



# Laboratory Studies of 2H Evaporator Scale Dissolution in Dilute Nitric Acid.

L. N. Oji

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# Laboratory Studies of 2H Evaporator Scale Dissolution in Dilute Nitric Acid.

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## EXECUTIVE SUMMARY

The rate of 2H evaporator scale solids dissolution in dilute nitric acid has been experimentally evaluated under laboratory conditions in the SRNL shielded cells. The 2H scale sample used for the dissolution study came from the bottom of the evaporator cone section and the wall section of the evaporator cone. The accumulation rate of aluminum and silicon, assumed to be the two principal elemental constituents of the 2H evaporator scale aluminosilicate mineral, were monitored in solution. Aluminum and silicon concentration changes, with heating time at a constant oven temperature of 90 °C, were used to ascertain the extent of dissolution of the 2H evaporator scale mineral.

The 2H evaporator scale solids, assumed to be composed of mostly aluminosilicate mineral, readily dissolves in 1.5 and 1.25 M dilute nitric acid solutions yielding principal elemental components of aluminum and silicon in solution. The 2H scale dissolution rate constant, based on aluminum accumulation in 1.5 and 1.25 M dilute nitric acid solution are, respectively,  $9.21\text{E-}04 \pm 6.39\text{E-}04 \text{ min}^{-1}$  and  $1.07\text{E-}03 \pm 7.51\text{E-}05 \text{ min}^{-1}$ . Silicon accumulation rate in solution does track the aluminum accumulation profile during the first few minutes of scale dissolution. It however diverges towards the end of the scale dissolution. This divergence therefore means the aluminum-to-silicon ratio in the first phase of the scale dissolution (non-steady state conditions) is different from the ratio towards the end of the scale dissolution. Possible causes of this change in silicon accumulation in solution as the scale dissolution progresses may include silicon precipitation from solution or the 2H evaporator scale is a heterogeneous mixture of aluminosilicate minerals with several impurities.

The average half-life for the decomposition of the 2H evaporator scale mineral in 1.5 M nitric acid is 12.5 hours, while the half-life for the decomposition of the 2H evaporator scale in 1.25 M nitric acid is 10.8 hours. Based on averaging the two half-lives from the 2H scale acid dissolution in 1.25 and 1.5 M nitric acid solutions, a reasonable half-life for the dissolution of 2H scales in dilute nitric acid is  $11.7 \pm 1.3$  hours. The plant operational time for chemically cleaning (soaking) the 2H evaporator with dilute nitric acid is 32 hours. It therefore may require about 3 half-lives or less to completely dissolve most of the scales in the Evaporator pot which come into contact with the dilute nitric acid solution.

On a mass basis, the Al-to-Si ratio for the scale dissolution in 1.5 M nitric acid averaged  $1.30 \pm 0.20$  and averaged  $1.18 \pm 0.10$  for the 2H scale dissolution in 1.25 M nitric acid. These aluminum-to-silicon ratios are in fairly good agreement with ratios from previous studies. Therefore, there is still more aluminum in the 2H evaporator scales than silicon which implies that there are no significant changes in scale properties which will exclude nitric acid as a viable protic solvent for aluminosilicate scale buildup dissolution from the 2H evaporator.

Overall, the monitoring of the scale decomposition reaction in 1.25 and 1.5 M nitric acid may be better ascertained through the determination of aluminum concentration in solution than monitoring silicon in solution. Silicon solution chemistry may lead to partial precipitating of silicon with time as the scale and acid solution is heated.

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## **LIST OF ABBREVIATIONS**

DWPF	Defense Waste Processing Facility
HLW	High-Level Waste
ICP-ES	Inductively Coupled Plasma–Atomic Emission Spectroscopy
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
XRD	X-Ray Diffraction
TTR	Technical Task Request

## 1.0 Introduction

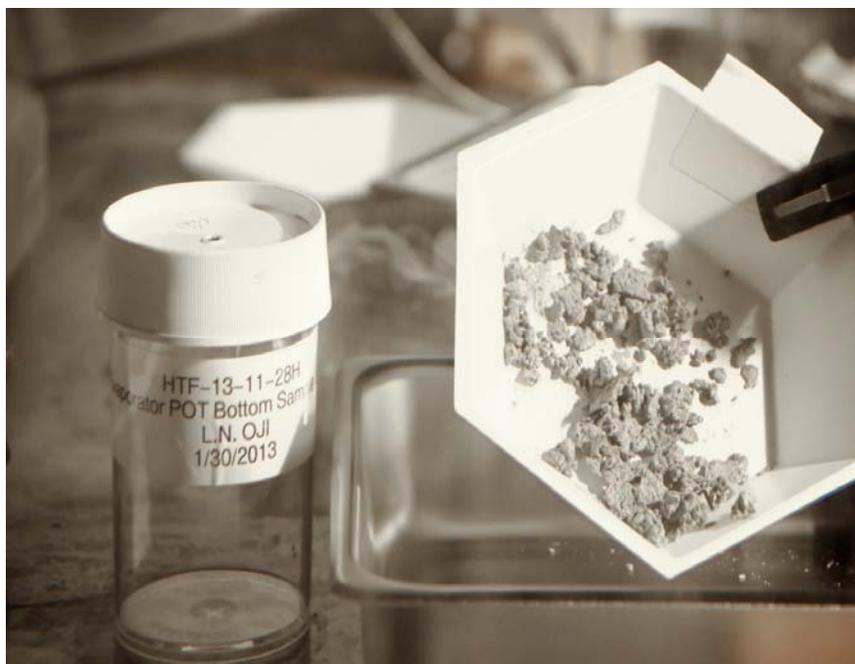
The 242-16H evaporator (2H evaporator) system concentrates recycle waste consisting primarily of Defense Waste Processing Facility (DWPF) recycle to the SRS H-Area Tank Farm. Historically, since the operation of DWPF, silicon in the recycle stream reacts with aluminum in to form sodium aluminosilicate mineral scale deposits in the evaporator pot and gravity drain line. The deposits are primarily nitrated sodium aluminosilicate with smaller amounts of clarkeite,  $\text{Na}((\text{UO}_2)\text{O}(\text{OH}))$ . Savannah River Remediation (SRR) has removed a buildup of the sodium aluminosilicate scale from the 2H-evaporator pot by the addition of dilute nitric acid solution<sup>i</sup>. Prior to the scale removal, two scale samples (HTF-13-10-28H evaporator wall scrape sample and HTF-13-11-28H evaporator pot bottom sample) were pulled by SRR and delivered to Savannah River National Laboratory (SRNL) in January 2013. These samples were sent to SRNL for characterization for primary fissile isotopes and non-fissile isotopes of uranium as well as determining the sodium aluminosilicate scale dissolution rate under laboratory conditions using 1.5 and later 1.25 M nitric acid. The laboratory dissolution studies with the scale samples also includes the goal of determining whether there are significant changes in evaporator scale properties which will exclude nitric acid as a viable solvent for scale buildup dissolution for the 2H evaporator.

However, when the evaporator wall scrape sample container (Sample HTF-13-10-28H) was opened in the shielded cell it was empty. Thus, both the phase 1 dissolution rate determinations (dissolution in 1.5 M nitric acid) and characterizations were now solely based on the pot sample [HTF-13-11-28H] as shown in Figure 1.

At the request of SRR, the original 2H scale dissolution test at 1.5 molar nitric acid was modified in phase 2 of the study to reflect a revision of the flow sheet used to clean the 2H Evaporator scales in 2013<sup>ii</sup>. The changes in the new flow sheet include dissolution at 1.25 M nitric acid at 90 °C. This new acid concentrations comes from the fact that 1,500 gallons of 1.5 M nitric acid along with 250 gallons of water and miscellaneous volumes of other water already in the pot is added to the pot per each strike. Thus, the final nitric acid concentration in the pot prior to the heating process will now be about 1.25M. Also, with the new flow sheet, the maximum targeted scale volume required to be accumulated in the evaporator before the initiation of chemical cleaning will now be 100 gallons instead of 200 gallons on which the initial 1.5 M nitric acid dissolution was based.

The 2H scale dissolution studies in 1.5 M nitric acid was based on the pot sample [HTF-13-11-28H] and because of inadequate amount of pot scale sample the dissolution studies in 1.25 M nitric acid was performed with a blend of 2H scale wall sample solids [combined 2H scale solid samples HTF-13-82 and HTF-13-77]. The dissolution studies at 1.25 M nitric acid called for the use of refined bulk density of the scale materials used instead of assuming that the scale mineral was 100 percent aluminosilicate mineral with a literature bulk density of 2.28 g/mL (value used for the 1.5 M nitric acid dissolution and phase ratio calculations).

