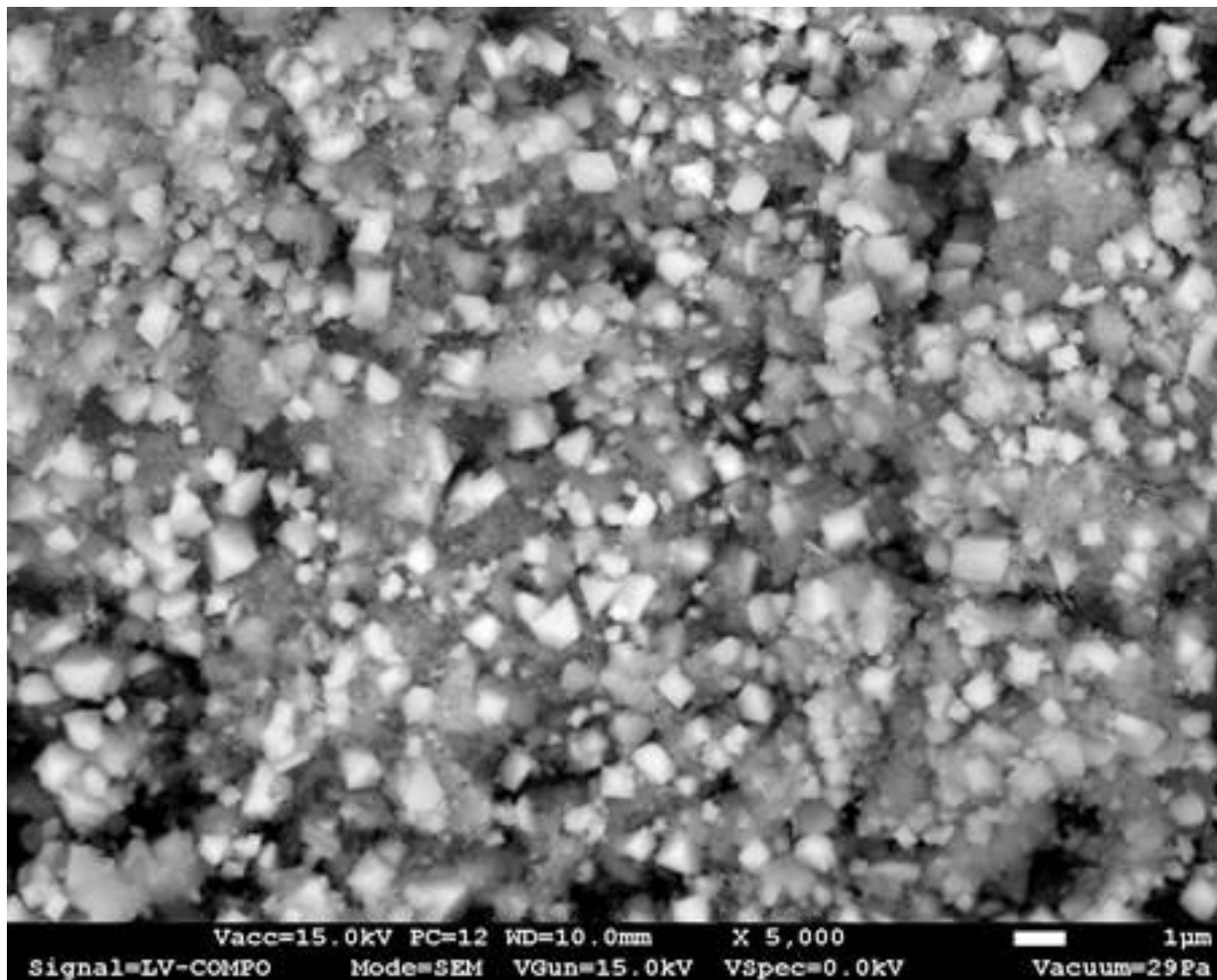
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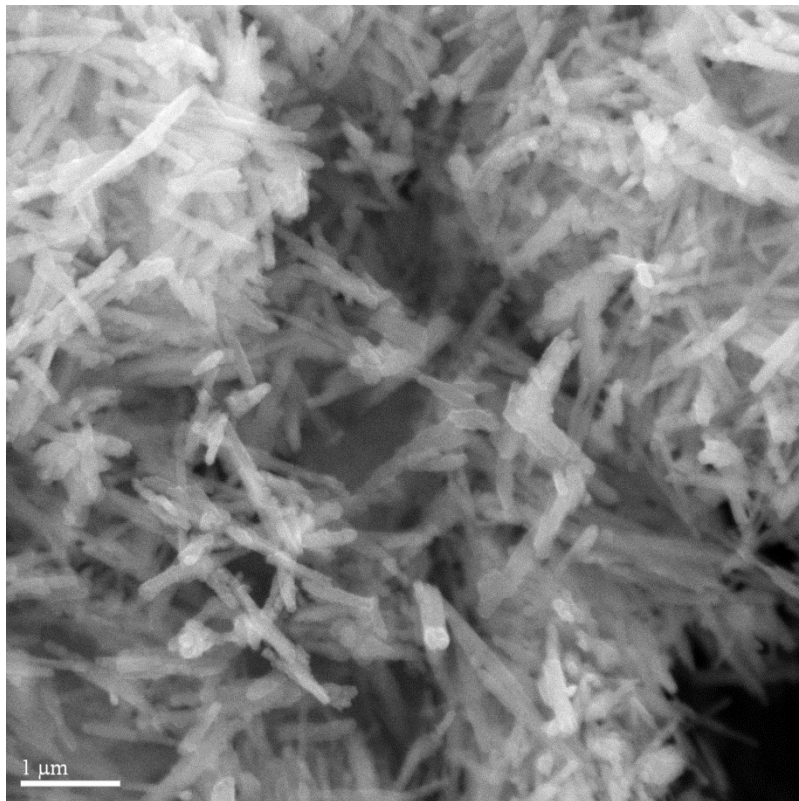


