

Calculation of the Aluminosilicate Half-Life Formation Time in the 2H Evaporator

RECORDS ADMINISTRATION



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by

F. F. Fondeur

Westinghouse Savannah River Company

Savannah River Site

Aiken, South Carolina 29808

W. R. Wilmarth

S. D. Fink

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F. F. Fondeur
W. R. Wilmarth
S. D. Fink

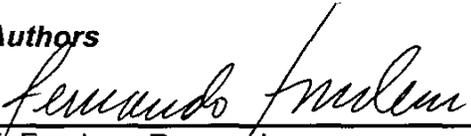
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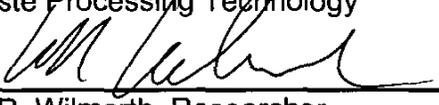


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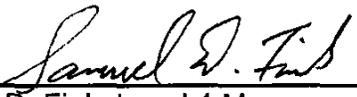

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Waste Processing Technology
Date 7-28-00


W. R. Wilmarth, Researcher
Waste Processing Technology
Date 7-31-00

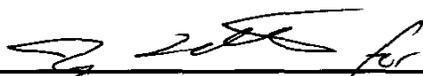
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CST Engineering Support
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Management


S. D. Fink, Level 4 Manager,
Waste Processing Technology
Date 7-29-00


Bill Van-Pelt, Level 4 Manager,
Waste Processing Technology
Date 7-31-00


B. L. Lewis
CST Engineering Support
Date 8-1-00

SUMMARY

The 2H Evaporator contains large quantities of aluminosilicate solids deposited on internal fixtures. The proposed cleaning operations will dissolve the solids in nitric acid. Operations will then neutralize the waste prior to transfer to a waste tank. Combining recent calculations of heat transfer for the 2H Evaporator cleaning operations and laboratory experiments for dissolution of solid samples from the pot, the authors estimated the re-formation rate for aluminosilicates during cooling. The results indicate a half-life formation of 17 hours when evaporator solution cools from 60 °C and 9 hours when cooled from 90 °C.

INTRODUCTION

The 242-16H High Level Waste Evaporator processes radioactive waste from the feed tank, concentrates the waste and discharges to the concentrate receipt tank. During this processing the waste concentrates by 30-40 vol %. However, during processing of Defense Waste Processing Facility Recycle stream, the concentration approaches 90 vol %. During processing DWPF recycle, the flow in the Gravity Drain Line decreased significantly, initially in July 1997. Video inspection indicated solid deposits present in the Gravity Drain Line.¹ Laboratory experiments of solids formed on the evaporator walls showed that compounds of the general formula, $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, form readily under the evaporator conditions.^{2,3} Recently, simulation experiments conducted at SRTC under conditions similar to the evaporator produced $\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solids.²

Prior to resuming normal operation of the evaporator, the solids must be removed. The proposed cleaning will use nitric acid and depleted uranium to dissolve the solids.⁴ Following dissolution, personnel will neutralize the acid by adding caustic, cool the pot contents, and transferring to a waste tank. This calculation estimates the rate at which aluminosilicates might form during the cooling.

One can determine the amount of aluminosilicates that form in the following fashion. First, reference data for the heats of reaction and heat capacity allow determination of the maximum temperature that results during neutralization of the acidic solution following the dissolution of solids. One may use recent laboratory data or literature information to derive a rate expression for the formation of aluminosilicates from caustic solution. Integration of the rate

¹ D. M. Grimm, R. L. Salizzoni, and T. A. Grzech, "Tank 38 Gravity Drain Line Back Flush Valve Action Plan," Rev. 1, August 1, 1997.

² W. R. Wilmarth, C. J. Coleman, A. R. Jurgensen, W. M. Smith, J. C. Hart, W. T. Boyce, D. Missmer, and C. M. Conley, "Characterization and Dissolution Studies of Samples from the 242-16H Evaporator," WSRC-TR-2000-00038, Rev. 0, January 31, 2000.

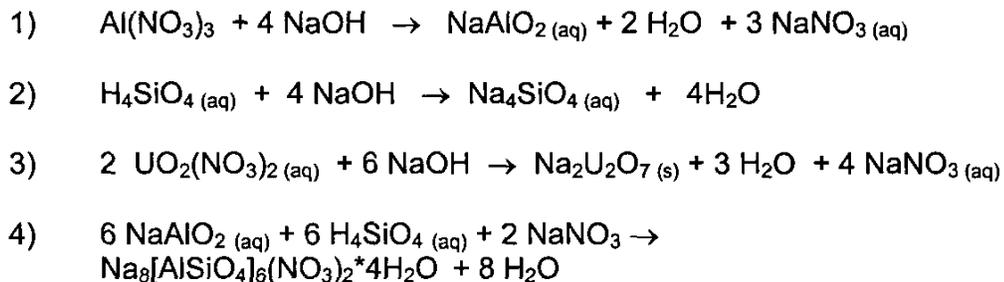
³ W. R. Wilmarth, C. J. Coleman, J. C. Hart, and W. T. Boyce, "Characterization of Samples from the 242-16H Evaporator Wall," WSRC-TR-2000-00089, March 20, 2000.