This report presents the laboratory dissolution results for the 2H scale pot sample HTF-13-11-28H in 1.5 M nitric acid and 2H scale dissolution results in 1.25 M nitric acid using mixed wall samples HTF-13-82 and HTF-13-77 as defined in the SRR Technical Task Request (TTR)<sup>ii</sup> and the SRNL Task Technical and Quality Assurance Plan<sup>iii</sup>. Additional radionuclide characterization results for this evaporator scale samples are also available in two reports.<sup>iv, v</sup>



**Figure 1** 2H-evaporator pot bottom scale sample (HTF-13-11-28H)

## 2.0 Experimental

### 2.1 Approach:

From the SRR 2012 initial chemical cleaning flow sheet for the 2H evaporator scale, the maximum targeted scale volume required to be accumulated in the evaporator before the initiation of chemical cleaning is 200 gallons (757 Liters), while the volume of 1.5 M nitric acid which would be introduced into the evaporator pot for the initial cleaning cycle process is 2000 gallons or  $7.57E+06$  mL (See enclosed flow sheet in the appendix A). Using the laboratory determined bulk density of 0.87 g/mL for the scale material, the calculated bulk weight in grams for maximum scale build up is  $6.59E+05$  g ( $0.87$  g/mL\* $757$  L\* $1000$  mL/L). Thus, the liquid (1.5 M HNO<sub>3</sub>)-to-solid (2H Evaporator scale) ratio, otherwise known as the phase ratio, in the SRR single pass cleaning process for the 2H evaporator is 11.5 mL/g ( $7.57E+06/6.59E+05$ ).

The laboratory approach (SRNL Shielded cell) for determining the 2H scale dissolution rate in 1.5 M nitric acid, at this given phase ratio of 11.5 mL/g, was to perform the dissolution tests at other phase ratios (7, 10, 15, 20 and 25 mL/g) and then extrapolate for the dissolution rates at a phase ratio of 11.5 mL/g if desired.

However, at the request of SRR, the original 2H scale dissolution test at 1.5M nitric acid was modified in phase 2 of this study to reflect a revision of the flow sheet used to clean the 2H Evaporator scales in 2013<sup>vi</sup>. The changes in the new flow sheet include dissolution at 1.25 M nitric acid at 90 °C. This new acid concentrations comes from the fact that 1,500 gallons of 1.5 M nitric acid along with 250 gallons of water and miscellaneous volumes of other water already in the pot is added to the pot per each strike; a total of 1,750 gallons of dilute nitric acid (approximately 1.29 M HNO<sub>3</sub>). Thus, the final nitric acid concentration in the pot prior to the heating process is now approximately 1.25M. Also, with the new flow sheet, the maximum targeted scale volume required to be accumulated in the evaporator before the initiation of chemical cleaning is 100 gallons instead of 200 gallons.

The bulk density of the combined 2H scale wall samples was determined in the shielded cell. The new value served as the basis for determining the phase ratios in the 1.25 M nitric acid dissolution studies. The refined shielded cell bulk density of 0.87 g/mL is less than half of that for pure aluminosilicate mineral.

The calculated bulk weight in grams for maximum scale build up is now  $3.29\text{E}+05$  g ( $0.87$  g/mL\* $3.785$  L/gallon\* $100$  gallons \* $1000$  mL/L). Thus, in the new flow sheet the liquid (1.25 M HNO<sub>3</sub>)-to-solid (2H Evaporator scale) ratio, otherwise known as the phase ratio, in the SRR single pass cleaning process for the 2H evaporator is 20.12 mL/g ( $6.62\text{E}+06$  mL/ $3.29\text{E}+05$  g). Here the total volume of 1.25 M nitric acid for dissolution in the tank is  $6.62\text{E}+06$  mL ( $1750$  gallons\* $3.785$  L/gallon\* $1000$  mL/L). Hence, the dissolution at 1.25 M nitric acid was repeated at the following phase ratios 15, 20 and 25 mL/g thus bounding the new calculated plant operational phase ratio of 20.12.

## 2.2 Methodology

The volume amount of 1.5 or 1.25 M nitric acid in each centrifuge tube depended on the desired liquid-to-solid ratio (phase ratio) for the dissolution test. The two laboratory dissolution studies were performed in the SRNL shielded cells. Five phase ratios (7, 10, 15, 20 and 25) for the 1.5 M nitric acid dissolutions and three phase-ratio preparations of scale and nitric acid solutions (15, 20 and 25) for the 1.25 M nitric acid dissolutions were used. For the five phase ratio preparations using 2H scale sample solids (sample HTF-13-10-28H),  $1.0 \pm 0.1$  grams of 2H scale sample was weighed out and introduced into a 50 mL capacity Teflon centrifuge tube already containing a definite amount of the 1.5 M nitric acid. Similarly, for the 1.25M nitric acid dissolutions the blended 2H scale wall samples (combined 2H scale solid samples HTF-13-82 and HTF-13-77)  $1.0 \pm 0.1$  grams of the material solids was weighed and introduced into a 50 mL capacity Teflon centrifuge tube already containing a given amount of the 1.25 M nitric acid. It is worth noting that the 2H scale material used for the 1.25 M nitric acid dissolution was a blend of two 2H scale samples as described above. The goal was to mechanically mix the two materials (equal portions by weight represented in the mixture) without necessarily changing or decreasing the particle size of the final product or mixture. Attaining this goal was not quite practical because a careful observation of the mixture after blending the two scale samples indicated that the particle size of the resulting mixture was smaller than the original 2H scale material used in the phase 1 study. Thus, during the phase 2 dissolution study it was expected that the dissolution/reaction rate of the blended material in the nitric acid, due to a reduction in particle size of the scale, was probably going to be faster or more erratic when compared with the phase 1 study.

Each 50 mL capacity Teflon centrifuge tube, containing the acid and scale samples corresponding to the desired phase ratio, was put on a rack inside an oven maintained at a temperature of  $90 \pm 2$  °C. The test for each phase ratio was performed one at a time. After heating each sample for the given time at  $90 \pm 2$  °C, the centrifuge was taken out of the oven and centrifuged for about 60 seconds (1200 rpm) and a 0.25 mL pipette inserted into the clear fraction inside the Teflon tube to extract 0.25 mL fraction for further dilution and analysis for Si and Al by ICP-ES. After the sample extraction, the centrifuge tube was put back into the oven to continue the heating until the next heating length of time was attained and the centrifuging and extraction cycles repeated. The heating interval was 15 minutes and sampling was performed every 15 minutes for a total of 5 times (15, 30, 45, 60 and 75 minutes) for each phase ratio. Each 0.25 mL portion extracted every

15 minutes from a single tube for each phase ratio was diluted with approximately 5 mL of DI water; giving an average total dilution factor of 21. The diluted samples were submitted to Analytical Development for Al and Si concentration analyses by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES).

The 2H evaporator scale sample used for the 1.5 M nitric acid dissolution study (sample HTF-13-10-28H), based on X-ray diffraction (XRD) and ICP-ES analysis results, contained a significant amount of impurities. These other non-aluminosilicate material components of the 2H evaporator scale included an average of 12 wt. % elemental mercury/mercuric compounds and 6.5 wt. % uranium mineral [3, 4]. The elemental analyses of the scale by ICP-ES also showed that scales impurities include a significant amount of Fe, Ca, Cr, Gd and Ni. Based on above summary information the estimated quantity of aluminosilicate in this particular 2H evaporator scale was put at 75%. On the other hand, the sample used for the 1.25 M nitric acid dissolution study contained about 3.5 wt% elemental mercury and 7 wt% other impurities and thus the estimated quantity of aluminosilicate in this particular 2H evaporator scale sample was pegged at 89.5%.

All kinetic and rate equations used to determine the decomposition rate constants for the scale material, as presented in column 2 of Table 4, are based on 75% of the true weight of the initial material used in each phase ratio for the dissolution in 1.5 M nitric acid and 89.5% for the 1.25 M nitric acid dissolution as shown in Table 6. In this thermal decomposition of 2H evaporator scale in nitric acid, the scale is considered as the decomposing material with initial concentration (a) and the aluminum ( $x_{al}$ ) and silicon ( $x_{si}$ ) are the principal decomposing products as shown in Tables 4 and 6.