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516 Figure 1. Tc-trevorite from $\text{Fe}(\text{OH})_2$ by SEM

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520 **Figure 2. Tc-goethite by SEM**

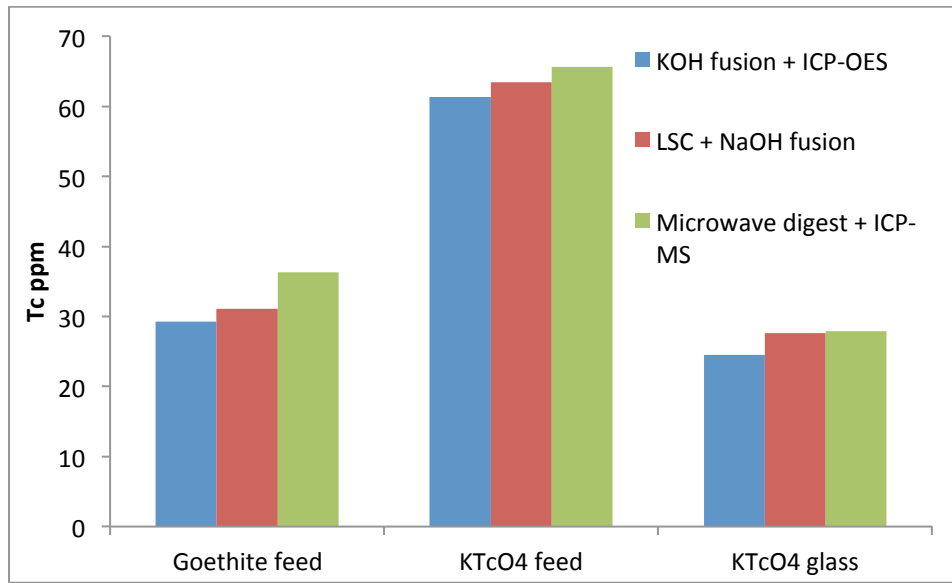
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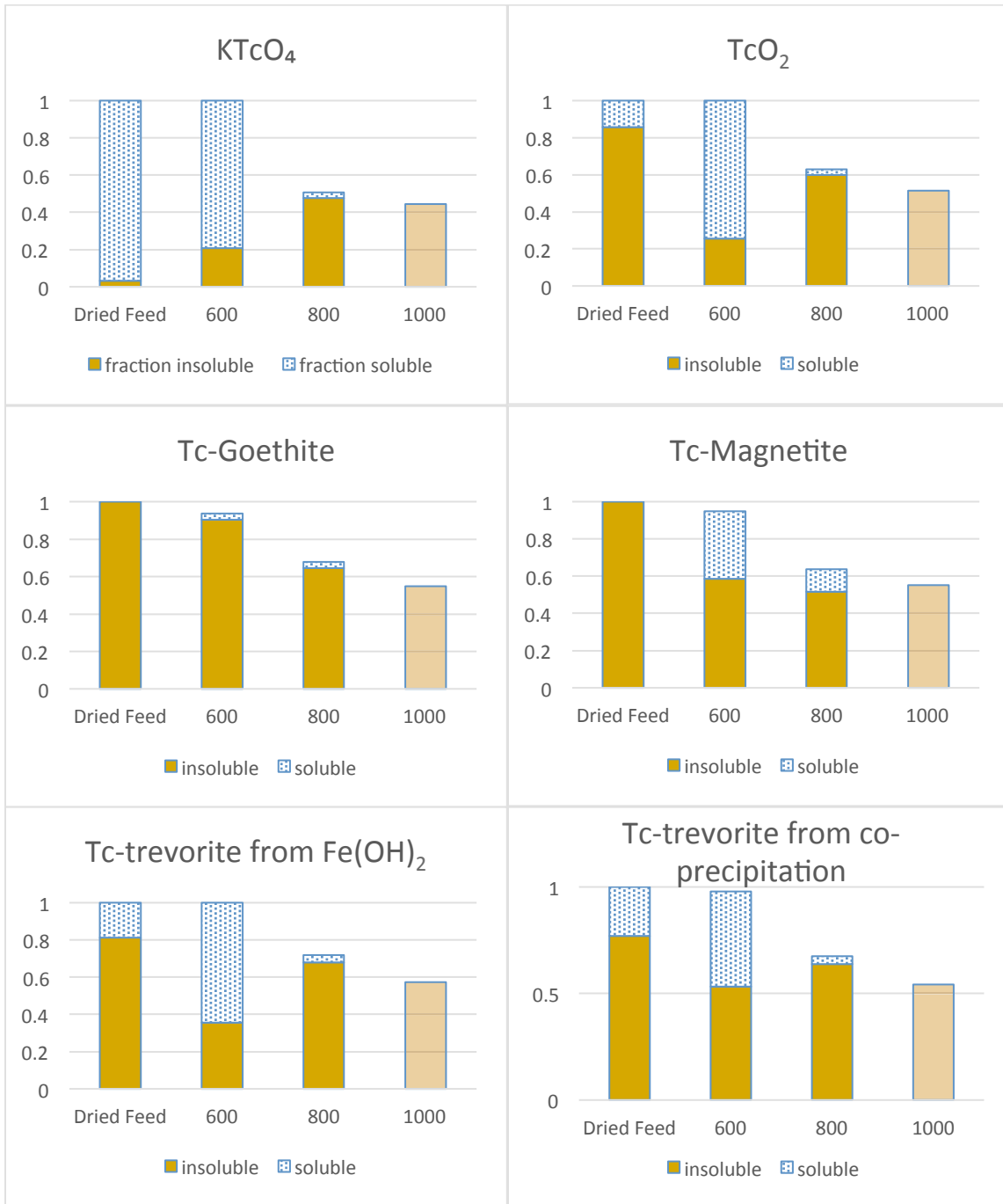
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527 **Figure 3. Comparative analyses of three powdered samples by KOH fusion and ICP-MS analysis by**
528 **SwRI, NaOH fusion and LSC at PNNL, and microwave digestion and ICP-MS analysis at PNNL.**

529



530

531

532 **Figure 4. Normalized results of leach tests and LSC on AN-102 feeds doped with six different Tc**
533 **sources in dried feed and heat treated to various temperatures. Y-axis is Tc concentration normalized**
534 **to the total concentration in dried feed. Blue portions of bars indicate the concentrations of Tc found**
535 **in each sample by leaching. Brown solid portions of bars indicate the total Tc concentraion minus the**
536 **leached Tc concentration. Transparent data at 1000°C are assumed to be fully insoluble but were not**
537 **measured by leach tests.**



