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Determination of the Crystalline Structure of Scale Solids from the 16H Evaporator Gravity Drain line to Tank 38H

L. N. Oji

October 2015

SRNL-STI-2015-00457, Revision 0

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EXECUTIVE SUMMARY

In August 2015, scale solids from the 16H Evaporator Gravity Drain Line (GDL) to the Tank 38H were delivered to SRNL for analysis. The desired analytical goal was to identify and confirm the crystalline structure of the scale material and determine if the form of the aluminosilicate mineral was consistent with previous analysis of the scale material from the GDL.

Analysis of the "as-received" material by X-ray diffraction and wet chemical techniques led to the following conclusions:

- The "as-received" scale solid from the 16H Evaporator gravity drain line is composed of both crystalline and amorphous solid materials.
- X-ray diffraction analysis of the "as-received" sample indicate the presence of two principal crystalline compounds; nitrated sodium aluminosilicate mineral called cancrinite $(Na_8(Al_6Si_6O_{24})(NO_3)_2 \cdot 4H_2O)$ and clarkeite $(Na\ [(UO_2)O(OH)](H_2O)$, which is a hydroxyl uranium mineral.
- The elemental analytical data for the "as-received" scale solid shows that the aluminum-to-silicon molar ratio is 1.08, which is in good agreement with the theoretical aluminum to silicon molar ratio of 1.0 for cancrinite aluminosilicate mineral. This information thus confirms that the bulk of the scale material is cancrinite $(Na_8(Al_6Si_6O_{24})(NO_3)_2 \cdot 4H_2O)$, which has a theoretical aluminum-to-silicon molar ratio of 1.0.

- Aluminosilicate formation modeling and experimental data shows that the solubility product, K_{sp}, for aluminosilicate mineral is directly proportional to the cube root of the free-OH concentration. This aluminosilicate K_{sp} and free-OH concentration relationship seems to answer the question dealing with the observed increase in the frequency of mechanical cleaning of the 2H evaporator experienced in the plant during the removals of accumulated aluminosilicate when the free-OH concentration in the 2H Evaporator feed tank dropped to a value of 1.5 molar or less.

- It is recommended that the free-OH concentration in Tank 43H be maintained at or above 2 molar to decrease mechanical cleaning frequency of the GDL due to excessive accumulation of sodium aluminosilicate scales.
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LIST OF ABBREVIATIONS

ICP-ES	Inductively Coupled Plasma – Emission Spectrometry
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
XRD	X-ray diffraction

1.0 Introduction

On August, 2015, Savannah River Remediation (SRR) obtained scale solid sample materials from the Evaporator Gravity Drain Line (GDL) to Tank 38H during mechanical cleaning of the evaporator. This scale material (sample ID: TK 38 HTF-15-60) was delivered to Savannah River National Laboratory (SRNL) for analysis. The desired goal was to identify the chemical nature (elemental make-up and crystalline structure of the solids) of the solids material, and to confirm that the crystallinity of the scale solids was consistent with previous analysis of scales from the GDL.[i]

The Technical Task Request, X-TTR-H-00056, defined the tasks and requirements for the performance of this scale sample characterization by SRNL. This report contains the results of the XRD and ICP-ES elemental analysis of the "as-received" GDL sample solids. Requirements for performing reviews of technical reports and the extent of review are established in Manual E7 Procedure 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.

As-received Sample ID: TK 38-HTF-15-60 (Tank 38 gravity drain Line solids) Sample description: Dark brown material Weight of "as-received" sample: 5.6 grams

Figure 1, Picture of the Evaporator gravity Drain Line scale solids (Sample HTF-15-60).