After time, t, of thermally decomposing the scale in nitric acid at 90 °C, when x mg of (a) must have decomposed, the remaining concentration of the aluminosilicate scale is a minus x (a-x) and x mg of aluminum and silicon are formed in solution. The rate of accumulation of aluminum and silicon in solution is dx/dt. For first-order decomposition reaction, this rate is proportional to the instantaneous concentration of the scale (aluminosilicate), so that

$$dx/dt = k_1(a-x)$$

Separating the variable in above equation and integrating, the resulting equation is

$$\ln(a/(a-x)) = k_1t + C \text{-----}(1)$$

A plot of  $\ln(a/(a-x))$  versus t in the above equation, gives a straight line, the slope of which is the first-order rate constant,  $k_1$ , for the decomposition of the scale mineral. Note that in the above equation C is the constant of integration or y-intercept value in the graph.

### 2.3 Quality Assurance

This work was performed in accordance with the requirements of the task technical request [1]. The experimental data are for these analyses are contained in Laboratory Notebook SRNL-NB-2013-00026 and various Analytical Development (AD) notebooks. Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

### 3.0 Results and Discussion

The principal elemental components of the 2H evaporator scale mineral, an aluminosilicate mineral classified as cancrinite or sodalite, are aluminum, silicon and sodium. The accumulation rate of aluminum or silicon in solution as a result of the dissolution of 2H evaporator scale sample with time was used as a

measure of the scale sample dissolution rate at constant temperature of  $90 \pm 2$  °C. The aluminum and silicon accumulation profiles at different phase ratios, for the 2H scale dissolution in 1.5 M nitric acid, are shown in Figures 2 and 3 and those for 2H scale dissolution in 1.25 M nitric acid are shown in Figures 4.

In general, during each heating and scale dissolution cycle the scale dissolved producing more aluminum and silicon with increase in heating time. After heating for a while, the amount of these analytes in solution decreased or tapered off in most of this study as shown in Figures 2, 3 and 4.

As shown in Figures 2, 3 and 4, within the 75 minute window of scale dissolution at 90 °C, the plots show an initial steep scale dissolution (non-steady state scale dissolution rate) followed by a nearly linear portion (equilibrium dissolution region of the plots). The accumulated aluminum and silicon data used in the generation of the plots in Figures 2 and 3 are presented in Table 1 for the 1.5 M nitric acid dissolution of the 2H scale and are shown in Table 2 for the 1.25 M nitric acid dissolution as presented in Figure 4.

During the scale dissolutions, the silicon accumulation rate in solution seems to track the aluminum accumulation profile during the first few minutes, but then it begins to diverge from then onwards. This divergence therefore means the aluminum-to-silicon ratio in the first phase of the scale dissolution (non-steady state conditions) is different from the ratio towards the end of the scale dissolution runs, as shown in Figures 2, 3 and 4. If the last three data points in each plot in figures 2 and 3 are considered to be in the steady state or equilibrium scale dissolution region (maximum aluminum and silicon in solution), then the value of the aluminum-to silicon ratio can be based on just those three data points. This aluminum-to-silicon ratio based on the three data points for all five phase ratios averages  $1.39 \pm 0.17$  (See values from Table 1). Similarly, using the first two data points in Figures 2 and 3 (non-steady state dissolution of the scale) a different aluminum-to-silicon ratio averages to  $1.18 \pm 0.09$ . The Al/Si ratio average of averages for these two conditions (steady state and non-steady state scale dissolution) is 1.29. These values for aluminum-to-silicon ratio are comparable to the  $1.32 \pm 0.2$  value obtained by simply averaging the individual aluminum and silicon accumulation shown in Table 1, column 4.

The maximum amounts of Al and Si in solution during each of the five phase ratio dissolutions of the scale material were calculated as follows. The milligrams of silicon or aluminum in solution in 60 minutes heating multiplied by the phase ratio corresponds to the total Al or Si that went into solution after heating at 90 °C ( $\text{mg/L} \cdot \text{mL/g-solid} \cdot \text{L}/1000 \text{ mL} = \text{mg/g-scale}$  of Al or Si that went into solution). The data is presented in Table 3 for all phase ratios for the 1.5 M nitric acid dissolution of the 2H scale material.

For the 1.5 M nitric acid dissolution, the phase ratio versus maximum aluminum or silicon in solution plots is shown in Figures 5 and 6, respectively. There are no significant changes in the amount of these two elements in solution with changes in the digestion phase ratios. Hence conclusion can be made that the 2H evaporator scale dissolution, as measured by total aluminum or total silicon in solution, appear to be independent of phase ratio employed in the scale dissolution in 1.5 M nitric acid.

Figures 5 and 6 show, respectively, plots of phase ratio versus the total aluminum or total silicon accumulated in solution. Taking into consideration that there is about a 20% ICP-ES instrument analytical uncertainties for measuring aluminum and silicon, the 2H scale dissolution in 1.5 M nitric acid appear to be generally independent of phase ratio. There are no significant changes in total aluminum or silicon accumulated in solution with changes in phase ratio.

Similarly, for the 2H scale dissolution in 1.25 M nitric acid the aluminum-to-silicon ratio averages to  $1.18 \pm 0.10$ . Again, although the silicon accumulation rate in solution seems to tracks the aluminum accumulation profile it diverges after about 30-45 minutes of heating and scale dissolution.

The data in Table 2 was used to generate the plots presented in Figure 4 (Al and Si concentration profiles for scale dissolution in 1.25 M nitric acid). It is worth pointing out that not all the data points in Table 2 were used in generating of plots in Figure 4. As expected and discussed earlier, the reduction in particle size of the blended 2H scale material used for the phase 2 study in 1.25 M nitric acid may have influenced the dissolution rates. In general, these increases in the dissolution rates, as measured by the relative increase in accumulation of Al and Si during some heating times (second and third 15-minute dissolution times for phase ratios 15 and 20, and first 15-minute dissolution time for phase ratio 25) resulted in data points which are here considered as outliers and thus were not included in generating the plots in Figure 4 and in the calculation of the rate constants. Thus, a total of 3 data points out of the 15 possible data points was not included in generating the Al or Si concentration profiles and thus not used in determining the dissolution rate. This problem was not encountered in phase 1 (scale dissolution at 1.5 M nitric acid) of this study where there was no blending of 2H scale solids.

The plots in Figures 5 and 6 for total aluminum and silicon in solution as a function of phase ratio illustrates that the amounts of these scale elemental components are independent of phase ratios, especially at the maximum accumulation of these elements which corresponds to the equilibrium conditions for the dissolution of the 2H evaporator scale. Therefore, based on the above conclusion, it is reasonable to compare the 2H evaporator scale dissolution rates in 1.25 or 1.5 M nitric acid with the 2H evaporator scale dissolution rates from earlier studies<sup>vii,viii</sup>.

In this dissolution study the calculated ratio of aluminum to silicon in solution was 1.3:1. In previous study with 2H evaporator scales dissolution in 1.5 M nitric acid, Wilmarth, et al. reported an Al/Si ratio of 1.5:1<sup>vii, viii, ix</sup>. Within experimental errors, the Al/Si ratio from current studies is in fairly good agreement with those of previous dissolution studies for 2H evaporator scale as reported by Wilmarth, et al.<sup>vii, viii</sup>

**Table 1. Aluminum and silicon accumulation with time during scale dissolution for different phase ratios: 1.5 M nitric acid study.**

<b>Phase ratio-minute</b>	<b>[Al], mg/L</b>	<b>[Si], mg/L</b>	<b>Al/Si ratio*</b>
7-15 min	6003	5476	<b>1.10</b>
7-30 min	7033	5935	<b>1.19</b>
7-45 min	7659	6054	<b>1.27</b>
7-60 min	8131	6044	<b>1.35</b>
7-75 min	8390	5908	<b>1.42</b>
10-15 min	5842	4877	<b>1.20</b>
10-30 min	6527	5511	<b>1.18</b>
10-45 min	7333	5966	<b>1.23</b>
10-60 min	7658	6390	<b>1.20</b>
10-75 min	8266	5931	<b>1.39</b>
15-15 min	2176	1934	<b>1.13</b>
15-30 min	3119	2414	<b>1.29</b>
15-45 min	3101	2177	<b>1.42</b>
15-60 min	5127	3418	<b>1.50</b>
15-75 min	5395	3450	<b>1.56</b>
20-15 min	3234	2961	<b>1.09</b>
20-30 min	3876	3480	<b>1.11</b>
20-45 min	3965	3404	<b>1.16</b>
20-60 min	4157	3427	<b>1.21</b>
20-75 min	4473	3567	<b>1.25</b>
25-15 min	686	614	<b>1.12</b>
25-30 min	1947	1414	<b>1.38</b>
25-45 min	2814	1857	<b>1.52</b>
25-60 min	3213	1909	<b>1.68</b>
25-75 min	2405	1423	<b>1.69</b>
<b>Average</b>			<b>1.3 ± 0.2</b>

\*Al/Si ratios seem to increase with increase heating time for each phase ratio. The largest difference in Al/Si ratio is manifested in phase ratio 25 runs.