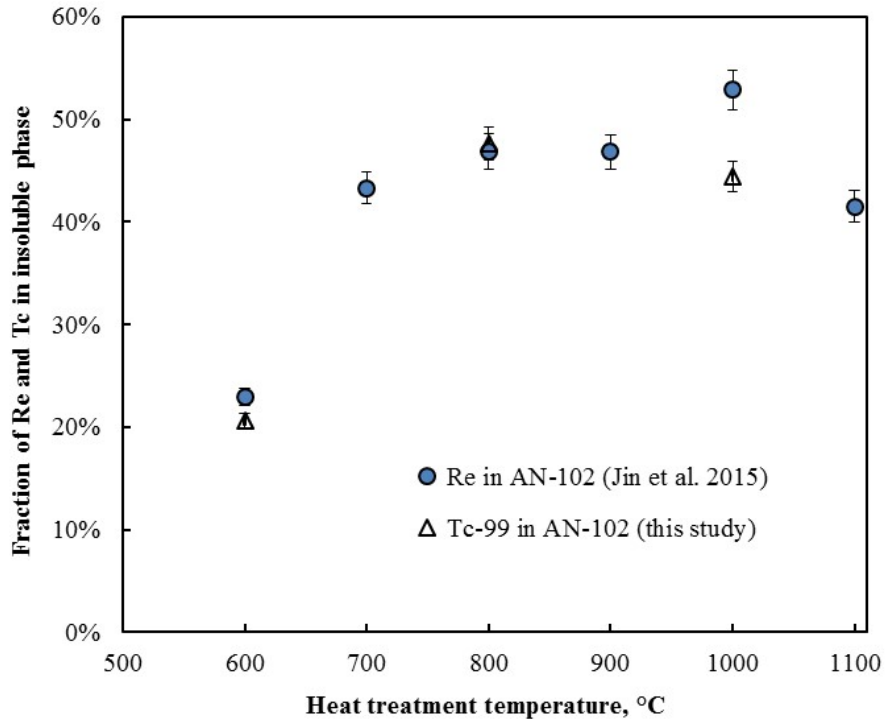
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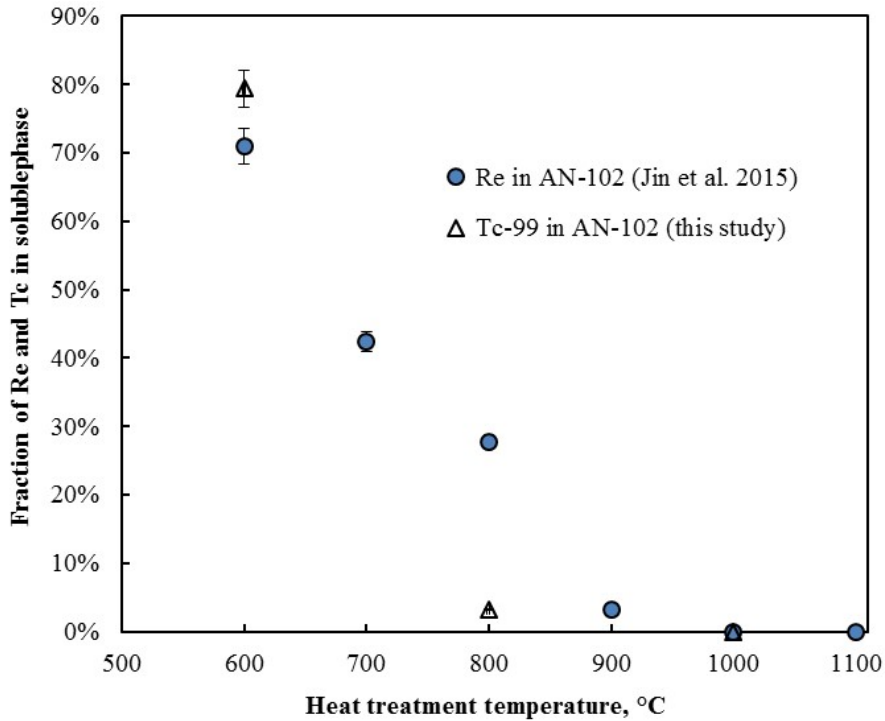
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541 **Figure 5. XANES analysis of Tc in feeds doped with six Tc sources in dried feed and heat treated to**
 542 **various temperatures. Black shaded columns indicate the Tc⁴⁺ fraction detected by XANES. The orange**