⁴ W. R. Wilmarth and S. W. Rosencrance, "Effect of Gadolinium and Depleted Uranium on the Nitric Acid Dissolution of Samples from the 242-16H Evaporator Pot," WSRC-TR-2000-00210, June 12, 2000.

expression over the period of cooling allows one to estimate the amount of solids that form.

TEMPERATURE RISE DURING NEUTRALIZATION

During the caustic addition, the calculation assumes no free nitrate exists with the nitrates bound to the aluminum and uranium. This condition gives the maximum heat generation during neutralization as illustrated in the reaction sequence written below.



The chemical species listed above do not represent an exhaustive list of all the possible species that may occur during neutralization. The listing also does not rigorously duplicate the composition determined in characterization of samples collected from the vessel. However, it provides the major plausible existing species during neutralization. With that in mind, the heats of reaction per mole of reactants for each reaction follow.^{5, 6}

- 1) $\Delta H = -10.76 \text{ kcal/mol}$
- 2) $\Delta H = -200 \text{ kcal/mol}^*$
- 3) $\Delta H = -18.77 \text{ kcal/mol}^*$
- 4) $\Delta H = 203.8 \text{ kcal/mol}$ (per mole of aluminate)

*These values differ from a previous document⁸ where data for aluminum nitrate, uranyl nitrate and silicic acid in the crystalline form instead of the aqueous form (these were not available at that time) were used.

⁵ F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," *Circular of the National Bureau of Standards* 500, February 1, 1952.

⁶ N. Komada et al, "Thermodynamic Properties of Sodalite at Temperatures from 15 K to 1000 K," *J. Chem. Thermodynamics*, Vol. 27, PP. 1119-1132, 1995.

Table 1 lists the values used in deriving the heat of reactions.

Table 1. Heat of formation of typical components in the evaporator.

Component	ΔH (kcal/mol)	Reference
$UO_2(NO_3)_2$	-342.6	7
$Na_2U_2O_7$	-763.5	7
$Al(NO_3)_3$	-273	5
H_4SiO_4	-349	5
$NaAlO_2$	-275.9	5
$Na_8[AlSiO_4]_6(NO_3)_2 \cdot 4H_2O$	-3212	6
Na_4SiO_4	-720	5

Additional heat (-3.3 kcal/mole)⁵ comes from adding the 32703 moles of caustic to the evaporator.⁸

The estimated reactant inventory after acid dissolution follows.

4019 moles of $UO_2(NO_3)_2$
 1457 moles of $Al(NO_3)_3$
 1457 moles of H_4SiO_4
 32703 moles of NaOH
 243 moles of $Na_8[AlSiO_4]_6(NO_3)_2 \cdot 4H_2O$ (s) (1/6 of the aluminum nitrate)
 12643.2 liters of total solution (1.25 specific gravity)⁸

The authors assume the heat evolution during neutralization results from hydration of the hydroxyls (during caustic addition) and the hydroxylation of the metallic cations (aluminum, silicon and uranium) by the hydrated hydroxyls. This will give a conservative upper bound for the temperature rise.

The total heat evolved equals the sum of the heat from each reaction (excluding the aluminosilicate formation reaction) or 4.9×10^5 kcal.

The total thermal inertia, or heat dampening, of the system depends on the mass and heat capacity of the water and steel⁹ as shown below.

$$(1.54 \times 10^7 \text{ g solution} \times 0.7 \text{ cal/(g } ^\circ\text{C)}) + (7.45 \times 10^6 \text{ g steel} \times 0.11 \text{ cal/(g } ^\circ\text{C)}) = 1.16 \times 10^7 \text{ cal/}^\circ\text{C}$$

An estimate of the temperature rise in this system during neutralization comes from the ratio of these two values:

⁷ J. Fuger and F. L. Oetting, "The Chemical Thermodynamics of Actinide Elements and Compounds, Part 2-The Actinide Aqueous Ions," International Atomic Energy Agency, Vienna, 1976.

