

MODELING HANFORD-RPP TREATED LAW FEED EVAPORATION



SRNLTM
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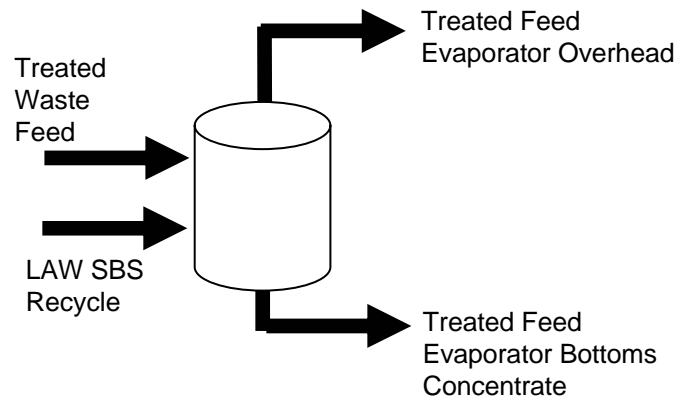
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Introduction

- **Goal - examine impact secondary-waste recycle streams on Treated Low Activity Waste (LAW) Evaporator**
 - Treated LAW Evaporator concentrates treated waste streams from Cs ion exchange blended with LAW melter offgas scrubbing recycle streams
- **Concern - Treated waste feed blends may form sodium-aluminum silicate precipitates**
- **Approach – Build OLI ESP model of Treated LAW Evaporator**
 - Examine range of waste feed compositions for Envelope A, B, and C waste feeds into evaporator
 - Use model to predict physical and chemical properties of evaporator concentrates
 - Additional runs used to compare chemical and physical property model predictions and experimental results for small scale radioactive tests (S-69) of the treated feed (AW 101) evaporation process

Basic Model Characteristics

- **Used OLI Environmental Simulation Program (OLI/ESP) version 6.6 with CARBONAT, HNO3DB, SILICA, URANIUM, and ZEOLITE private databases**
- **OLI ESP only performs steady state calculations**
- **Used OLI Flash Calculation Block:**



Model Description

- Waste feeds first diluted to target density of 1.22 g/ml \cong 5 Molar Na
- Waste feeds next filtered to approximate Cs removal from pre-treatment steps
- SBS to feed rate ratio controlled to match volume ratio from 0 and 2
- Waste feeds from pre-treatment and SBS stream evaporated at 50°C
- Evaporator bottoms stream then cooled at 1 atm to desired temperature of 15 to 66 °C
- Na Molarity of cooled evaporator bottoms (product) stream compared to targets of 6, 8, or 10.
 - If desired Na Molarity not reached, evaporator molar vapor fraction adjusted until desired set point achieved
- Waste feed flow rates based on LAW glass production rate of 30 metric tons per day (two melters) at a Na₂O loading of 19.5, 5.0, and 11.2 wt% for Envelope A, B, and C wastes, respectively
- LAW SBS flow rate not tied directly to treated feed evaporator process but to downstream LAW vitrification off gas treatment
- SBS flow rate treated as independent variable for physical property models

Model Description Continued

- OLI/ESP does not have ability to calculate heat capacity directly
 - Used OLI Scratch Pad tool in OLI/Express to generate enthalpy vs. temperature plot at each calculated steady-state composition for temperature range 15 – 66°C in one-degree increments

Factor Space Design

- Simulation design matrices derived from model factor space defined by model variables and ranges
- Design matrices consist of two types of design points
 - Fit points -used for model fits and consist of extreme (minimum and maximum) values of each of variable
 - Validation points - generated using the Orthogonal Latin Hypercube (OLH) technique, which produces points uniformly distributed over the linear factor space
- Validation points used to validate property model predictions against simulation results

