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Aspen/OLI Model of Waste Evaporation and Neutralization Process for MOX Waste Solidification Building

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Introduction

The Mixed Oxide Fuel Fabrication Facility (MOX or MFFF) at the Savannah River Site includes a Waste Solidification Building (WSB), which was built to house the process for converting aqueous wastes from the MFFF and the proposed Pit Disassembly and Conversion Facility (PDCF) into cements for long-term storage in either onsite repositories or at the Waste Isolation Pilot Plant (WIPP). The WSB process design required flowsheet modeling of the mixing tanks, batch evaporators, and neutralization tanks included in the WSB process.

A steady state computer simulation was developed, using Aspen Plus® to model the mixing tanks and evaporators and OLI® to model the chemistry. The simulation is configured so that both inputs and outputs appear on a Microsoft Excel® spreadsheet.

Aspen Model Details

Simulations for expected and maximum flow rates and acid and salt concentrations were requested for characteristic MOX feeds from the Pit Disassembly and Conversion Facility (PDCF) and from the Alternate Feed Stock (AFS). Each set of inputs includes specifications for three High Activity Waste (HAW) streams, a stream containing significant concentrations of Am-241 (AM241 in the simulation), an alkaline stream (ALKALINE), and an excess concentrated nitric acid stream (XSACID), and two Low Activity Waste (LAW) streams, a stream carrying the PDCF laboratory wastes (PDCFLAB), and a strip solution stream with a high concentration of primarily depleted uranium (STRIPU).

All input stream compositions are defined in terms of a list of chemical basis species, which comprise the OLI chemistry model. All input species are required to be neutral acids, salts, or hydroxides included in the OLI databooks. Each chemical element corresponds to one chemical basis species in the OLI chemistry model, with a few exceptions. The primary exception is sodium (Na), which is listed as both sodium nitrate ($NaNO_3$), for acidic waste streams, and sodium hydroxide (NaOH), for caustic waste streams.

The WSB process simulation includes adiabatic and constant temperature mixing tanks, evaporators, and condensers. In the simulation, all tanks, evaporators, and condensers operate at a default pressure of one atmosphere, and all constant temperature mixing tanks and condensers operate at a default ambient temperature of 25 °C.

To expedite the simulation calculation, the solids in the OLI chemistry model are limited to precipitates known to form from the chemical species present in the feed solutions. These species include silver (Ag), which precipitates as Ag_2O, and the actinide species thorium (Th), uranium (U), neptunium (Np), plutonium (Pu), and americium (Am). Of the elemental species whose precipitation is suppressed, the alkali metals (+1 valence) and the alkali earth metals (+2 valence) are likely to be soluble at the concentrations present in the WSB process solutions, and the remaining metals and anions are present only at low concentrations and

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therefore would not contribute significantly to the overall solids content if they were to precipitate.

The simulation model is a steady state, continuous flow model. All output flows are reported in units of kg/year, and all cooling duties are reported in units of kcal/hr. These units assume that operation of the WSB processes continues at a constant rate 24 h/day, seven days/week, year-round.

OLI Chemistry Model Development

Aspen Technologies, Inc., utilizes an aqueous chemistry model developed by OLI Systems, Inc., in the form of thermodynamic equilibrium databases (called databooks in the OLI terminology). On the recommendation of OLI, the WSB evaporation and neutralization process model uses the most recently developed OLI databook, MSEPUB (Mixed Solvent Electrolyte, Public). Notably, the MSEPUB databook bases ionic speciation on the H_3O^+ ion, so acid concentrations are reported in terms of H_3O^+ concentrations. Historically, the OLI databooks have been used successfully to model nitric acid-based waste solution evaporators for the Hanford River Protection Project.

The OLI models for the ionic speciation and solubility of the actinide elements are of particular concern for the WSB model. The MSEPUB databook contains models for the most probable ionic states of all actinides of interest, including thorium(VI) (Th(IV)), uranium(VI) (U(VI)), neptunium(IV) (Np(IV)), plutonium(IV) (Pu(IV)), and americium(III) (Am(III)). Models for the majority of Th(IV), Np(IV), and Am(III) species are based on data from the Lawrence Berkeley Laboratory thermodynamic database.[1] Data for Pu(IV) were obtained from work at Hanford[2-6] and in Russia.[7] MSEPUB includes models for monatomic U(VI) ions[8] and for polyatomic U(VI) ions.[9] These models are restricted to cationic species, which predominate in acidic solutions, and MSEPUB contains only one solid U species, uranyl hydroxide ($UO_2(OH)_2$).