⁸ C. S. Boley, M. C. Thompson, and W. R. Wilmarth, "Technical Basis for the 242-16H Evaporator Cleaning Flowsheet," WSRC-TR-2000-00211, July, 2000.

⁹ K. Kwon, "2H Evaporator Pot Liquid Heating With Warming Coil," HLW-STE-2000-00267, June 26, 2000.

$$4.9 \times 10^8 \text{ cal} \div 1.16 \times 10^7 \text{ cal/}^\circ\text{C} = 42 \text{ }^\circ\text{C}.$$

When one includes the aluminosilicate heat of reaction (i.e., an endothermic reaction), the total temperature rise becomes 38 °C.

Since a 50 wt % caustic solution is more dense than 1.5 M nitric acid solution (for example the caustic solution will sink to the bottom of the evaporator) it will not immediately hydrate. Under this condition one can ignore the heat of hydration (-3.3 kcal/mole) evolution when the caustic solution sees the water associated with the nitric acid. The net temperature rise is 33 °C ($3.82 \times 10^8 \text{ cal} / 1.16 \times 10^7 \text{ cal/}^\circ\text{C}$). Including aluminosilicate heat of formation the temperature rise then is 28.7 °C.

ALUMINOSILICATE FORMATION DURING NEUTRALIZATION

Barnes et al.^{10, 11} carefully studied the formation of sodium aluminosilicate in caustic solutions. Under isothermal, unseeded and sodalite/cancrinite seeded conditions, the aluminosilicate crystallization rate depended on the desilication rate to the second power. The study also determined an activation energy of $7.1 \pm 0.5 \text{ kcal/mol}$ and a pre-exponential factor of $1560 \pm 60 \text{ m}^2/\text{h}$ for sodalite crystallization.

One can derive similar kinetic parameters from the data obtained at SRTC in solutions that roughly approximate the contents of the evaporator during cleaning.¹² The authors assume the data satisfies a second-order degree of supersaturation approximation in the temperature range of interest.¹⁴ This assumption implies that one can assume a constant area available for growth and incorporate the area within the rate constant. In other words, one treats the reaction as a second order process.¹³

¹⁰ M. C. Barnes, J. A. Mensah and a. R. Gerson, "The Kinetics of Desilication of Synthetic Spent Bayer Liquor Seeded with Cancrinite and Cancrinite/Sodalite Mixed-Phase Crystals", J. of Crystal Growth, Vol. 200, PP. 251-264, 1999.

¹¹ M. C. Barnes, J. A. Mensah and A. R. Gerson, "The Kinetics of Desilication of Synthetic Spent Bayer Liquor and Sodalite Crystal Growth," International Journal of Colloids and Surfaces A, Vol. 147, PP 283-295, 1999.

¹² W. R. Wilmarth, D. D. Walker and S. D. Fink, "Sodium Aluminosilicate Formation in Tank 43H Simulants," WSRC-TR-97-00389, November 15, 1997.

¹³ J. A. Mensah, M. C. Barnes, R. Jones and A. R. Gerson, "The Mechanism and Kinetics of Sodium AluminoSilicate Scale Formation in Bayer Heat Exchangers," 1999 Engineering Foundation Conference on Scale Formation and Mitigation on Heat Exchanger Surface, Banff, Canada, July 1999.

Examination of the data provides the following kinetic parameters.

- One obtains an activation energy for formation of $\text{Na}_6[\text{AlSiO}_4]_6$ of 7.16 kcal/mol.
- The corresponding pre-exponential factor becomes 9259 L/(mol*h).¹²

These values agree reasonably well with literature data.¹⁴ The chosen pre-exponential factor incorporates the area of the sodalite precipitates obtained in ref. 11. The authors assume heat accumulates faster during neutralization than removed by the tube bundle resulting in a temperature rise of 42 °C (under adiabatic conditions).

The authors next assume that dissipation of heat generated by the neutralization occurs only through the tube bundle coil. The temperature would only decrease 4 °C (4.95×10^4 kcal/ 1.16×10^7 kcal/°C) due to aluminosilicate formation, a small change compared to the 42 °C temperature rise. The authors assume the temperature of the evaporator (which decreases with time) affects the aluminosilicate formation rate. In that case, equation 5 provides the temperature decrease in the evaporator. (A rigorous approach would solve the equations simultaneously. This approximation only introduces a minor error given the small heat of formation for the compound.)

