Steady-State Simulation of Steam Reforming of INEEL Tank Farm Waste

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ABSTRACT

A steady-state model of the Sodium-Bearing Waste steam reforming process at the Idaho National Engineering and Environmental Laboratory has been performed using the commercial ASPEN Plus process simulator. The preliminary process configuration and its representation in ASPEN are described. An assessment of the capability of the model to mechanistically predict product stream compositions was made, and fidelity gaps and opportunities for model enhancement were identified, resulting in the following conclusions: 1) Appreciable benefit is derived from using an activity coefficient model for electrolyte solution thermodynamics rather than assuming ideality (unity assumed for all activity coefficients). The concentrations of fifteen per cent of the species present in the primary output stream were changed by more than 50%, relative to Electrolyte NRTL, when ideality was assumed; 2) The current baseline model provides a good start for estimating mass balances and performing integrated process optimization because it contains several key species, uses a mechanistic electrolyte thermodynamic model, and is based on a reasonable process configuration; and 3) Appreciable improvement to model fidelity can be realized by expanding the species list and the list of chemical and phase transformations. A path forward is proposed focusing on the use of an improved electrolyte thermodynamic property method, addition of chemical and phase transformations for key species currently absent from the model, and the combination of RGibbs and Flash blocks to simulate simultaneous phase and chemical equilibria in the off-gas treatment train.

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TABLES

ACRONYMS

DOE	U.S. Department of Energy
GAC	Granular Activated Carbon
HEME	High-Efficiency Mist Eliminator
HEPA	High-Efficiency Particulate Air (filter)
HLLWE	High Level Liquid Waste Evaporator
HLW	High Level Waste
INEEL	Idaho National Engineering & Environmental Laboratory
INTEC	Idaho Nuclear Technology & Engineering Center
LET&D	Liquid Effluent Treatment & Disposal
MACT	Maximum Achievable Control Technology
NRTL	Non-Random Two Liquid
PEWE	Process Equipment Waste Evaporator
PFD	Process Flow Diagram
SBW	Sodium Bearing Waste
SL	Solid-Liquid (equilibrium)
TRU	Transuranic
TTP	Technical Task Plan
VL	Vapor-Liquid (equilibrium)
WIPP	Waste Isolation Pilot Plant

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INTRODUCTION

This report documents one phase of work in a larger, multi-year Tanks Focus Area-funded Technical Task Plan (TTP) project at the INEEL to develop an effective simulation tool to support high level waste (HLW) management. The scope of this effort has been documented elsewhere (Nichols et al, 2001a). Its current focus is on enhancement of previous simulation capability to support conceptual and detailed design of a SBW treatment process. Simulation capabilities are needed to support the entire synthesis/optimization life cycle from process configuration design to continuous improvement during operations. Specific application areas that are expected to benefit from availability of a high-fidelity simulation tool include: 1) Low-level unit operations modeling support for Tank Farm management; 2) Support for design of process control; 3) Process/cost optimization; 4) Emissions estimating for regulatory purposes; 5) Planning for trial burns; 6) Estimation of emissions that are physically unmeasurable on a continuous basis; and 7) Characterization of process variability for safety analysis.

Background

Steam Reforming Process

Steam reforming has been used extensively in industry for many years in a wide variety of applications. Only recently, however, has steam reforming been seriously considered for treatment of radioactive wastes. In July of 1999, a commercial steam reforming process was commissioned in Erwin, Tennessee to treat high activity (up to 100 R/hr beta/gamma) ion exchange resins produced by the nuclear power industry (Studsvik, 2000).   Due to the success demonstrated at the Erwin facility, interest in steam reforming technology has increased in the DOE complex (Gentilucci, 2001). Steam reforming may be an economical method for treating liquid wastes currently stored at the INEEL and at other DOE sites.