The MSEPUB model for U is not adequate for basic solutions, for which the precipitate takes the form of a sodium polyuranate ($Na_6U_7O_{24}.nH_2O$, where n is 12 or 16),[10] or, when fully dehydrated, crystalline sodium diuranate ($Na_2U_2O_7$).[11] This stoichiometry implies that, when an acid solution is neutralized by caustic, each U atom is associated with an ionic or molecular species such as $UO_2(OH)_3^-$ with a charge of -1 rather than a species with a neutral charge, as would be the case for a $UO_2(OH)_2$ precipitate. The predominant U species in acidic solution is UO_2^{2+}. Thus, substitution of $UO_2(OH)_2$ for $Na_2U_2O_7$ as the precipitate in caustic solution underestimates by 50% the amount of caustic that would have to be added to precipitate soluble U.

To address this discrepancy in the MSEPUB databook, a so-called private, or user, databook, named DRNA, was created with three new species added, a singly charged anion, $UO_2(OH)_3^-$, and soluble and solid forms of a sodium diuranate hydrate precipitate, $Na_2U_2O_7.5H_2O$. (The number of waters of hydration was selected to most closely match the stoichiometry of the most highly hydrated aqueous precipitate, $Na_6U_7O_{24}.16H_2O$.) The anion species was added so that the calculated solubility would drop as the solution becomes more caustic. For the WSB model, a simple empirical approach is taken in which the anionic uranyl species is assigned the simplest possible formula, $UO_2(OH)_3^-$; this approach is consistent with the uranyl species already present in the MSEPUB databook.

The private OLI databook DRNA was generated using the OLI ESP (Environmental Simulation Package) software. The $UO_2(OH)_3^-$ anion was added using the COMPLEX function, with UO_2OH^+ and OH^- specified as the basis ions. Initially, two species, UO_2OHOH

(The default name assigned by COMPLEX automatically and fortuitously differentiated this neutral species from the $UO_2(OH)_2$ species already in the public MSEPUB databook.) and $UO_2(OH)_2OH^-$ were added. Values for the thermodynamic state variables for $UO_2(OH)_2OH^-$ (the free energy (ΔG_{ref}) and the enthalpy (ΔH_{ref})) were then copied and transferred to a new species, $UO_2(OH)_3^-$. The two species created by the COMPLEX function then were deleted.

The last step in the creation of the database entry for $UO_2(OH)_3^-$ was to specify the logarithm of the equilibrium constant for the ionic reaction

$$UO_2(OH)_3^- \Leftrightarrow UO_2(OH)_2 + OH^-$$

No equilibrium data was available for hydroxide-complexed uranyl ions, so the equilibrium constant was empirically adjusted based on the "best value" equilibrium constants for chemically similar uranyl fluoride solutions.[12] By trial and error extrapolation that compared equilibrium constants for uranium oxyfluorides with those for uranium hydroxides, the value of the equilibrium constant for $UO_2(OH)_3^-$ was set at -4.8.

For sodium diuranate, two databook entries were made, one for a soluble aqueous species and one for a solid precipitate. The diuranate hydrate $Na_2U_2O_7.5H_2O$ was converted to an equivalent monouranate species, $NaUH_5O_6$, to simplify the chemistry within the OLI databook. Both the aqueous species and the precipitate were assigned the same thermodynamic properties.

Initial estimates for the free energy, enthalpy, and entropy (S_{ref}) were based on weighted averages of the thermodynamic properties of sodium diuranate ($Na_2U_2O_7$)[13,14] and water.[15] The enthalpy was adjusted by trial and error to match the calorimetrically-measured heat of solution of 44.03±0.27 kcal/mole for the diuranate species dissolving in 6 M HNO_3 at 25 °C.[16,17] Subsequently, the free energy and entropy were scaled by multiplying by the ratio of the adjusted enthalpy to the original estimate of the enthalpy. The molar volume was calculated from a sodium diuranate particle density of 3.93 g/cm^3, measured by the falling drop method.[18]

The entry for sodium diuranate also requires values for the logarithms of the equilibrium constants for the dissolution of the precipitate and the dissociation of the neutral aqueous species, by the reactions:

$$NaUH_5O_6(ppt) \Leftrightarrow Na^+ + UO_2(OH)_3^- + H_2O$$

and $$NaUH_5O_6(aq) \Leftrightarrow Na^+ + UO_2(OH)_3^- + H_2O$$

The equilibrium constants were adjusted to fit sodium diuranate solubility data for caustic waste supernate solutions with various concentrations of added NaOH.[11] By trial and error, the logarithm of the equilibrium constant for the aqueous species was set at 0.7, and the logarithm of the equilibrium constant for the precipitate was set at -3.9. Figure 1 compares the model predictions with the measured solubilities.