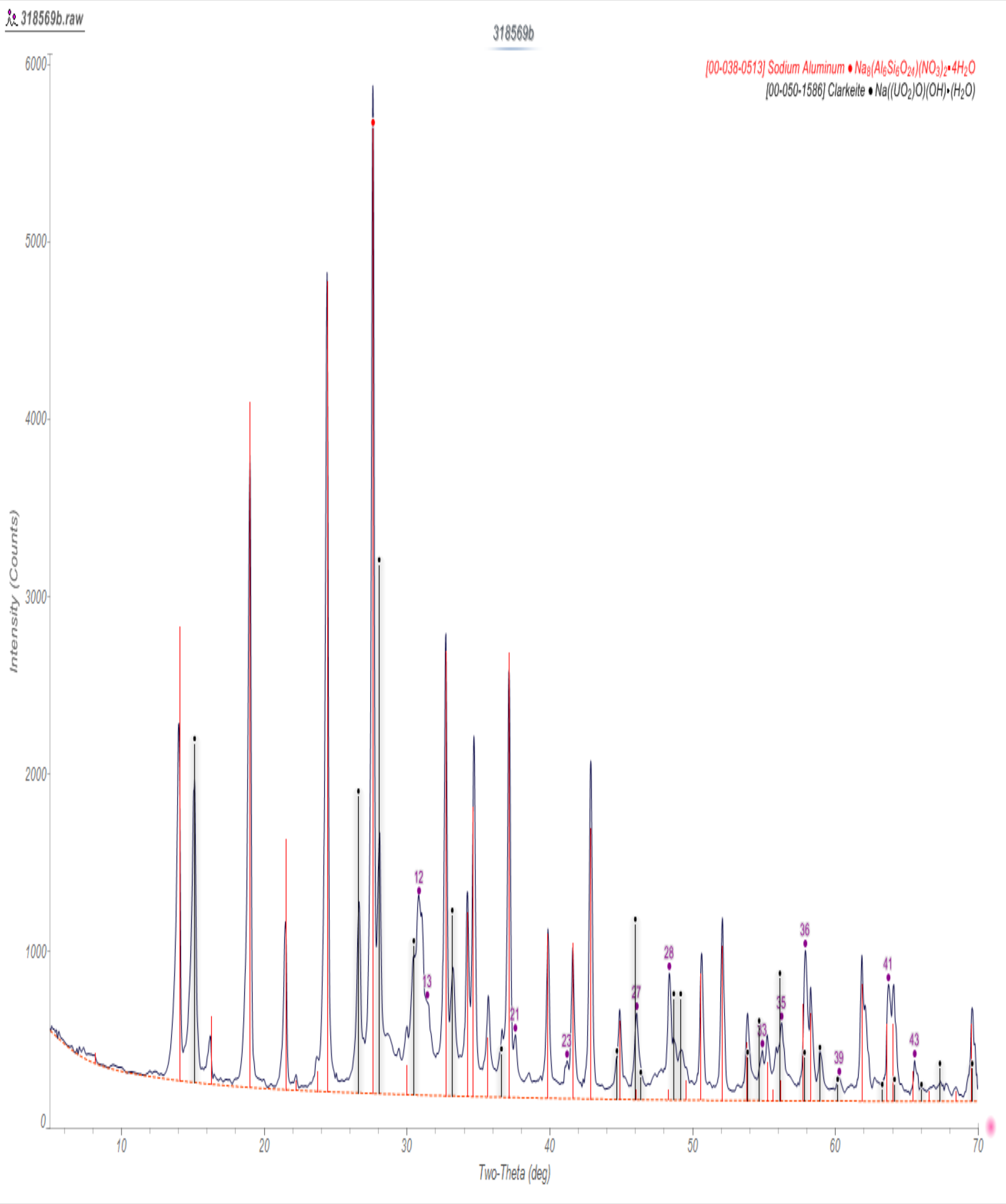

Figure 2 XRD spectra of scale solids from the Tank 16H Evaporator gravity drain line to Tank 38H. Spectra show both crystalline and amorphous material (Sample HTF-15-60).

2.0 Sample Description, Preparation for Analysis and Experimental Details

A picture of the GDL scale sample solids inside a transparent and clear polymethyl pentene beaker is shown in Figure 1. About 5.6 grams of the fairly dry material was received and one half of it was air-dried in the Shielded cell for 48 hours. The resulting air-dried solids were put in a new glass mortar and pestle and ground to a fine powder. This fine powder was sent to Analytical Development (AD) for X-Ray characterization.