In FY-2000, a brief steam reforming pilot-scale test was performed using a low activity INEEL waste simulant (Marshall & Pao, 2000).   Although not identical in composition to that expected for SBW, the acid, nitrate, and aluminum compositions in the simulant were comparable to anticipated SBW compositions for these constituents. Hence, results from this test may provide an indication of how steam reforming would perform if implemented for SBW treatment. Conclusions from this test were: 1) Steam reforming appears technically viable for effectively denitrating low-activity wastes containing primarily sodium, aluminum, and calcium nitrate salts, and 2) Gaseous effluent NOx can be controlled using reductants and metal-based additives.

More recently, steam reforming has been evaluated as a treatment option for low activity Hanford tank wastes. An initial pilot-scale test was performed in December 2001 (WGI, 2002).   Conclusions from this test were: 1) The steam reforming process shows potential for converting low activity waste into a ceramic waste form suitable for disposal at Hanford, 2) Steam reforming can potentially reduce the period required to process all waste from the Hanford waste tanks (relative to the baseline low activity waste vitrification process), 3) Steam reforming can remove and destroy nitrates and organics present within the waste, and 4) A steam reforming process could potentially treat wastes that vary considerably in chemical composition.

Steady State Simulation

The current steady-state simulation model of steam reforming of SBW using a commercial process simulation package includes the capability to perform rigorous thermodynamic equilibrium calculations. This capability was only available to a very limited extent in past efforts at process modeling to support high level waste program planning at the INEEL. At one point process mass balances used in planning and feasibility studies were performed with linked EXCEL spreadsheets which lacked a physical properties database. Later this process was automated using Visual Basic programs native to EXCEL. However, the modeling still lacked mechanistic predictive capability and was intended primarily to track feed components through process streams based on empirical or estimated partitioning data.

A major short-term objective of the TTP during FY-2002 has been to assemble a baseline steady state simulation of the integrated SBW steam reforming treatment process using the selected commercial software with its native thermodynamic database. This baseline simulation model has been used to provide "first estimate" type information in the following areas:

- Mass balance estimates focusing on stream sizes, composition and mass flow rates of waste product streams, and required input streams;

- Sizing information needed to assemble a preliminary equipment list and cost estimates;

- An integrated flowsheet with quantitative estimates of flow rates to stimulate and direct the thinking of process design personnel toward recommendations for improving subprocess efficiencies and robustness, reducing capital and operating costs, and minimizing the number and complexity of potentially problematic equipment.

Long Term Simulation Objectives

The current baseline model provides mostly empirically-based mass balance accounting which is needed at the current stage in the development of the SBW treatment flowsheet. Technically it represents no improvement (or only slight improvement) over the prior spreadsheet-based modeling approach. However, this baseline is a first and necessary step towards a longer-term objective to utilize (and possibly expand) the full thermodynamic predictive capability of the commercial process simulator. The steady-state baseline model utilizes a portion of that capability and provides a starting point to incrementally reduce the number of empirically-based submodels and correspondingly increase the number that are mechanistically-based.

Purpose of This Report

This report describes the current status of a steady-state model developed for steam reforming of INEEL SBW process using ASPEN Plus. The process configuration and its representation in ASPEN Plus are described. The principal objective in this effort is to supply the following types of information:

- Needed process mass and energy inputs
- Operational issues that may require attention in laying out the process
- Product stream compositions

For the current phase of the project the main focus has been on the third type of information and this report is similarly focused. An assessment of the capability of the model to predict product stream compositions is made, and fidelity gaps are identified. These gaps deal primarily with (a) the choice

of the species that must be represented in the model, (b) the specification of the chemistry (set of possible reactions) that the model must account for, and (c) the selection of appropriate physical properties models to be used. From the identified fidelity gaps, opportunities for model enhancement are identified and a path forward is proposed.

STEAM REFORMING PROCESS CONFIGURATION

A preliminary process configuration for steam reforming treatment of SBW was previously developed (Taylor et al., 2002) and is reproduced in Figure 1. After that configuration was developed and documented some minor changes were made before the configuration was modeled in ASPEN Plus. The revised configuration is shown in Figure 2. The changes to the original configuration and their rationale are described below.