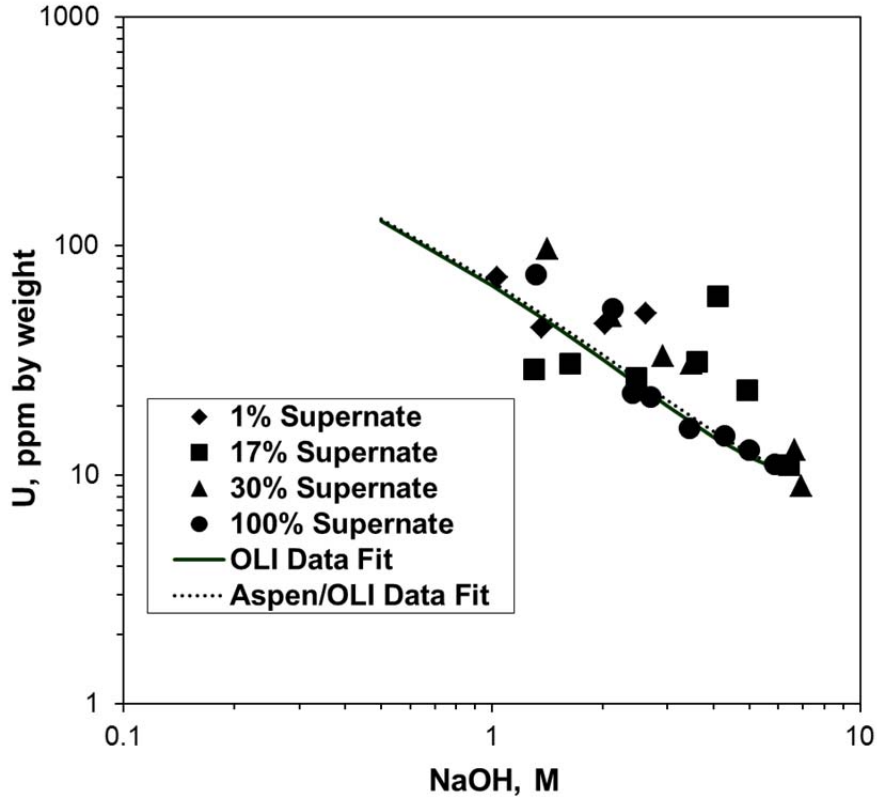

Figure 1. Comparison of OLI Model of Sodium Diuranate with Measurements of Hobbs and Karraker for Waste Tank Supernate/NaOH Mixtures

The sodium diuranate solubility correlation was tested by applying it to reproduce laboratory titrations of concentrated simulated transuranic waste solutions. Two titrations were reproduced, one starting at 30 °C and a second starting at 70 °C. At the start of the titrations, the solutions contained 0.75 L, with 290 g/L U, 0.34 M Al, 0.19 M Si, and 1.5 M HNO_3. Concentrated caustic (50 wt % NaOH) was added at a rate of 11.4 mL/min. Figure 2 compares calculated and measured pH values at 70 °C. According to the OLI calculations, the plateau in this figure at low pH is caused by neutralization of Al^{3+} and UO_2^{2+} and the precipitation of gibbsite ($Al(OH)_3$), boehmite (AlOOH), and uranyl hydroxide ($UO_2(OH)_2$). The gradual increase at intermediate pH's is due to the conversion of $UO_2(OH)_2$ to sodium uranates of varying stoichiometry, one of which, $Na_2(UO_2)_6(OH)_{14}.4H_2O$, was detected by x-ray diffraction analyses of the precipitates. The OLI model does not include any intermediate species between $UO_2(OH)_2$ and $Na_2U_2O_7.5H_2O$, so the model predicts an abrupt shift in the titration curve slightly into the caustic range. However, the OLI model accurately predicts the stoichiometry for the complete conversion to the diuranate species, as indicated by the agreement between the measured and predicted pH's where the pH levels out in the caustic region.