An aliquot of the "as-received sample" solids (average of 0.5 g) was digested by aqua-regia with nitric/hydrochloric acid and the resulting digested liquid sample was analyzed by Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-ES) for elemental constituents. The principal cations detected were mainly aluminum, silicon, calcium, and iron as presented in Table 1.

3.0 Analytical Results and Discussion

The theoretical molar ratio of Al to Si, based on the formula for nitrated sodium aluminosilicate ($Na_8(Al_6Si_6O_{24})(NO_3)_2{\cdot}4H_2O$) mineral (cancrinite), is 1 (6 moles Si/ 6 moles Al). Analytical data for the "as-received" material by Inductively Coupled Plasma-Mass Spectrometry (ICP-ES) gave an aluminum concentration of 145,000 µg/g (5.37E-03 moles/g) and silicon concentration of 139,000 µg/g (4.95E-03 moles/g). The calculated silicon to aluminum molar ratio is 1.08. Taking into consideration the ICP-ES measurement uncertainties for both Al and Si, this value is in fairly good agreement with the theoretical Al/Si molar ratio of 1.0 for Cancrinite. It is assumed that the amorphous material does not contain significant amounts of Al and Si.

X-Ray diffraction spectrum of the air-dried GDL scale sample, as shown in Figure 2, matched the spectrum of two crystalline materials; nitrated sodium aluminosilicate mineral ($Na_8(Al_6Si_6O_{24})(NO_3)_2{\cdot}4H_2O$).and clarkeite ($Na[(UO_2)O(OH)](H_2O)$). Clarkeite is a hydroxy uranium mineral. There are other non-crystalline materials in the GDL scale material as indicated by the upward shift in the XRD spectral base line in Figure 2.

Based on these characterization results, it is concluded that the 16H Evaporator GDL scale material solids is composed mostly of nitrated sodium aluminosilicate mineral (cancrinite) and clarkeite minerals.

Figure 3 shows a plot of the free hydroxide concentration (OH) in Tank 43H, which is the feed tank to the 2H evaporator, over time between 2010 and 2015[ii]. The data contains real measured free-OH data (in blue) with estimated free-OH data (in brown) for these time periods. It is worth noting that the estimated free-OH data does not take into account the concentrating effects of the evaporator process and so the estimated value may not be reliable. There are three real measured free-OH concentration regions of interest in Figure 3; (1) region between August 2010 and February 2012 when the Free-OH concentration was greater than or equal to 2.0 molar, (2) region between December 2013 and September 2014 when the free-OH concentration was consistently lower than or equal to 1.5 molar and (3) region after September 2014 when the free-OH concentration started staying consistently above 1.5 molar.

According to the 2H Evaporator operational information from the plant, there was less frequent need for mechanical cleaning of the GDL due to a reduction in the accumulation rate for aluminosilicate scale when the free-OH concentration in the feed tank (tank 43H) average above a value of 2 molar [region one of Figure 3, as described in paragraph above]. On the other hand, during the periods in region 2 there were more frequent need for mechanically cleaning the GDL to remove accumulated scale materials [free-OH concentration 1.5 molar or less]. However, in region 3, when the free-OH concentration started creeping back upwards above a concentration greater than 1.5 molar, the amount of accumulated aluminosilicate scale solids in the GDL was observed to be less compared to when the free-OH concentration was less than or equal to 1.5 molar.

The operational plant observation summarized above indicates that there seems to be a free-OH concentration level (1.5 M and below) in the evaporator feed tank below which there is significant accumulation of aluminosilicate scale and a free-OH concentration level (greater 1.5 M) when there is a consistent reduction in accumulated aluminosilicate mineral. The second condition, greater 1.5 M free-OH concentrations, leads to infrequent mechanical cleaning of the GDL because of the reduced accumulation of aluminosilicate scale in the evaporator feed tanks.