$$5) (m^{\text{water}} C_p^{\text{water}} + m^{\text{steel}} C_p^{\text{steel}}) \frac{dT}{dt} = -UA(T - T_{\text{coil}})$$

$$6) T = T_{\text{coil}} + \Delta T e^{-\lambda t}$$

$$7) \lambda = \frac{UA}{m^{\text{water}} C_p^{\text{water}} + m^{\text{steel}} C_p^{\text{steel}}}$$

The symbol “ ΔT ” in equation 5 represents the temperature difference between the maximum temperature of the solution after neutralization and the coil temperature ($T_{\text{coil}} = 25$ °C). For the heat transfer rate (UA) term of the tube bundle coil, we use a value of 2.38×10^6 cal/h as recommended by Ki Kwon.⁹ Consequently the time constant for heat removal (λ) as given in equation 6 equals 0.2144 h^{-1} . The rate constant calculation includes this temperature which decreases with time. This makes the aluminosilicate formation rate a function of time as well.

One can determine the half-life for formation of aluminosilicate by integrating the rate expression as a function of time. One calculates the half-life as equal to the area under the rate versus time curve from zero time to 50% completion.

¹⁴ M. C. Barnes, J. Addi-Mensah and A. R. Gerson, “The Kinetics of Desilication of Synthetic Spent Bayer Liquor Seeded with Pure Sodalite, Pure Cancrinite and Their Dimorphic Phase Mixtures,” in “Light Metals 1999” by C. E. Eckert, The Mineral, Metals and Materials Society, pg. 121-129, 1999.

For second-order supersaturation dependency, the rate expression takes the following form.

$$8) \frac{dC}{C^2} = - \int_0^{t_{\frac{1}{2}}} k dt; \left(\frac{2}{C_0 + C_{final}} \right) = \text{Area under the curve} = \int_0^{t_{\frac{1}{2}}} k dt$$

After some manipulation,

$$\text{Area at half life is} = \frac{1}{C_0 + \frac{2}{\text{Total area under the curve}}}$$

In this case, the area must equal $(C_0 + 2/ \text{Total Area under the curve})^{-1}$ where C_0 equals the initial concentration of the limiting reagent, either aluminum or silicon in this application.

We calculated the area under the rate constant-time curve and Table 2 contains the results.

Table 2. The half-life (in hours) for aluminosilicate formation from cooling at different neutralization temperatures.

Temperature after neutralization	60 °C	70 °C	80 °C	90 °C	100 °C	110 °C
Second Order (1/C ²)	17.06	14.1	10.49	8.93	7.89	7.06

Table 2 also shows half-life values for other maximum temperatures after neutralization. The computed numbers clearly show a faster aluminosilicate formation with higher temperatures. This indicates the cleaning procedure should cool the evaporator contents as low as possible (nearly 30 °C) to prevent significant formation of solids during the post-neutralization step. If one can control the rate of caustic addition in such a way as to maintain isothermal conditions in the evaporator, then the following expression gives the half-life of formation for the aluminosilicate.

$$9) t_{\frac{1}{2}} = \frac{1}{kC_0}$$

In this expression, k is the rate constant and C_0 is the initial aluminate or silicate ion concentration. Table 3 provides the half-life times for different isothermal temperatures.

Table 3. Aluminosilicate formation under approximate isothermal conditions.

Temperature (°C)	t _{1/2} (hours)
30	139
35	115
40	95
45	79
50	66.6
60	47.6
70	35
80	26

Achieving approximate isothermal conditions requires the net rate of heat generated during neutralization must exactly match the heat withdrawal rate of the tube bundle.

The arithmetical translation of this condition follows.

$$10) \Delta H_{\text{neutralization}} F C_{\text{OH}} - \Delta H_{\text{alu min osilicate}} (k C_{\text{OH}}^2) V_{\text{evaporator}} = UA(T - T_{\text{coll}})$$

In this expression, F is the volumetric flow rate of the caustic solution and "V_{evaporator}" is the volume of liquid in the evaporator. The symbol "C_o" stands for caustic concentration (50 wt%) and the symbol "k" stands for the rate constant which depends on temperature. We again neglect the small heat loss due to aluminosilicate formation. Therefore, one can readily determine the required flow rate from the heat balance equation. The symbol ΔH_{neutralization} in equation 10 stands for the heat of neutralization per mole of sodium hydroxide (1.02 x 10³ cal/mol). Substituting in for the values in equation 10 and choosing isothermal temperatures of 30 through 60 °C, one determines that the caustic addition rate can not exceed 0.01 gallons per hour to keep the vessel contents isothermal. The early facility plans included an addition rate of 10 gallons per hour. Maintaining isothermal caustic addition appears impractical. Furthermore, even at these slow caustic additions, without mixing, researchers reported gel formation.¹³

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