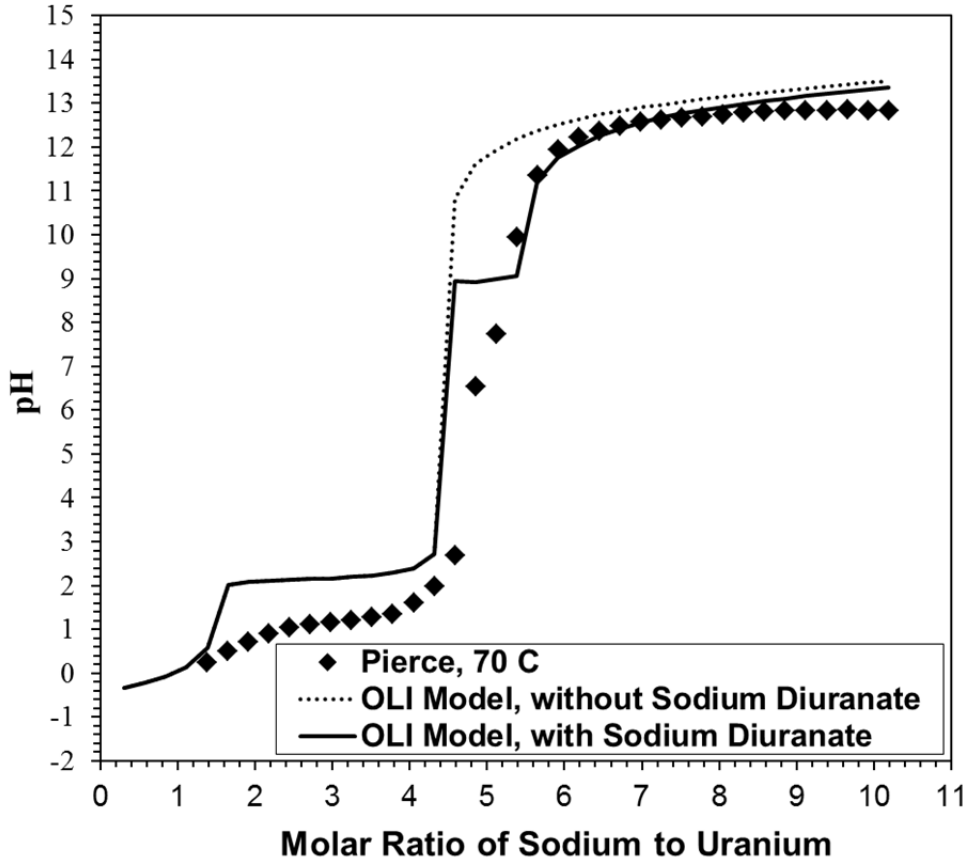

Figure 2. Comparison of OLI Uranium Solubility Predictions with Measurements of Pierce in a Solution with an Initial Temperature of 70 °C

A second private databank was added to correct density calculations for aqueous NaOH solutions. These density calculations are required for the HAW and LAW caustic neutralization streams. For a 50 wt % NaOH solution at 20 °C, the MSEPUB databook gives a density of 1.7176 kg/L, compared to a tabulated density of 1.5253 kg/L.[19] OLI Systems, Inc., was apprised of this error and provided a private databook called NAOH that contains corrected density calculations.

The solubility of NaOH must be modeled to ensure that the HAW and LAW caustic neutralization streams will not precipitate solids during their make-up and transfer to the neutralization tanks. At 25 °C, the solubility of NaOH in water is about 53 wt %. The solubility rapidly drops, however, as the caustic solution absorbed carbon dioxide (CO_2) from the air to form Na_2CO_3. Figure 3 depicts the variation of both measured and predicted Na_2CO_3 solubilities at 25 °C as a function of the NaOH concentration. It may be seen that Na_2CO_3 solubilities remain low at NaOH concentrations in excess of approximately 30 wt %, and then rise as the NaOH concentration decreases.