 543 **columns indicate the fraction of Tc⁷⁺ detected by XANES. Transparent column were not measured and**
 544 **are assumed to be fully Tc⁷⁺.**
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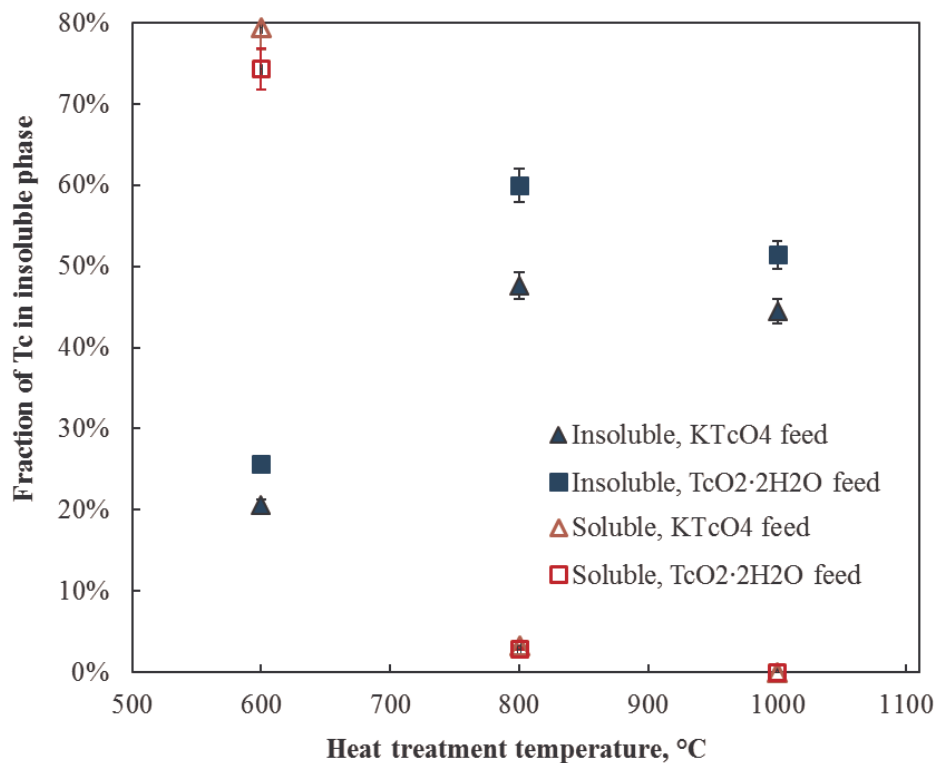
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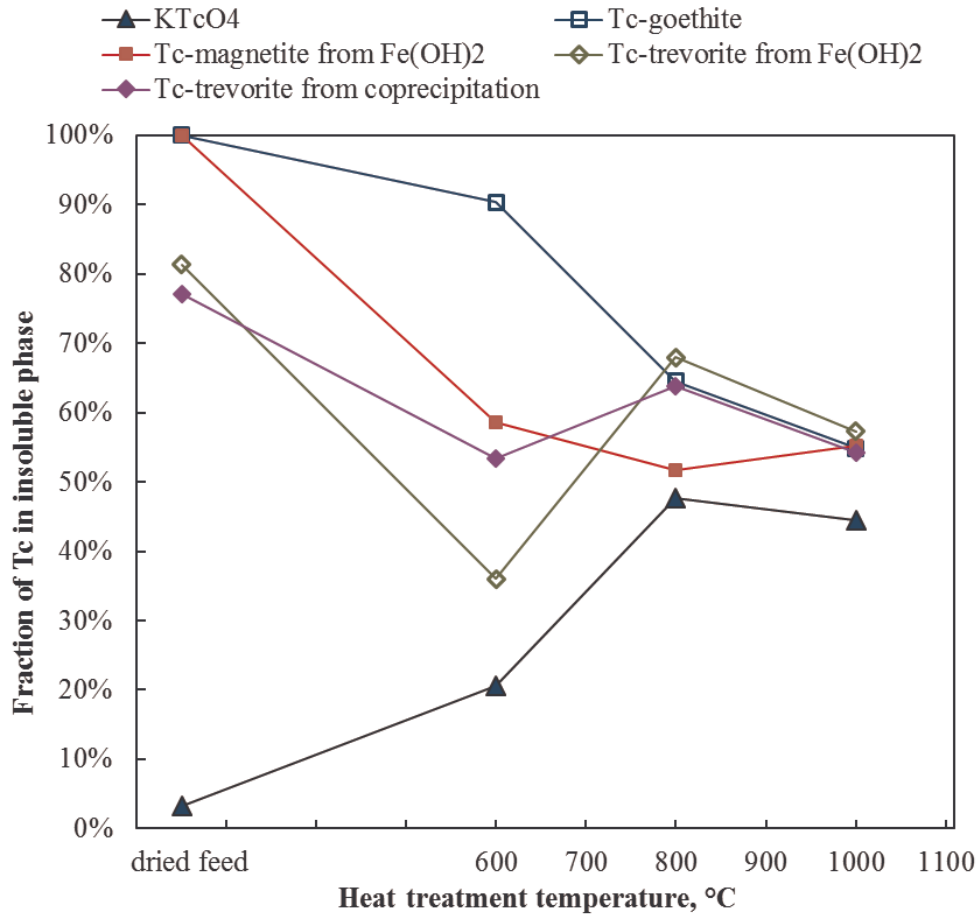
548