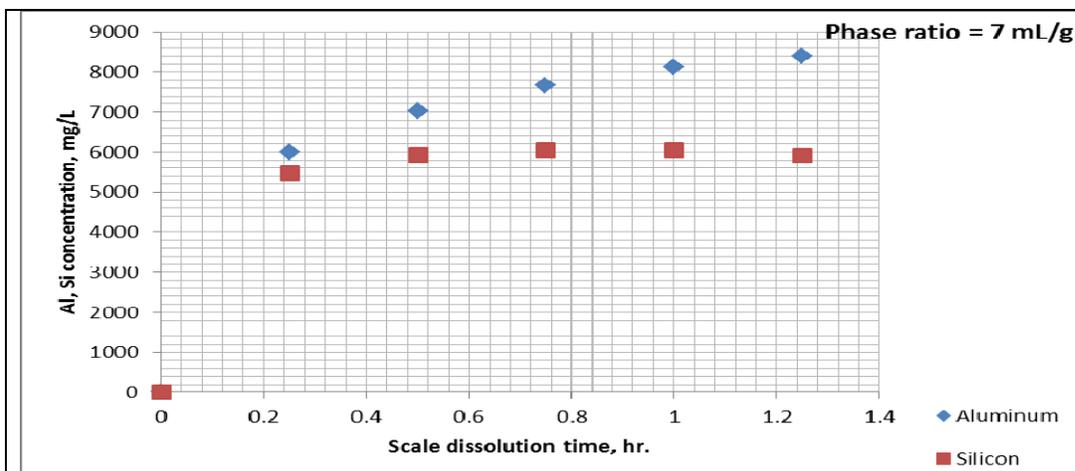
**Table 2. Aluminum and silicon accumulation with time during scale dissolution for different phase ratios: 1.25 M nitric acid study.**

Phase ratio-minute	[Al], mg/L	[Si], mg/L	Al/Si ratio*
15-15 min	2905	2685	<b>1.08</b>
15-30 min	6092	5405	<b>1.13</b>
15-45 min	5148	4401	<b>1.17</b>
15-60 min	6000	4685	<b>1.28</b>
15-75 min	6661	4995	<b>1.33</b>
20-15 min	1819	1721	<b>1.06</b>
20-30 min	2358	2124	<b>1.11</b>
20-45 min	4661	3604	<b>1.29</b>
20-60 min	4264	3328	<b>1.28</b>
20-75 min	4247	3159	<b>1.34</b>
25-15 min	6499	6096	<b>1.07</b>
25-30 min	2306	2138	<b>1.08</b>
25-45 min	3060	2913	<b>1.05</b>
25-60 min	3596	3079	<b>1.17</b>
25-75 min	4035	3302	<b>1.22</b>
<b>Average</b>			<b>1.18 ± 0.10</b>

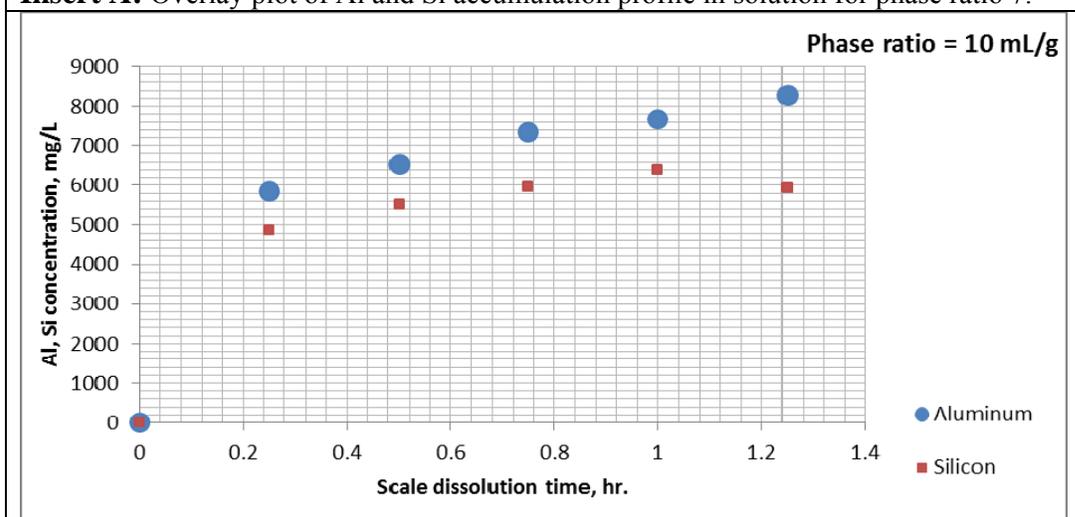
\*Again, the Al/Si ratios seem to increase with increase heating time for each phase ratio.

**Table 3. Maximum accumulation of aluminum and silicon in solution [1.5 M nitric acid dissolution]**

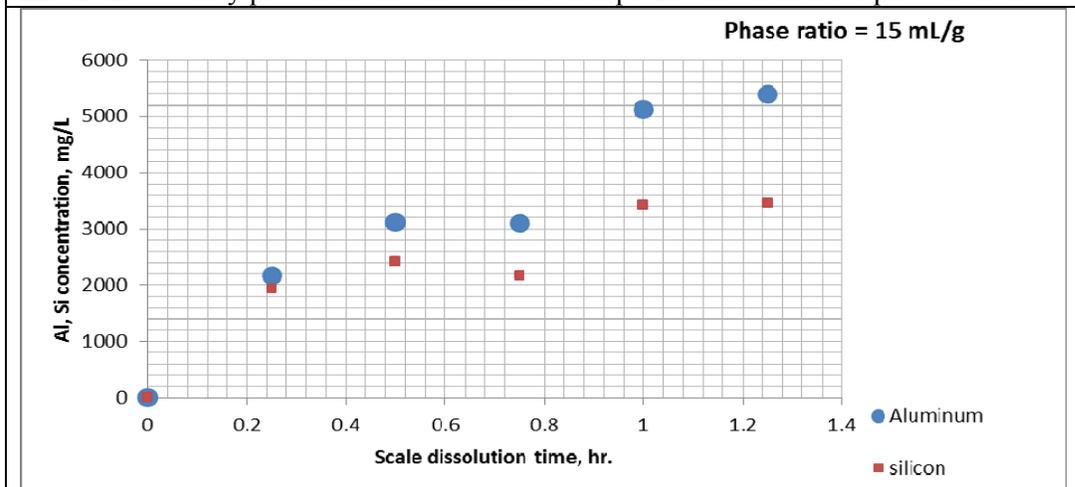
Phase ratio, mL/g	7	10	15	20	25	Average/ St.dev
Al in solution after heating for 1 hr.(mgL <sup>-1</sup> hr <sup>-1</sup> )	8200	7962	5300	4316	3200	
Total Al that went into solution (mg/L*mL/g(phase ratio) * L/1000 mL = mg/g-scale)	<b>57.4</b>	<b>79.6</b>	<b>79.5</b>	<b>86.3</b>	<b>80</b>	<b>76.6</b> <b>± 11.1</b>
Si in solution after heating for 1 hr.(mg L <sup>-1</sup> hr <sup>-1</sup> )	6000	6330	3500	3427	1900	
Total Si that went into solution (mg/L*mL/g(phase ratio) * L/1000 mL = mg/g-scale)	<b>42</b>	<b>63.3</b>	<b>52.5</b>	<b>68.5</b>	<b>47.5</b>	<b>54.8</b> <b>± 11</b>