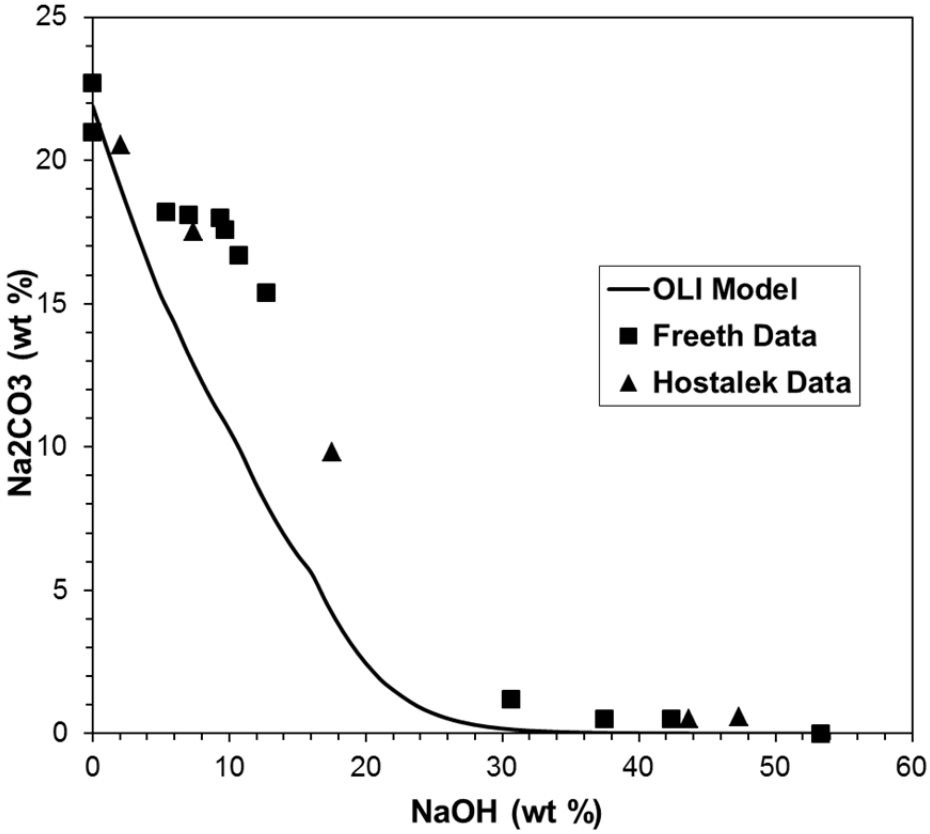

Figure 3. Comparison of OLI Carbonate Solubility Predictions with Measurements of Freeth[20] and Hostalek[21] at 25 °C

Simulation Methodology

In the Aspen Plus simulation package, chemical processing blocks are connected by flow streams. Using built-in vapor/liquid/solid equilibrium databases, Aspen iteratively calculates chemical and thermodynamic equilibria for each block in sequence. Figure 4 depicts the Aspen/OLI simulation of the WSB waste evaporation and neutralization process. Low activity waste (LAW) and high activity waste (HAW) are segregated into separate processing lines. The only connection between the HAW and the LAW processes is the transfer of the HAW evaporator condensate to the LAW feed tank. In the simulation, each processing line consists of a feed tank, an evaporator, and a neutralization tank. (The actual process design includes multiple tanks, pumps, and transfer lines which are not explicitly modeled by the simulation.) Each feed and neutralization tank is modeled as an adiabatic mixer to calculate the maximum possible temperature due to the heats of mixing and neutralization, followed by a heat exchanger to calculate the cooling duty required to bring the mixed stream back to ambient temperature. Each evaporator also includes a condenser, with the outlet stream set to ambient temperature and pressure.