Physical Property Models

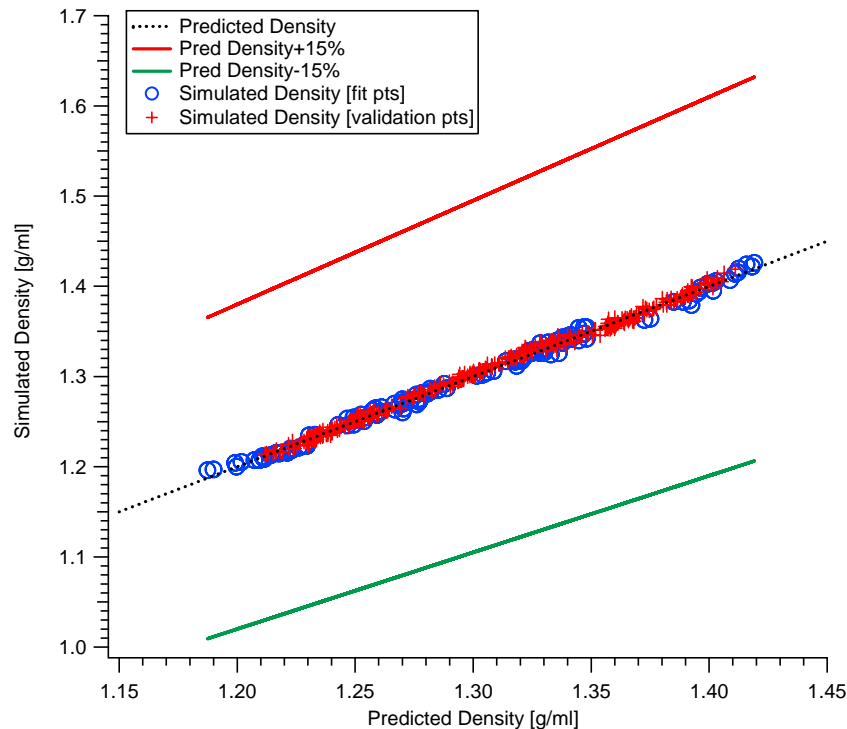
- Physical property models expressed in terms of two variable types:
 - mixture variables - define composition of waste feed streams
 - process variables - define “state” of process: evaporator bottoms temperature, Na molarity, and SBS to Feed volume ratio
- For all envelopes, temperature range used for bottoms concentrate was 15-66°C and LAW SBS to treated waste feed volume flow ratio was varied 0 to 2
- Bottoms concentrate Na molarity was varied between 6 and 10 molarity to match prior experimental work

Envelope Factor Space

- From prior modeling work - waste feeds expressed in terms of mass of non-water species
 - Amount of water evaporated will change depending on dilution of waste feed via pre-treatment and/or addition of LAW SBS recycle
 - Non-water species will always be present and thus have greatest impact on properties of the bottoms stream
- Waste feed compositions for each envelope analyzed and significant species chosen to define waste feed composition factor space
- Factor space subject to constraint that sum of molar charge of mixture variables must be equal to 4.73648

Example Predictive Model-Density

$$\text{density}_{\text{EnvA}} \left[\frac{\text{g}}{\text{ml}} \right] = 1.1117 \cdot x_{\text{AlO}_2} + 1.1110 \cdot x_{\text{CO}_3} + 1.075 \cdot x_{\text{F}} + 1.072 \cdot x_{\text{NO}_2} + 1.096 \cdot x_{\text{NO}_3} + \\ 0.9813 \cdot x_{\text{OH}} + 1.141 \cdot x_{\text{PO}_4} - 1.119\text{E-}3 \cdot \text{Temp} + 7.046\text{E-}3 \cdot \text{SBS} / \text{Feed} + \\ 0.03258 \cdot [\text{Na}] - 4.438\text{E-}5 \cdot (\text{SBS} / \text{Feed} - 1) \cdot (\text{Temp} - 40.5) - \\ 1.150\text{E-}4 \cdot ([\text{Na}] - 8) \cdot (\text{Temp} - 40.5)$$