549 **Figure 6. Fractions of total Re and Tc remained in the insoluble (top plot)**
550 **phases of the heat-treated samples as a function of temperature. The error bars represent the**
551 **standard deviation of chemical analyses with RSD = 3.6% for Re (from Jin et al. 2015 [5]) and 3.4% for**
552 **Tc (Table 2).**

553



554
 555 **Figure 7. Fraction of total Tc-99 remained in the insoluble and soluble phases of the heat-treated**
 556 **samples as a function of temperature for the feeds with KTcO_4 and $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$. The error bars**
 557 **represent the standard deviation of chemical analyses with RSD = 3.4% (Table 2).**
 558
 559



560

561 **Figure 8. Fraction of total Tc-99 remained in the insoluble phase of the heat-treated samples for the**
 562 **feeds with minerals compared to the KTcO_4 feed as a function of temperature. The error bars were**
 563 **not included to avoid the plot being too cluttered. Duplicate leach tests for feeds showed relative**
 564 **percent differences between 0.77% and 4.24% when testing for water-soluble Tc.**

565 **11 Tables**566 **Table 1. Composition of AN-102 Glass Feed to make 1 Liter slurry [25]**

Material	
Simulated waste	g/l
Al(NO ₃) ₃ ·3.9H ₂ O, 60% sol.	142.07
H ₃ BO ₃	0.11
Ca(NO ₃) ₂ ·4H ₂ O	1.47
Na ₂ CrO ₄ ·4H ₂ O	2.78
KOH	8.12
NaOH, 50% sol. D=1.53	102.73
NiO	0.09
PbO	0.09
SiO ₂	0.1
NaCl	3.74
NaF	1.99
Na ₃ PO ₄ ·12H ₂ O	7.56
Na ₂ SO ₄	12.2
NaNO ₂	65.13
NaNO ₃	94.65
Na ₂ CO ₃	48.96
Sodium Formate (C1)	24.91
Sodium Oxalate (C2)	1.44
Glycolic Acid (C2)	30.22
Citric Acid (C6)	9.07
Target Glass Weight	1145.23
Total Simulant Weight	1246.58
Kyanite (Al ₂ SiO ₅) 325 Mesh (Kyanite Mining) (g)	96.64
H ₃ BO ₃ (US Borax – Technical Granular) (g)	200.67
Wollastonite NYAD 325 Mesh (NYCO Minerals) (g)	158.24
Fe ₂ O ₃ (97% Alfa) (g)	59.21
Li ₂ CO ₃ (Chemetall Foote Co. Technical grade) (g)	90.77
Olivine (Mg ₂ SiO ₄) 325 Mesh (#180 Unimin) (g)	33.18
SiO ₂ (Sil-co-Sil 75 US Silica) (g)	358.02
TiO ₂ (Rutile Airfloated Chemaloy) (g)	16.75
ZnO (KADOX – 920 Zinc Corp. of America) (g)	39.63
Zircon ZrSiO ₄ (Flour) Mesh 325 (AM. Mineral) (g)	51.13
Measured Simulant Weight for 1 liter (g)	1247