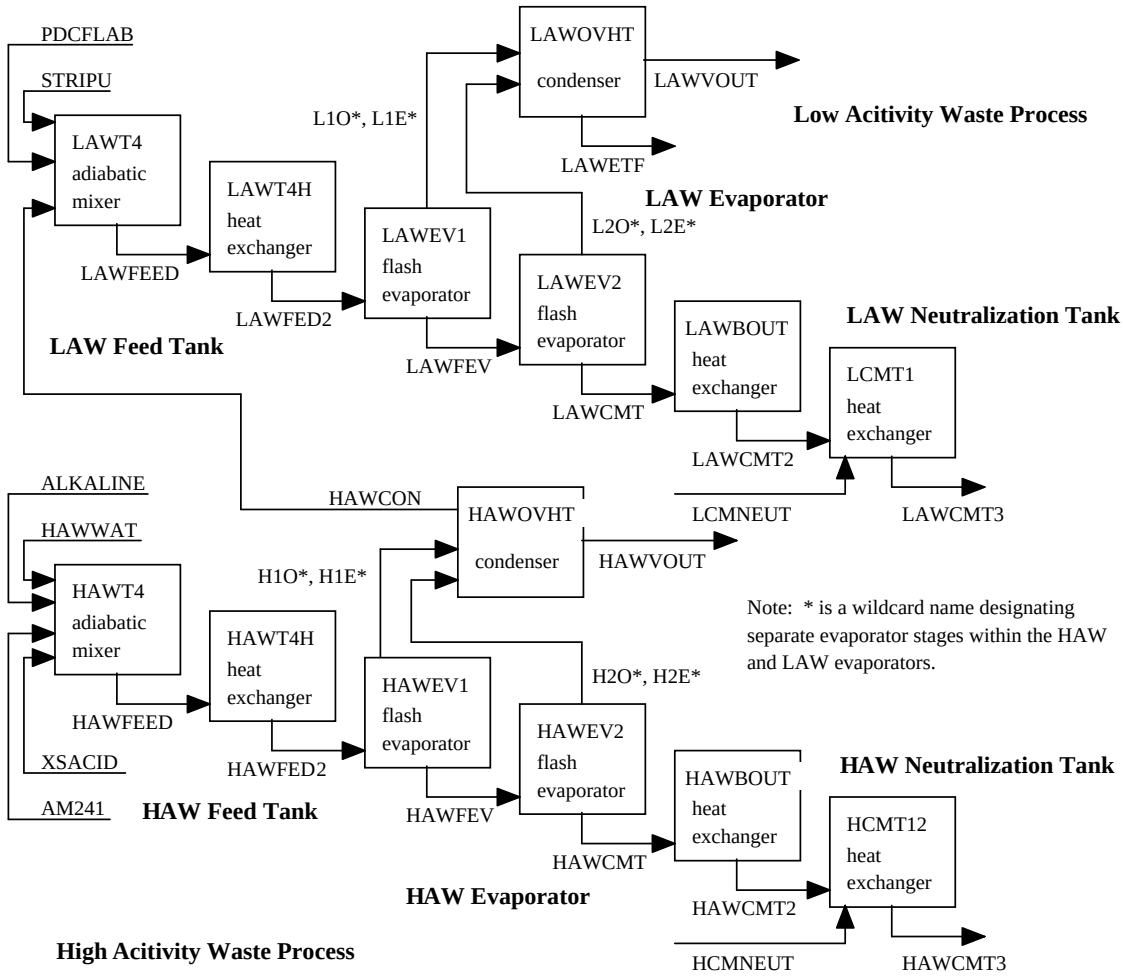

Figure 4. Schematic of Aspen/OLI Model of the Waste Solidification Building Evaporation and Neutralization Process

Feed-forward controls are used to set the flow rates of the HAW water dilution stream, the HAW and LAW caustic neutralization streams, and the fractions of flow that are evaporated in the HAW and LAW evaporators. The HAW water dilution stream is set to give an acid concentration of 1 M in the HAW evaporator feed stream, based on the combined total HNO_3 and NaOH concentrations in the other HAW feed streams. The HAW evaporator operation is set to concentrate the HAW evaporator bottoms acid concentration to 6 M, again based on the HNO_3 concentration. The LAW evaporator operation is set to concentrate the LAW evaporator bottoms to either 0.4 g/L Cl or 200 g/L U, whichever is reached first. The Cl limit is set to minimize corrosion in the process vessels and pipes, and the U limit is set to prevent U precipitation and solids handling problems in the LAW evaporator and piping downstream from the evaporator. The HAW and LAW caustic neutralization stream flow rates are set to add OH^- to the neutralization feed streams in concentrations that are approximately 10% in excess of those required to neutralize major acid and salt constituents, include HNO_3, H_2SO_4, and uranyl salts.

The target acid concentration in the HAW bottoms stream and the target Cl and U concentrations in the LAW evaporator bottoms stream are applied at the bottoms stream temperature. It is recommended that these targets be set lower than the desired concentrations in the cooled streams to account for solution density changes with temperature.