- HEPA filter added upstream of thermal oxidizer. This operation is deemed necessary in order to (a) protect the oxidizer from particulate in the offgas that could present plugging and/or fouling problems (in the case of a catalytic unit), and (b) permit placement of the unit outside the hot cell. (The unit is quite large due to a large residence time requirement due to high water content of the input stream. In addition, it should be accessible for hands-on maintenance.)

- Condenser blowdown routed to caustic scrubber rather than to acid scrubber. This change reflects common operating practice to route contaminated fluids to the next higher area of contamination in order to minimize generation of contaminated streams. The condenser blowdown should be fairly clean and the caustic scrub liquor would likely be the next higher contaminated liquid in the offgas system.

- Condensate is not used for boiler feedwater. Condensate from the offgas will contain some radioactive contamination. The capital and operating expense associated with operating a contaminated boiler and feedwater system were deemed the overshadow the benefit of reduced water consumption through recycle of the condensate. Therefore consumptive use of uncontaminated water to supply steam to the reformer was used instead of condensate recycle.

- Liquid/solid separation for scrubber blowdown eliminated. The current assumption is that the steam reformed waste product will be packaged and disposed at WIPP. For this disposal option it was decided not to separate the high-activity reformer waste from the low-activity (and probably TRU-contaminated) salt waste. (This decision could be changed if higher disposal costs associated with higher volumes of remote-handled waste outweigh higher capital and operating costs associated with separate processing, packaging, and disposal of high- and low-activity waste products.) With the two product streams combined there is no need to separate solids from the scrubber blowdown, prior to drying.

- Evaporation pretreatments (PEWE, LET&D, HLLWE) of tank farm liquids eliminated. To simplify the baseline model none of the existing evaporative pretreatment processes at Idaho Nuclear Technology and Engineering Center (INTEC) for tank farm feeds were included in the model. Such pretreatments are already well characterized on the basis of longstanding experience.

- Mercury condensation and amalgamation eliminated. To simplify the process and eliminate one waste stream (amalgamated Hg) it was decided to route Hg-laden offgas from the salt drier into the main offgas stream and thus capture the mercury in the GAC beds. This may increase the volume of waste GAC that must be disposed. Testing would be required to assess this impact.

- Replacement of final offgas cooler (condenser) with dry quench. In the original process configuration the 1000°C exhaust from the thermal oxidizer was assumed to be cooled in a heat exchanger and any condensation was recycled as makeup to the caustic scrub. However, the need for high-temperature materials and a specially-designed heat exchanger to handle the high temperature for this configuration suggest that a dry quench may be a better choice. This will increase the volume of offgas as a result of the evaporative cooling but the increased robustness of the system was deemed to justify the change.

- Submerged Bed Scrubber eliminated. As discussed in Taylor & Nichols (2002), the target models for the spray quench and the submerged bed scrubber are conceptually the same, the only difference being particle collection efficiencies owing to different operating characteristics. In the current baseline model, however, only vapor/liquid phase and chemical equilibrium is represented for these unit operations, and they are therefore equivalent. Thus, for the ASPEN Plus model their combined effect is the same as either alone, so the two were lumped into a single FLASH2 computational block.

For a more complete description of the unit operations represented in Figures 1 and 2 the reader is referred to the discussion in Taylor & Nichols (2002).

PROCESS REPRESENTATION IN ASPEN PLUS

ASPEN Plus was selected as the commercial process simulator of choice because of its apparent wide array of modeling capabilities (Nichols et al., 2001b). The baseline model constructed in ASPEN Plus has underlying assumptions which are described in detail in Wood (2002) and Barnes et al (2002). A brief review of pertinent details and assumptions used in constructing the model is presented below:

- The reactions that take place in the reformer are limited by the specie set, and a few have presumed extents. Thus, the portion of the model that represents the steam reformer is semi-mechanistic.

- Steam reformer operates at 600°C and 12 psia.

- Steam reformer offgas from the sintered metal product filter is quenched to 94°C.

- Caustic scrub makeup maintains the scrub solution at a pH of 8.0.

- Blowdown of scrubbing liquors is required to limit buildup of dissolved and undissolved solids. As noted previously, the design philosophy for the wet offgas cleaning train was to route recycled liquid from each unit operation to the operation having the next higher level of contamination. In this manner, makeup is minimized as is the production of waste liquid that must be treated and disposed.