**Insert A:** Overlay plot of Al and Si accumulation profile in solution for phase ratio 7.

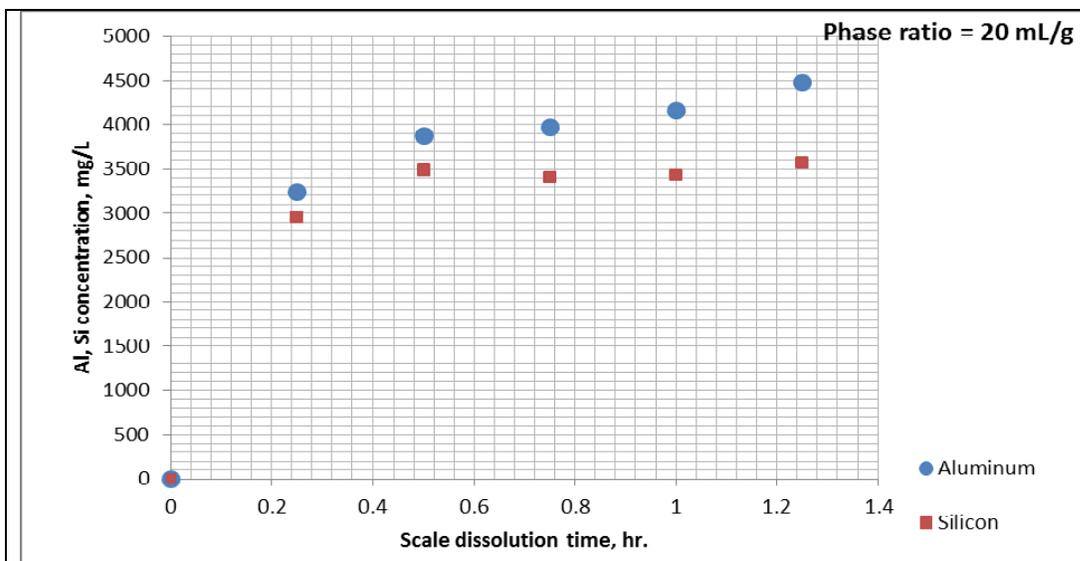


**Insert B:** Overlay plot of Al and Si accumulation profile in solution for phase ratio 10.

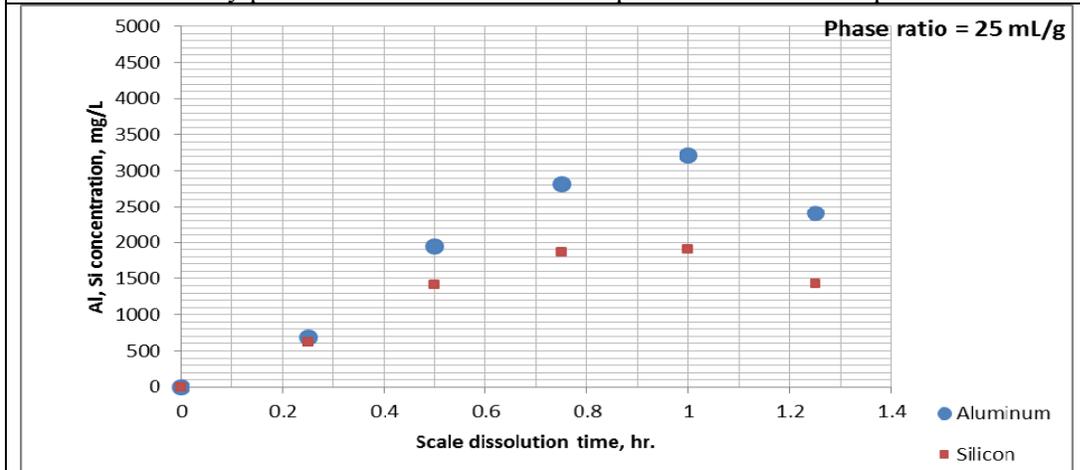


**Insert C:** Overlay plot of Al and Si accumulation profile in solution for phase ratio 15.

**Figure 2.** Aluminum and silicon concentration profiles for 2H evaporator bottom pot scale dissolution in 1.5 M HNO<sub>3</sub> for phase Ratios 7, 10 and 15. Oven Temperature maintained constant at 90 ± 2° c.



**Insert E:** Overlay plot of Al and Si accumulation profile in solution for phase ratio 20.



**Insert G:** Overlay plot of Al and Si accumulation profile in solution for phase ratio 25.

**Figure 3.** Aluminum and silicon concentration profiles for 2H evaporator bottom pot scale dissolution in 1.5 M HNO<sub>3</sub> for phase ratios 20 and 25. Oven temperature maintained constant at 90 ± 2 °C.

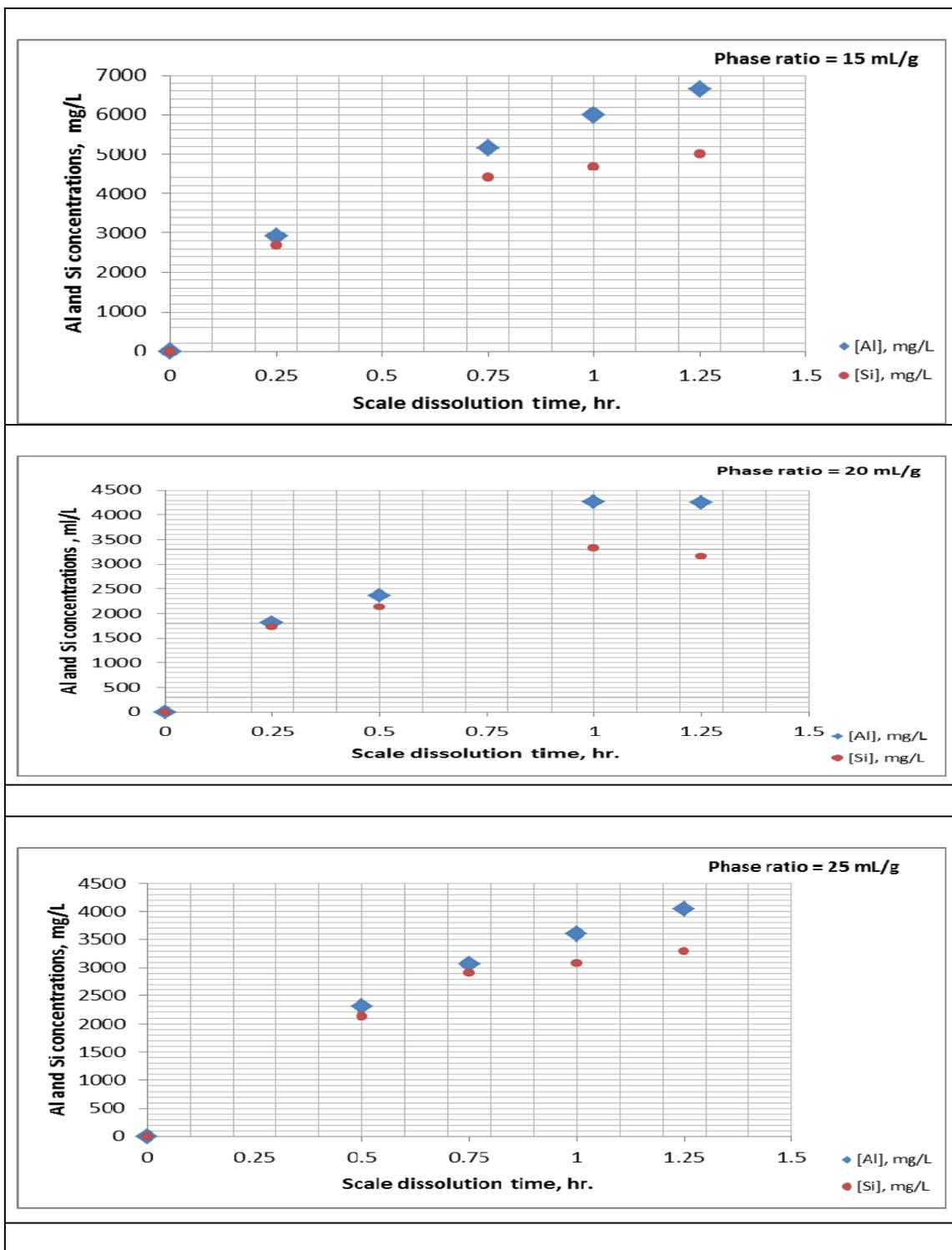
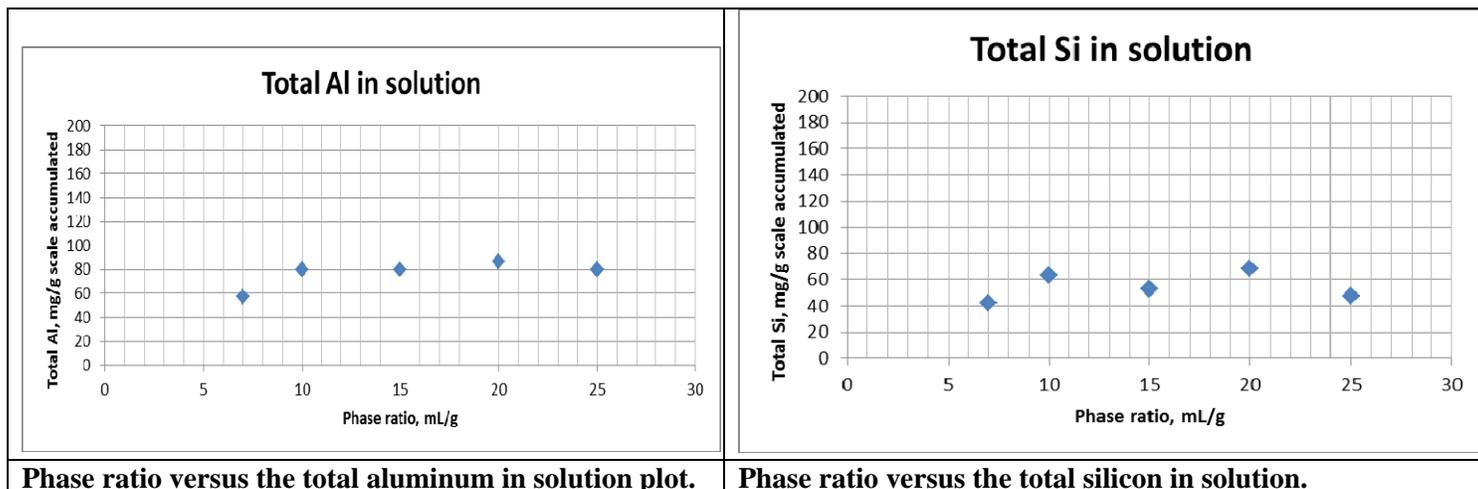
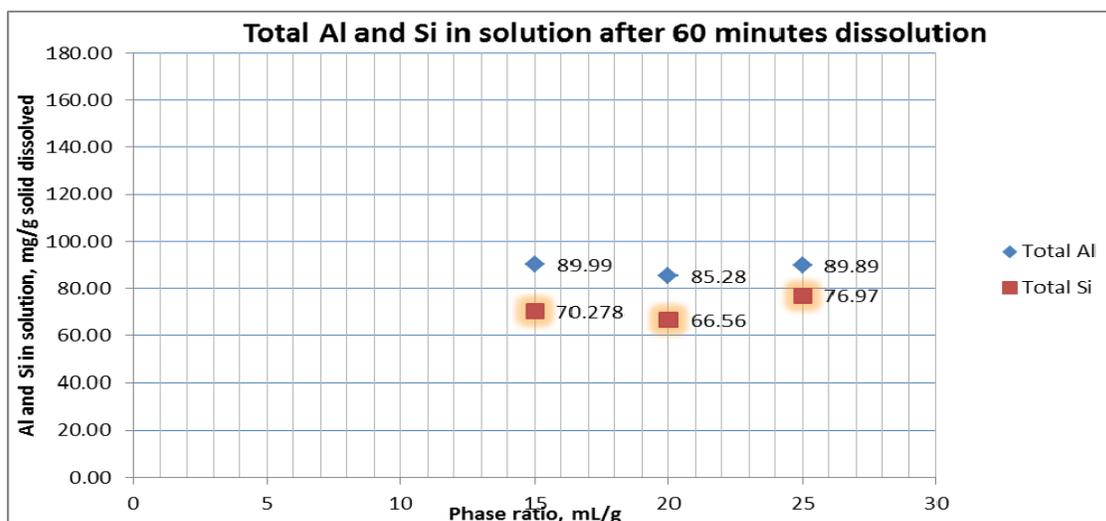