For the simulation calculations in this study, the target acid concentration in the HAW bottoms stream is set at 5.7 M HNO_3, and the target concentrations in the LAW bottoms stream are set at 0.37 g/L Cl and 185 g/L U. Caustic is added to the HAW and LAW neutralization tanks in amounts 10% in excess of those required to neutralize all principal anionic species. The composition of the caustic neutralization streams is set at 69 wt % H_2O, 30 wt % NaOH, and 1 wt % $NaHCO_3$, which is within the measured soluble range for caustic-carbonate solutions at 25 °C (see Figure 3).

Both the HAW and the LAW evaporators are modeled as 12-stage flash evaporators. Entrainment from each evaporator stage is modeled by splitting the bottoms stream from each stage so that a small fraction of the liquid, nominally set at 1 ppm by weight for each stage of both the HAW and LAW evaporators, is entrained with the vapor. The effective entrainment from all the stages of the HAW and LAW evaporators can be obtained by adding the entrainments from each of the stages; this gives an effective entrainment of about 10 ppm for each evaporator.

The staging of the evaporation process minimizes the fraction of vapor that is lost in any given stage and therefore minimizes the effect of partial vapor pressures on the vapor-liquid equilibria. In this way the modeling accounts for the effect of the process ventilation system in sweeping away vapors, without including any specific design component of the ventilation system. The only elements lacking in the model are the requirement for sensible cooling of the process ventilation gas, which should be small compared to cooling required for condensation and cooling of the vapor, and loss of volatile vapors due to evaporation in the condensers.

Discussion of Results

For the four simulation cases that were requested, tabulated comparisons of maximum temperatures, heat duties, and stream compositions at key locations in the WSB process follow. Table 2 compares heat duties (actually, cooling duties) for the evaporator feed tanks, evaporator condensers and bottoms tanks, and neutralization tanks. The highest cooling requirements are for the HAW and LAW condensers. The cooling requirements for the HAW and LAW evaporator bottoms streams are determined by the concentration maximums specified for these streams, and the cooling requirements for the HAW and LAW neutralization tanks are fixed by the salt concentrations in the HAW and LAW evaporator bottoms streams.

Table 2. Comparison of Heat Duties for Evaporator Feed Tanks, Evaporators, and Cementation Feed Tanks

	PDCF Feed Exp. Flow (kcal/h)	**PDCF Feed Max. Flow (kcal/h)**	**AFS Feed Exp. Flow (kcal/h)**	**AFS Feed Max. Flow (kcal/h)**
HAW Evaporator Feed Tank	108	114	42	45
LAW Evaporator Feed Tank	0	0	0	0
HAW Evaporator Condenser	17433	18420	7755	8468
LAW Evaporator Condenser	28772	30046	18519	19464
HAW Condenser Bottoms	342	361	150	164
LAW Condenser Bottoms	188	407	199	414
HAW Neutralization Tank	523	553	231	252
LAW Neutralization Tank	144	154	112	118

Results show that the LAW condensate stream carries most of the bulk effluent from the simulation process. The neutralized feeds to the HAW and LAW cementation processes both include precipitated solids. The HAW solids consist primarily of silver oxide (Ag_2O), and the LAW solids are comprised primarily of sodium diuranate ($Na_2U_2O_7.5H_2O$) and, for the AFS feed at the maximum flow rate and concentration, some uranyl hydroxide ($UO_2(OH)_2$).

Conclusion

An Aspen Plus/OLI model of the WSB process has been constructed and tested. The model includes separate mixing tanks, evaporators, and neutralization tanks for High Activity Waste (HAW) and Low Activity Waste (LAW) flow streams. The HAW and LAW evaporators separate the feeds into bottoms streams that are neutralized with concentrated caustic and overhead streams that are sent to condensers. The neutralized bottoms streams feed cementation processes, which are not modeled. The HAW condensate is mixed with the feed to the LAW evaporator, and the LAW condensate stream goes to an Effluent Treatment Facility (ETF), which is not part of the model. The Aspen Plus/OLI model has been tested successfully using WSB input data. Tabulated results are presented for four simulation cases, two each for feeds from the Pit Disassembly and Conversion Facility (PDCF) and from an Alternate Feed Stock (AFS).

As part of the modeling effort, a so-called private, or user, databook was created within OLI to model the neutralization and precipitation of uranium salts. The private databook extends the applicability of the existing OLI model into the basic pH range, where uranium forms sodium diuranate salts. The change in OLI was needed to accurately model the neutralization stoichiometry of uranium, which is present in high concentrations in the LAW evaporator bottoms.

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