Example Predictive Model-Conductivity

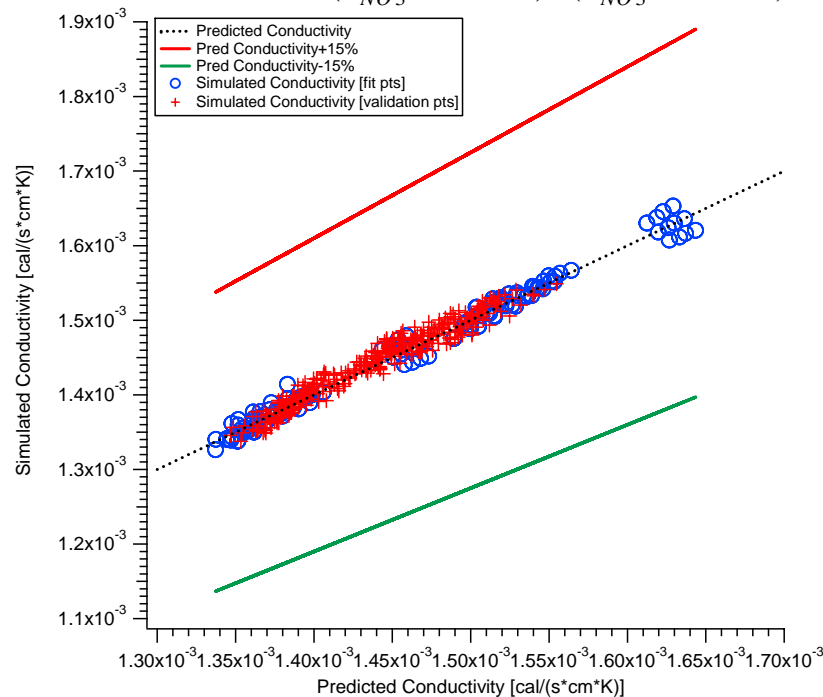
$$\text{conductivity}_{\text{EnvA}} \left[\frac{\text{cal}}{\text{s} \cdot \text{cm} \cdot \text{K}} \right] = 1.271\text{E-}3 \cdot x_{\text{AlO}_2} + 1.326\text{E-}3 \cdot x_{\text{CO}_3} + 1.392\text{E-}3 \cdot x_{\text{F}} + 1.304\text{E-}3 \cdot x_{\text{NO}_2} +$$

$$1.272\text{E-}3 \cdot x_{\text{NO}_3} + 1.863\text{E-}3 \cdot x_{\text{OH}} + 1.402\text{E-}3 \cdot x_{\text{PO}_4} + 3.087\text{E-}6 \cdot \text{Temp} -$$

$$5.159\text{E-}6 \cdot \text{SBS} / \text{Feed} - 3.590\text{E-}6 \cdot [\text{Na}] +$$

$$1.639\text{E-}6 \cdot (\text{Temp} - 40.5) \cdot (x_{\text{OH}} - 0.1422) +$$

$$4.555\text{E-}4 \cdot (x_{\text{NO}_3} - 0.4156) \cdot (x_{\text{NO}_3} - 0.4156)$$