Figure 4. Aluminum and silicon concentration profiles for 2H evaporator bottom pot scale dissolution in 1.25 M HNO<sub>3</sub> for phase ratios 15, 20 and 25. Oven temperature maintained constant at 90 ± 2 °C.



**Figure 5. Phase ratio versus the total aluminum and silicon in solution plots (Dissolution in 1.5 M nitric acid). Scale dissolutions, as measured by total aluminum in solution, appear to be generally independent of phase ratio.**



**Figure 6. Phase ratio versus the total aluminum and silicon in solution overlay plots (Dissolution in 1.25 M nitric acid). Scale dissolutions, as measured by total aluminum in solution, appear to be generally independent of phase ratio.**

Representative first-order dissolution kinetic plots (based on equation 1) for phase ratios 10 and 15 are shown in Figures 7 and 8, respectively, for aluminum and silicon accumulation in solution for 1.5 M and 1.25 M nitric acid dissolutions. Data presented in Tables 4 and 6 are the basis for all the plots for the different phase ratios employed in the determination of all dissolution rate constants presented in Tables 5 and 7. The coefficient of linear regression ( $R^2$ ) for these plots averages better than 0.95, which indicates that dissolution of 2H scale in dilute nitric acid is a well behaved first-order process.

Tables 5 and 7 show the different rate constant at different phase ratios for both aluminum and silicon accumulations, respectively, for dissolutions in 1.25 and 1.5 M nitric acid. For the 1.5 M nitric acid dissolution, the average rate constant for aluminum accumulation is  $9.20\text{E-}04 \pm 6.61\text{E-}04 \text{ min}^{-1}$  and that for silicon is  $5.60\text{E-}04 \pm 4.93\text{E-}04 \text{ min}^{-1}$ . For the 1.25 M nitric acid dissolution of the 2H scale, the average rate constant for aluminum accumulation is  $1.10\text{E-}03 \pm 1.00\text{E-}04 \text{ min}^{-1}$  and that for silicon is  $6.00\text{E-}04 \pm 1.00\text{E-}04 \text{ min}^{-1}$ .

The half-life of a first-order reaction (dissolution of the scale) is independent of the initial material (scale) concentration. Therefore, for the 2H scale dissolution in 1.5 M nitric acid using the average rate constant for aluminum accumulation, one obtains a calculated average half-life of 12.6 hours ( $\tau_{1/2} = \ln 2/k_1 = 0.693/9.20\text{E-}04 \text{ min}^{-1}$ ). Based on the aluminum accumulation rate constants displayed in Table 5, this calculated half-life has a very large uncertainty. Similarly, for the 1.25 M nitric acid dissolution of 2H scale solids the average aluminum accumulation rate constant (Table 7), the calculated average half-life for scale dissolution is 10.8 hours ( $\tau_{1/2} = \ln 2/k_1 = 0.693/1.107\text{E-}03 \text{ min}^{-1}$ ).

Averaging the half-lives from the two 2H scale acid dissolution in 1.25 and 1.5 M nitric acid, a reasonable half-life for the dissolution of 2H scales in dilute nitric acid is  $11.7 \pm 1.3$  hours. The plant operational time for chemically cleaning of the scale (soaking) the 2H evaporator with dilute nitric acid is 32 hours.<sup>vi</sup> Therefore, it can be concluded that it requires about 3 half-lives or less to completely dissolve most of the scales in the Evaporator pot which come into contact with the dilute nitric acid solution.