Information from the aluminosilicate formation modeling of Gasteiger et al[iii] and previous work by Wilmarth and others[iv, v] shows that the solubility product, K_{sp}, for the aluminosilicate mineral is directly proportional to the cube root of the free-OH concentration in the solution matrix and inversely proportional to the ionic strength as presented in the equation below.

$$K_{sp} \propto \frac{\left(OH^{-}\right)^{3}}{\left(I\right)^{1.666}}$$

Based on the equation above, any significant reduction in free-OH concentration will translate to corresponding changes in the solubility of the aluminosilcate minerals in the evaporator; in this case this means an increase in the accumulation of aluminosilicate minerals formed in the evaporator due to a reduction in aluminosilicate solubility. This faster accumulation of the aluminosilcate mineral leads to an increase in the mechanical cleaning frequency to prevent a complete shutdown of the evaporator. Therefore, it is recommended that the free-OH concentration in the 2H Evaporator feed tank (Tank 43H) be maintained at or above 2.0 M to reduce the aluminosilicate scale accumulation rate and thus reduce the mechanical cleaning frequency.

Table 1 ICP-ES data from Peroxide fusion digestions of the “as-received” GDL sample, ug/g

Elements	Concentration, ,ug/g
Al	145000
Ca	3310
Fe	854
Si	139000

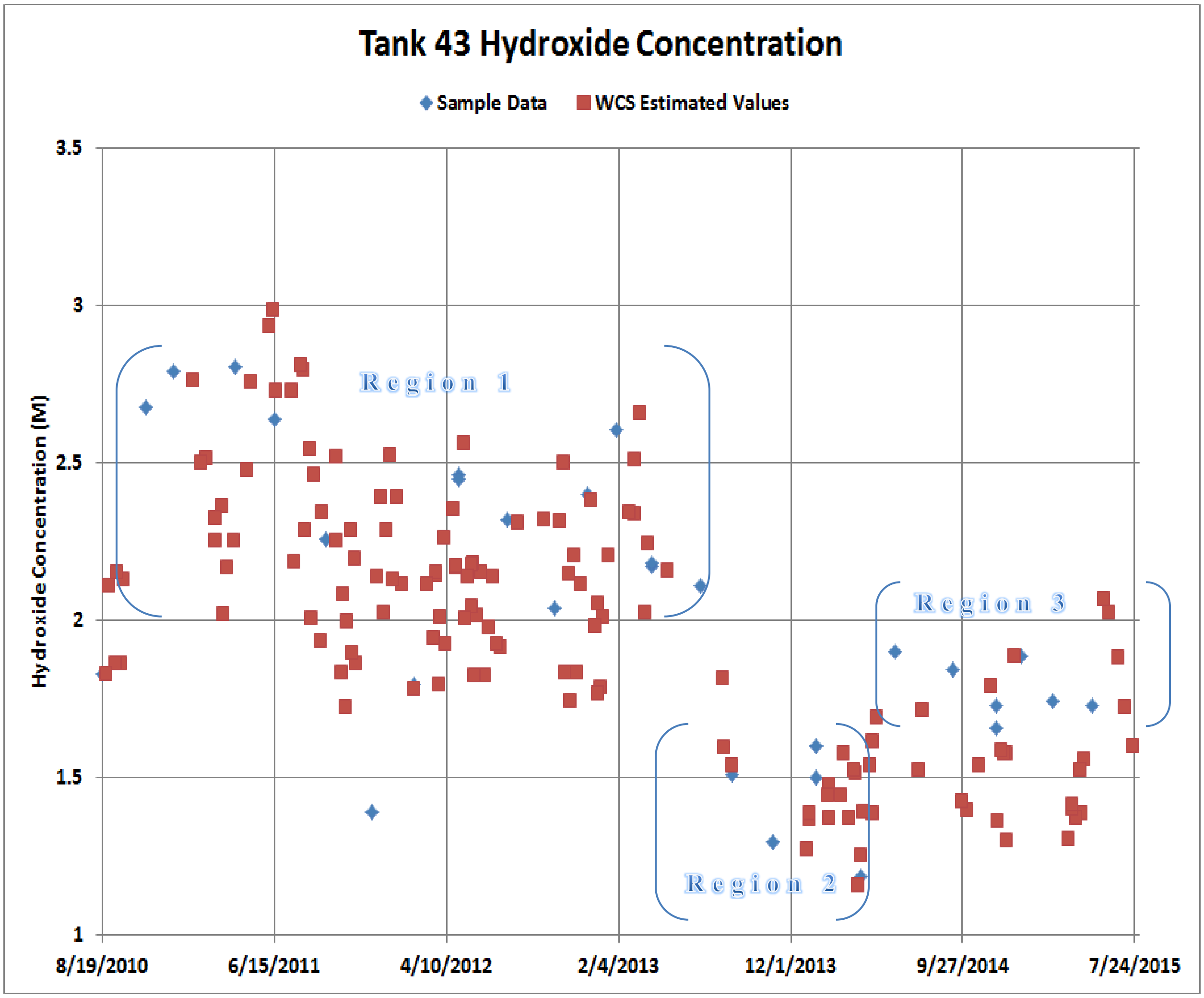

Figure 3 Free hydroxide concentration variations over time in the Tank 43H –Feed tank to the 2H Evaporator. There is more accumulation of aluminosilicate mineral in region 2 with low free-OH concentration values, which corresponds to the more frequent need for mechanical cleaning of the GDL.

4.0 Conclusions

Characterization of the scale solid sample from the 16H Evaporator gravity drain line (GDL) to Tank 38 by X-ray diffraction and wet chemical techniques led to the following conclusions:

- The "as-received" scale solid from the 16H Evaporator gravity drain line is composed of both crystalline and amorphous solid materials.

- X-ray diffraction analysis of the "as-received" sample indicate the presence of two principal crystalline compounds; nitrated sodium aluminosilicate mineral $(Na_8(Al_6Si_6O_{24})(NO_3)_2 \cdot 4H_2O)$[vi, vii] and clarkeite $(Na[(UO_2)O(OH)](H_2O)$, which is a uranium mineral.