Example Predictive Model-Heat Capacity

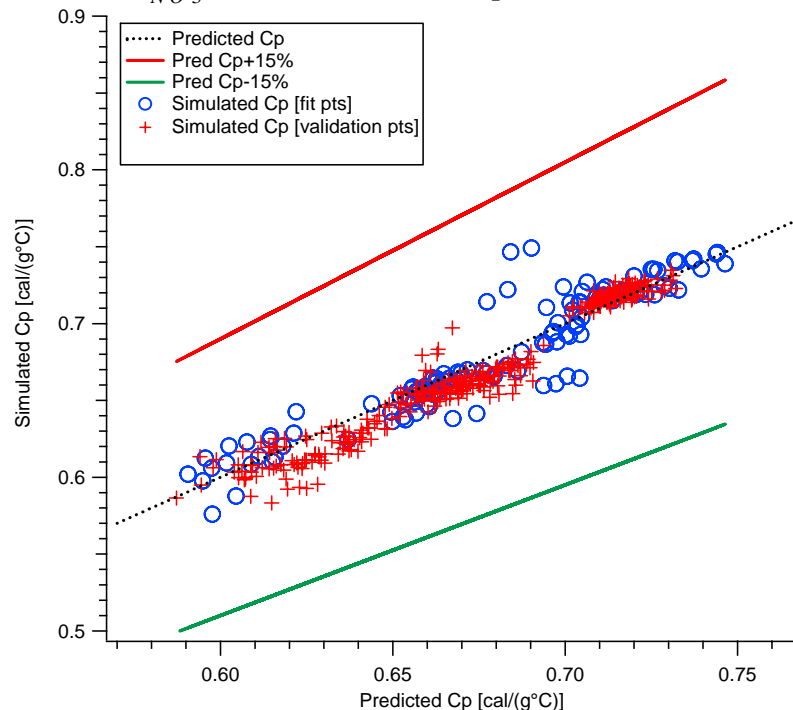
$$Cp_{EnvA} \left[\frac{\text{cal}}{\text{g} \cdot \text{oC}} \right] = 0.8824 * x_{AlO_2} + 0.7165 * x_{CO_3} + 0.9227 * x_F + 0.7351 * x_{NO_2} +$$

$$0.8640 * x_{NO_3} + 0.9586 * x_{OH} + 0.8870 * x_{PO_4} - 3.443E-3 * SBS / Feed -$$

$$2.020e-2 * [Na] - 0.05588 * (x_{CO_3} - 0.0510) * ([Na] - 8) +$$

$$-0.03794 * (x_{NO_2} - 0.2331) * ([Na] - 8) + 0.02999 * (x_{NO_3} - 0.4156) * ([Na] - 8) +$$

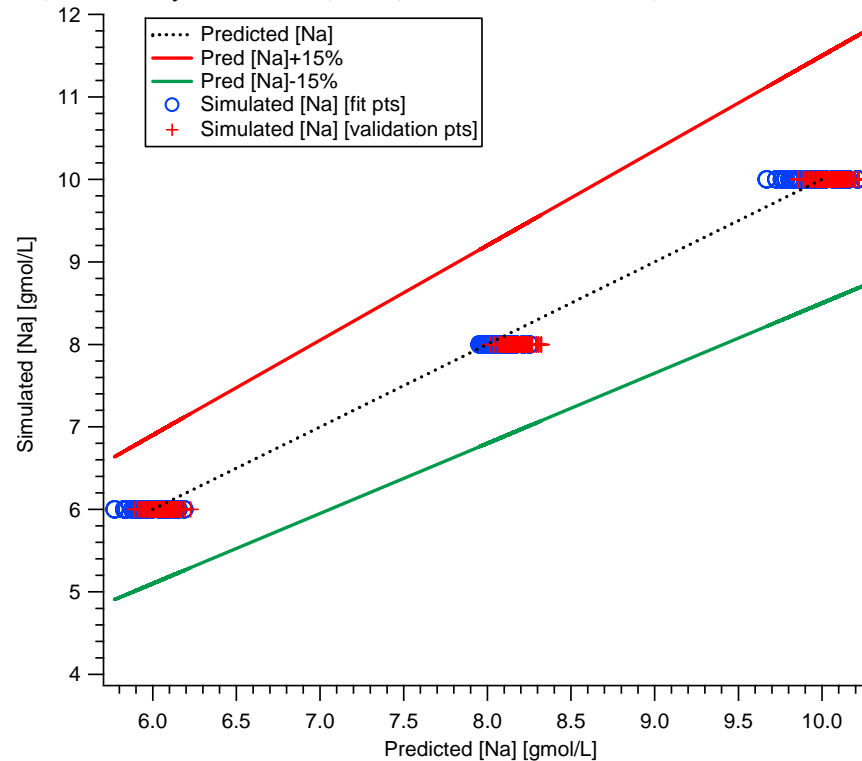
$$0.002053 * (x_{NO_3} - 0.4156) * (Temp - 40.5) + 9.093e-5 * ([Na] - 8) * (Temp - 40.5)$$