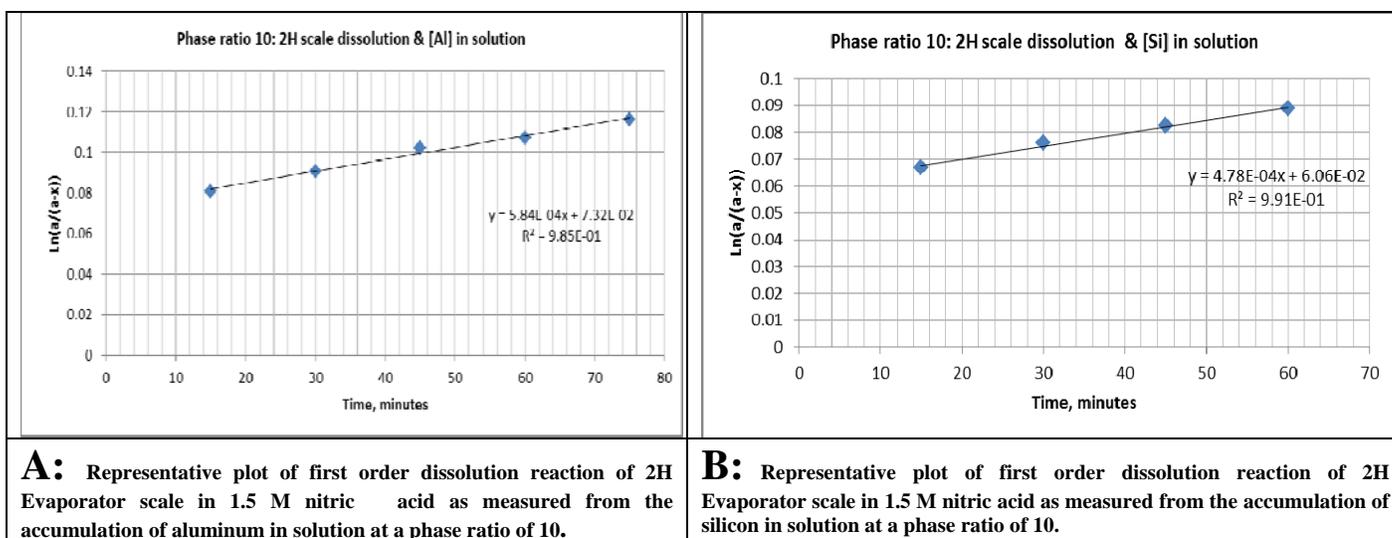
These half-life data are not calculated based on silicon accumulation because of the known abnormal precipitation chemistry of silicon in nitric acid. There appears to be an apparent difference in the 2H scale dissolution rate in 1.5 M nitric acid when compared with the scale dissolution in 1.25 M nitric acid. This slight difference may be attributed to the nature of the scale solids which were used in the two dilute acid concentration dissolutions. The scale sample used in the 1.5 M acid dissolution were larger scale particles as shown in Figure 1, while the scale samples used in the 1.25 M acid dissolution were finer scale particles which would tend to dissolve slightly faster.

**Table 4. Dissolution of 2H evaporator scale in 1.5 M nitric acid at 90 °C**

Phase ratio/ minutes	Aluminosilicate initial concent. (a), mg	[Al], mg $X_{al}$	[Si], mg $X_{si}$	$\ln[a/(a-X_{al})]$	$\ln[a/(a-X_{si})]$	Time, t, minutes
7-15 min	740.25	42.021	38.332	<b>0.06</b>	<b>0.05</b>	<b>15</b>
7-30 min	740.25	49.231	41.545	<b>0.07</b>	<b>0.06</b>	<b>30</b>
7-45 min	740.25	53.613	42.378	<b>0.08</b>	<b>0.06</b>	<b>45</b>
7-60 min	740.25	56.917	42.308	<b>0.08</b>	<b>0.06</b>	<b>60</b>
7-75 min	740.25	58.73	41.356	<b>0.08</b>	<b>0.06</b>	<b>75</b>
10-15 min	753	58.42	48.77	<b>0.08</b>	<b>0.07</b>	<b>15</b>
10-30 min	753	65.27	55.11	<b>0.09</b>	<b>0.08</b>	<b>30</b>
10-45 min	753	73.33	59.66	<b>0.10</b>	<b>0.08</b>	<b>45</b>
10-60 min	753	76.58	63.9	<b>0.11</b>	<b>0.09</b>	<b>60</b>
10-75 min	753	82.66	59.31	<b>0.12</b>	<b>0.08</b>	<b>75</b>
15-15 min	807.75	32.64	29.01	<b>0.04</b>	<b>0.04</b>	<b>15</b>
15-30 min	807.75	46.785	36.21	<b>0.06</b>	<b>0.05</b>	<b>30</b>
15-45 min	807.75	46.515	32.655	<b>0.06</b>	<b>0.04</b>	<b>45</b>
15-60 min	807.75	76.905	51.27	<b>0.10</b>	<b>0.07</b>	<b>60</b>
15-75 min	807.75	80.925	51.75	<b>0.11</b>	<b>0.07</b>	<b>75</b>
20-15 min	756	64.68	59.22	<b>0.09</b>	<b>0.08</b>	<b>15</b>
20-30 min	756	77.52	69.6	<b>0.11</b>	<b>0.10</b>	<b>30</b>
20-45 min	756	79.3	68.08	<b>0.11</b>	<b>0.09</b>	<b>45</b>
20-60 min	756	83.14	68.54	<b>0.12</b>	<b>0.10</b>	<b>60</b>
20-75 min	756	89.46	71.34	<b>0.13</b>	<b>0.10</b>	<b>75</b>
25-15 min	771.75	17.15	15.35	<b>0.02</b>	<b>0.02</b>	<b>15</b>
25-30 min	771.75	48.675	35.35	<b>0.07</b>	<b>0.05</b>	<b>30</b>
25-45 min	771.75	70.35	46.425	<b>0.10</b>	<b>0.06</b>	<b>45</b>
25-60 min	771.75	80.325	47.725	<b>0.11</b>	<b>0.06</b>	<b>60</b>
25-75 min	771.75	60.125	35.575	<b>0.08</b>	<b>0.05</b>	<b>75</b>

**Table 5. Dissolution of 2H evaporator scale in 1.5 M nitric acid at 90 °C: Rate constants**

Phase ratio	Al in solution Rate constant, min <sup>-1</sup>	Si in solution Rate constant, min <sup>-1</sup>
7	3.98E-04	1.93E-04
10	5.84E-04	4.78E-04
15	1.13E-03	5.27E-04
20	5.42E-04	2.24E-04
25	1.95E-03	1.40E-03
Average	<b>9.21E-04</b>	<b>5.64E-04</b>
Standard dev.	<i>6.39E-04</i>	<i>4.90E-04</i>



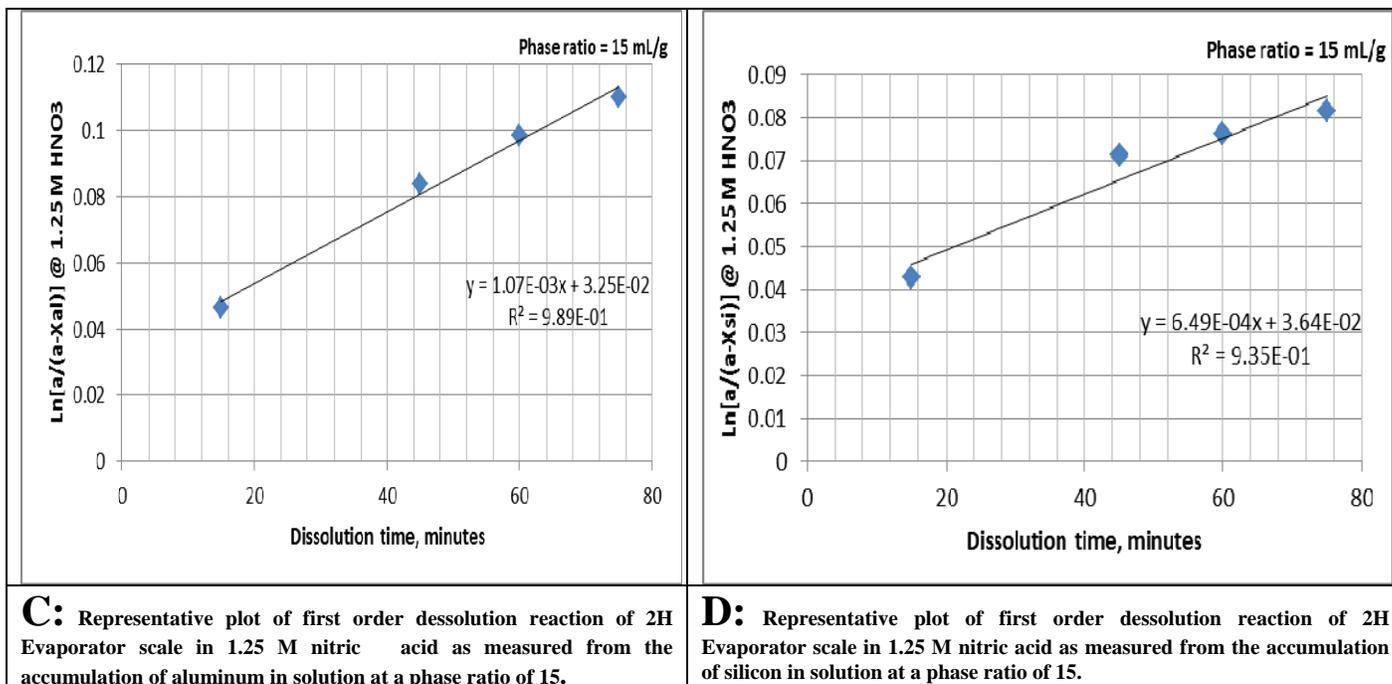
**Figure 7. Representative first order reaction plots for 2H scale dissolution in 1.5 M nitric acid.**