- The elemental analytical data for the "as-received" scale solid shows that the aluminum to silicon molar ratio of 1.08 is in good agreement with the theoretical aluminum to silicon molar ratio of 1.0 for cancrinite aluminosilicate mineral. This information thus confirms that the bulk of the scale material is cancrinite $(Na_8(Al_6Si_6O_{24})(NO_3)_2 \cdot 4H_2O)$, which has a theoretical aluminum to silicon molar ratio of 1.0.

- Information from aluminosilicate formation modeling and experimental data shows that the solubility product, K_{sp}, for aluminosilicate mineral is directly proportional to the cube root of the free-OH concentration in a solution matrix and inversely proportional to the ionic strength of the medium. This cube root concentration relationship between the solubility product of aluminosilicate mineral and free-OH seems to answer the plant question dealing with the observed increase in the frequency of mechanical cleaning of the GDL when the free-OH concentration in Tank 43H (2H Evaporator feed tank) drops to a value of 1.5 molar or less.

- Between August 2010 and February 2013, as shown in Figure 3, when the free-OH concentrations in the 2H Evaporator feed tank remained above 2 molar, the plant did not experience frequent mechanical cleaning of the GDL due to the accumulation of aluminosilicate scales. However, between February 2013 and December 2013, when the free-OH concentration dropped to ≤ 1.5 molar, there was an increase in the frequency of mechanical cleaning of the GDL due to excessive accumulation of aluminosilicate scales. As the free-OH concentration in the evaporator feed tank started creeping upwards above 1.5 molar in early part of 2014 the need for mechanical cleaning became less frequent. Therefore, there is a correlation between the changes in free-OH concentration in the evaporator feed tank, the aluminosilicate scale accumulation rate and the need or frequency for de-scaling of the GDL.

- Therefore, it is recommended that the free-OH concentration in Tank 43H be maintained at or above 2 molar to decrease mechanical cleaning frequency of the GDL due to excessive accumulation of sodium aluminosilicate scales.

5.0 Quality Assurance

Data are recorded in SRNL Electronic Notebook: L5575-00080 SRNL Electronic Notebook (Production); SRNL, Aiken, SC 29808 (2014) and various AD notebooks contain the analytical/experimental data.

6.0 Acknowledgements

I acknowledge the contributions of R. Sullivan, J. Fawbush and J. Mixon for preparing the samples in the SRNL shielded cells, Mark Jones, John Young, David Missimer and Dr. C. Colleman for providing analytical services.

7.0 References

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