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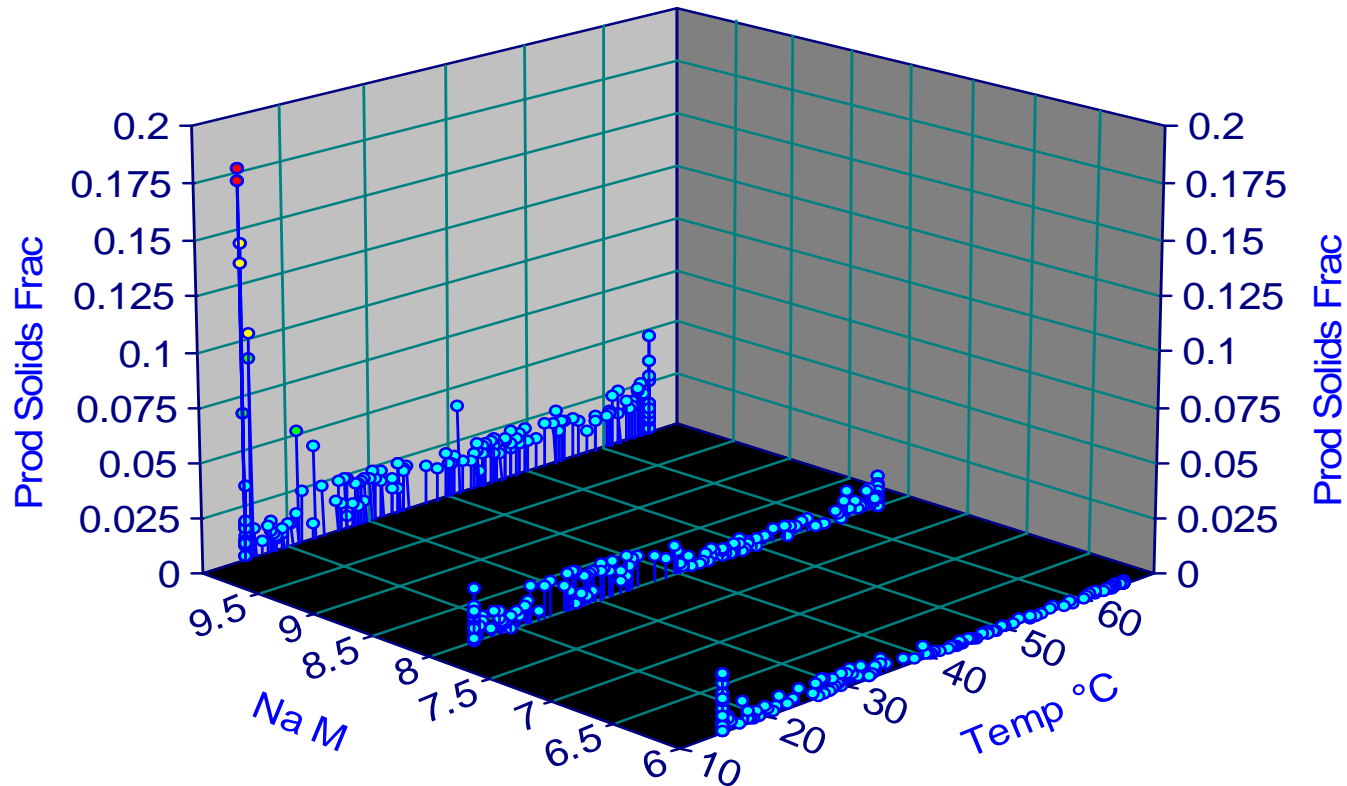
Example Predictive Model-Na Molarity