**Table 6. Dissolution of 2H evaporator scale in 1.25 M nitric acid at 90 °C**

Phase ratio/ minutes	Aluminosilicate initial concent. (a), mg	[Al], mg $X_{al}$	[Si], mg $X_{si}$	$\ln[a/(a-X_{al})]$	$\ln[a/(a-X_{si})]$	Time, t, minutes
15-15 min	957.65	43.58	40.28	<b>0.047</b>	<b>0.043</b>	<b>15</b>
15-30 min	957.65	91.38	81.08	<b>0.100</b>	<b>0.088</b>	<b>30</b>
15-45 min	957.65	77.23	66.02	<b>0.084</b>	<b>0.071</b>	<b>45</b>
15-60 min	957.65	89.99	70.28	<b>0.099</b>	<b>0.076</b>	<b>60</b>
15-75 min	957.65	99.91	74.93	<b>0.110</b>	<b>0.081</b>	<b>75</b>
20-15 min	963.915	36.38	34.41	<b>0.038</b>	<b>0.036</b>	<b>15</b>
20-30 min	963.915	47.15	42.48	<b>0.050</b>	<b>0.045</b>	<b>30</b>
20-45 min	963.915	93.23	72.08	<b>0.102</b>	<b>0.078</b>	<b>45</b>
20-60 min	963.915	85.28	66.56	<b>0.093</b>	<b>0.072</b>	<b>60</b>
20-75 min	963.915	84.93	63.18	<b>0.092</b>	<b>0.068</b>	<b>75</b>
25-15 min	907.6195	162.49	152.40	<b>0.197</b>	<b>0.184</b>	<b>15</b>
25-30 min	907.6195	57.64	53.45	<b>0.066</b>	<b>0.061</b>	<b>30</b>
25-45 min	907.6195	76.50	72.84	<b>0.088</b>	<b>0.084</b>	<b>45</b>
25-60 min	907.6195	89.89	76.97	<b>0.104</b>	<b>0.089</b>	<b>60</b>
25-75 min	907.6195	100.89	82.54	<b>0.118</b>	<b>0.095</b>	<b>75</b>

**Table 7. Dissolution of 2H evaporator scale in 1.25 M nitric acid at 90 °C: Rate constants**

Phase ratio	Al in solution Rate constant, min <sup>-1</sup>	Si in solution Rate constant, min <sup>-1</sup>
15	1.07E-03	6.49E-04
20	1.00E-03	5.96E-04
25	1.15E-03	7.26E-04
Average	<b>1.07E-03</b>	<b>6.57E-04</b>
Standard dev.	<i>7.51E-05</i>	<i>6.54E-05</i>



**Figure 8. Representative first order reaction plots for 2H scale dissolution in 1.25 M nitric acid.**

#### 4.0 Conclusions

The 2H evaporator scale aluminosilicate mineral readily dissolves in 1.25 and 1.5 M dilute nitric acid at 90 °C yielding principal elemental components of aluminum and silicon in solution. The 2H scale dissolution rate constant, based on aluminum accumulation in 1.5 and 1.25 M nitric acid solution are, respectively,  $9.21E-04 \pm 6.39E-04 \text{ min}^{-1}$  and  $1.107E-03 \pm 7.51E-05 \text{ min}^{-1}$ . The dissolution rate constant for 2H scale in 1.5 M nitric acid has a very large uncertainty when compared to the dissolution rate in 1.25 M nitric acid. Silicon accumulation rate in solution does track the aluminum accumulation profile during the first few minutes of scale dissolution. It diverges towards the end of the scale dissolution. This divergence therefore means the aluminum-to-silicon ratio in the first phase of the scale dissolution (non-steady state conditions) is different from the ratio towards the end of the scale dissolution. Possible causes of this change in silicon accumulation in solution as the scale dissolution progresses may include silicon precipitation from solution or the 2H evaporator scale is a heterogeneous mixture of aluminosilicate minerals with several impurities.

On a mass basis, the Al-to-Si ratio for the scale dissolution in 1.5 M nitric acid averaged  $1.30 \pm 0.20$  and averaged  $1.18 \pm 0.10$  for the 2H scale dissolution in 1.25 M nitric acid. These aluminum-to-silicon ratios are in fairly good agreement with ratios from previous studies. Therefore, there is still more aluminum in the 2H evaporator scales than silicon which implies that there are no significant changes in scale properties which will exclude nitric acid as a viable protic solvent for aluminosilicate scale buildup dissolution from the 2H evaporator.

The average half-life for the decomposition of the 2H evaporator scale mineral in 1.5 M nitric acid is 12.5 hours, while the half-life for the decomposition of the 2H evaporator scale in 1.25 M nitric acid is 10.8

hours. It therefore requires about 3 half-lives or less to completely dissolve most of the scales in the Evaporator pot which come into contact with the dilute nitric acid solution.

In order to adequately use the information provided in this study, such as the first-order rate constant,  $k_1$ , for the dissolution of the 2H scale mineral solids in the 2H evaporator, a more acceptable value for the true percent composition of aluminosilicate in the 2H evaporator scale material is required. This would make it easier to calculate as well as predict the scale soaking times required during scale cleaning cycles with dilute nitric acid.

The 2H evaporator scale decomposition data provided in plots in figures 7 and 8 illustrates that the decomposition of 2H evaporator scale follows first-order reactions kinetics. However, the monitoring of the scale decomposition reaction in 1.5 or 1.25 M nitric acid may be better ascertained through the determination of aluminum concentration in solution than monitoring for silicon. Silicon solution chemistry may lead to partial precipitating of silicon with time as the scale in acid is heated at 90 °C.

The elemental mercury/other mercury compound content of the 2H evaporator scale used in this dissolution study was significantly higher than mercury analytical results from previous 2H evaporator scale materials submitted to SRNL for analyses. This high mercury content, in this case averaging 12 wt. % for the 1.5 M nitric acid scale dissolution, may affect the scale dissolution chemistry in nitric acid. For future 2H evaporator scale samples, sent to SRNL for characterizations, it is therefore recommended that the bulk density, mercury content and relative amount of aluminosilicate mineral content be analytically determined.

## 5.0 References

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- <sup>i</sup> H. Bui, “2H Evaporator Scale Sampling Analysis,” X-TTR-H-00021, Rev. 0, January 16, 2013.
- <sup>ii</sup> H. Bui, “2H Evaporator Scale Sampling Analysis,” X-TTR-H-00021, Rev. 1., March 27, 2014.
- <sup>iii</sup> L N. Oji, “Task Technical and Quality Assurance Plan for 2H Evaporator Scale Sample Analysis and Dissolution Studies” SRNL-RP-2013-00033, Rev. 1, April 14, 2014.
- <sup>iv</sup> L N. Oji, “Analysis of 2H-Evaporator Scale Pot Bottom Sample [HTF-13-11-28H],” SRNL-STI-2013-00267, Revision 0, July 2013.
- <sup>v</sup> L N. Oji, “Analysis of 2H-Evaporator Scale Wall [HTF-13-82] and Pot Bottom [HTF-13-77] Samples,” SRNL-STI-2013-00352 June 2013.
- <sup>vi</sup> H. Bui, “Flowsheet and operating plan for the 242-16H evaporator acid cleaning process using neutralization in the evaporator (U),” WSRC-TR-2006-00259, Rev. 1, May 22, 2013.
- <sup>vii</sup> W.R. Wilmarth, C. J. Coleman, A. R. Jurensen, W. M. Smith, T.C. hart and W.T. Boyce, “Characterization and Dissolution Studies of Samples from the 242-16 Evaporator” Evaporator Cleaning Studies” WSRC-TR-2000-00038, Rev. 0, January 31, 2000.
- <sup>viii</sup> W.R. Wilmarth, “Evaporator Cleaning Studies” WSRC-TR-98-00406, Rev. 0, November 16, 1998.
- <sup>ix</sup> W.R. Wilmarth, “Effect of Gadolinium and Depleted uranium on the Nitric Acid Dissolution of Samples from the 242-16 Evaporator Pot” WSRC-TR-2000-00210, Rev. 0, June 12, 2000.

Appendix A: 2H Evaporator Cleaning Flow Sheet