567

568

569 **Table 2. Summary of results for Tc concentrations by LSC, weight-loss factor after 1000°C heat**
 570 **treatment, and calculated Tc retention from K₂TcO₄-spiked original and duplicate feed batches**

Feed batch	Tc concentration (ppm)		Weight-loss factor	Tc retention
	Pre-heat treatment	Post-heat treatment (weight corrected)		
Original	63.4	27.6	0.819	0.436
Duplicate	63.0	28.3	0.813	0.448
Duplicate	63.0	27.8	0.813	0.441
Duplicate	62.5	26.1	0.812	0.418
RSD	0.6%	3.4%		

571

RSD: relative standard deviation

572

573 **Table 3. Comparison of three analytical methods for Tc concentrations in selected feed and heat-**
 574 **treated samples**

Analytical method	Goethite feed	K ₂ TcO ₄ feed	K ₂ TcO ₄ 1000°C heat treated (weight corrected)
ICP-MS after KOH fusion (SwRI)	29.3	61.3	24.5
LSC after NaOH fusion	31.1	63.4(0.37)*	27.6(0.95)*
ICP-MS after microwave-assisted digestion	36.3	65.6	27.9

575

*Number in parenthesis is standard deviation calculated from RSD value given in Table 2

576

577 **Table 4. Summary of results for Tc concentrations by LSC, weight loss factors, and Tc valences by XANES**
 578 **and calculated values for Tc retention and fraction of soluble Tc**

Tc source	HT temp. (°C)	Tc conc. (ppm)		Weight-loss factor	Tc retention after HT	XANES results	
		In whole sample	In leach solution*			Fraction of Tc ⁷⁺	Fraction of Tc ⁴⁺
KTcO ₄	Dried feed	63.4	61.5	NA	NA	0.94±0.06	0.06±0.05
	600	63.4	50.2	0.886	1.000	1.00±0.02	0.00±0.01
	800	32.4	1.8	0.819	0.511	1.00±0.03	0.00±0.03
	1000	27.6	NM	0.819	0.436	1.00±0.04	0.00±0.03
Tc Goethite	Dried feed	31.1	0.1	NA	NA	0.00±0.04	1.00±0.03
	600	28.9	1.5	0.891	0.928	0.00±0.04	1.00±0.03
	800	20.8	1.3	0.811	0.669	0.95±0.04	0.05±0.04
	1000	16.5	NM	0.812	0.531	0.99±0.04	0.01±0.04
Tc Magnetite from Fe(OH) ₂	Dried feed	57.8	0.5	NA	NA	0.00±0.03	1.00±0.02
	600	55.4	20.8	0.886	0.959	0.54±0.02	0.46±0.02
	800	37.5	6.6	0.812	0.649	1.00±0.02	0.00±0.01
	1000	32.3	NM	0.802	0.559	0.97±0.04	0.03±0.03
Tc-trevorite from Fe(OH) ₂	Dried feed	74.9	13.6	NA	NA	0.10±0.03	0.90±0.03
	600	75.8	49.1	0.871	1.000**	0.66±0.04	0.34±0.04
	800	53.7	2.6	0.800	0.717	NM	NM
	1000	43.3	NM	0.821	0.579	NM	NM
Tc-trevorite from co-precipitation	Dried feed	104.9	23.9	NA	NA	0.10±0.03	0.90±0.04
	600	103.4	47.0	0.864	0.986	0.85±0.03	0.15±0.04
	800	71.4	4.1	0.787	0.681	NM	NM
	1000	57.5	NM	0.815	0.548	NM	NM
TcO ₂ •2H ₂ O	Dried feed	34.9	5.0	NA	NA	0.23***	0.77***
	600	34.5	26.1	0.870	0.989	0.96±0.04	0.00±0.06
	800	21.7	1.2	0.806	0.622	NM	NM
	1000	18.4	NM	0.816	0.527	NM	NM

579 *weight corrected to the dried feed for heat-treated samples
 580 **assumed value (Tc concentration in 600C sample was slightly higher than in dried feed)
 581 ***XANES analysis fitted several percentage of Tc¹⁺, which has been disregarded and Tc⁴⁺ and Tc⁷⁺ have been
 582 normalized to 1.
 583 HT: heat treatment, NM: not measured, NA: not applicable
 584

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