$$\begin{aligned}
 [\text{Na}]_{\text{EnvA}} \left[\frac{\text{gmol}}{\text{L}} \right] = & -34.36 \cdot x_{\text{AlO}_2} - 34.10 \cdot x_{\text{CO}_3} - 33.09 \cdot x_F - 32.95 \cdot x_{\text{NO}_2} - 33.72 \cdot x_{\text{NO}_3} - 30.24 \cdot x_{\text{OH}} - \\
 & 35.14 \cdot x_{\text{PO}_4} + 0.03444 \cdot \text{Temp} - 0.2139 \cdot \text{SBS} / \text{Feed} + 30.82 \cdot \text{Density} + \\
 & 0.1106 \cdot (\text{Density} - 1.300) \cdot (\text{Temp} - 40.5) - \\
 & 0.9262 \cdot (\text{Density} - 1.300) \cdot (\text{SBS} / \text{Feed} - 1)
 \end{aligned}$$



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Example Predictive Model-Solids Formation



Comparison of Simulation Results with Experimental Results

- Density predictions for Envelope A were within +/-6% of measured values for bottoms concentrate with a Na molarity between 2 and 10
- Viscosity predictions for Envelope A were within +/-20% for the 25°C measurements but only +/-50% for 15°C and 60°C tests
 - Lower and higher temperature extremes produced solids not accounted for by viscosity prediction
 - Model based only on supernate phase of bottoms concentrate
 - Model Bottoms concentrate ranged from 6 to 10 M Na while experimental test data covered 2 to 10 M Na
- Thermal conductivity predictions for Envelope A were within +/-25% of all measured values for bottoms concentrate
 - Discrepancy due to simulated conductivity based only on supernate and experimental values based on entire slurry

Comparison of Simulation Results with Experimental Results Continued

- Heat capacity predictions for Envelope A were within +/-15% of all but 4 measured values for bottoms concentrate with a Na Molarity between 2 and 8
- Sodium Molarity predictions for Envelope A were within +/-15% of measured values for bottoms concentrate with a Na Molarity between 6 and 10
 - For initial samples at 2 molar, predicted values within +/-50%
 - Discrepancy due to prediction being derived from data with Na M between 6 and 10 not 2
 - Difficult to derive predictive relationship relating waste feed composition (dry basis), SBS/Feed ratio, bottoms temperature, and bottoms density to bottoms Na molarity
- No accurate prediction equations for the solubility of the evaporator bottoms stream in terms of the total insoluble solids present could be derived in either linear or nonlinear forms for Envelopes A, B, or C.
 - Waste feed compositions, SBS to Waste Feed ratio, bottoms temperature, and Na molarity did not provide enough data to describe this phenomena

Conclusions

- Development of equations successful based on goal of developing physical property correlations for each waste envelope with an error no greater than $\pm 15\%$ between calculated and modeled physical properties
- Equation to predict solubility or amount of total solids in the Treated LAW evaporator bottoms concentrate could not be developed to satisfy this goal
- Predicted physical properties compared well with experimental results:
 - Predicted densities and heat capacities within $\pm 15\%$ of the measured values for Envelopes A, B, and C
 - Na molarity predictions for Envelope A and B also within $\pm 15\%$
 - Other predicted physical properties outside $\pm 15\%$ of the measured values
 - Mismatch with measured values due in part to being outside range of predictions, comparing a measured slurry property with a predicted supernate property, and exclusion of solids in the predictions
- More details in Extended Abstract on AIChE Conference CD
- Full paper at <http://sti.srs.gov/fulltext/tr2003269/tr2003269.pdf>