- A temperature of 1000°C will be required in the thermal oxidizer to reduce residual H_2, CO and hydrocarbons below the MACT limits. (Lower temperatures are undesirable because complete oxidation may not be achieved while higher temperatures may cause undesirable thermal NO_x formation.)

- Thermal oxidizer air rate adjusted to achieve 2 mol% O_2 in effluent gas.

- Offgas from the thermal oxidizer is quenched to 105°C.

- To simplify the model minor species were grouped together based on valence. Mass balance results provided by the model were transferred to a spreadsheet and the grouped species were separated back into individual components. The list of minor species treated in this way is provided in Barnes et al (2002).

- The following additives are mixed with SBW to provide the stream reformer feed:

  - One mole of sucrose ($C_{12}H_{22}O_{11}$) for every 5 moles of HNO_3 in the waste.
  - Si and Al in amounts to stoichiometrically convert all Na in SBW liquid to aluminum ortho-silicate ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$).
  - Bed material sufficient to comprise 4 wt% of the final product (4% of final product assumed to be generated from ellutriated bed material).
  - NOx catalyst at 21.6% of the bed addition rate (weight basis).
  - 384 kg/hr of steam for fluidization.
  - Carbon at a rate sufficient to maintain 600°C temperature in the reformer (based on heat of combustion), based on assumption of 4 wt% carbon carryover to the primary reformer product.
  - Oxygen corresponding to an assumed reducing environment in the reformer (defined as a reformer outlet H_2 concentration of 1 mol%).

- 0.5% of the reformer feed slurry carries over into the offgas treatment system.

- Composition of the reformer offgas is adjusted via specified chemical reactions with prescribed extents to achieve the following mol% values:

  - [CO] = 2%
  - [HCl = 0.73% of $[Cl]_{total}$
  - [HF] =19.5% of $[F]_{total}$

- Ten wt% of the reformer product is carried into the quench tower.

- Offgas scrubbing system parameters:

  - Quench is adiabatic
  - Quench liquid mass flow rate is 2.6 times gas flow rate
  - Quench blowdown rate is 0.05 x total offgas flow rate from steam reformer
  - Scrubber is adiabatic
  - Scrubber liquid mass flow rate is 7.5 times gas flow rate
  - Scrubber blowdown rate is about 376 kg/hr (~4% of flow out scrub tank)
  - pH of scrub makeup is equivalent to that of 0.1 M NaOH solution
  - Condenser is adiabatic
  - HEME is adiabatic
  - HEME wash flowrate is 0.03 x total offgas flow rate from steam reformer

- Air inflow to offgas due to vacuum flow control is 0.1 x offgas mass flow from final HEPA filter.

The process configuration in Figure 2 was represented in ASPEN Plus with the PFD shown in Figure 3. As is customary in the use of a generic process simulation program like ASPEN Plus, multiple computational "blocks" may be required to simulate each unit operation in the process. The block/unit operation correspondence is mapped in Table 1. Target modeling approaches for the process unit operations were previously identified (Taylor, et al, 2002).

MODEL ASSESSMENT

The steam reforming process simulation model is expected to provide the following kinds of information:

- Product stream compositions--Based on the input stream compositions and flowrates, the corresponding product stream characteristics are calculated based on the unit operation models and physical properties data and methods available to the simulation. The output stream characteristics can thus be compared with requirements, to the extent that the unit operation models accurately represent the underlying chemical and physical properties.

- Required feed and energy inputs--The model provides estimates of the compositions and flow rates of product streams, based on the compositions and feeds of the input streams. By adjusting the input streams the product streams can be tailored toward meeting requirements. In this way the simulation engineer can derive information about required feed inputs. The model also provides directly the required heat, work, and cooling inputs to the unit operations, according to the modeling assumptions (e.g., pump efficiencies, heat exchanger effectiveness, etc.).

- Operational feasibility--In addition to compositions and flowrates of product streams, similar information is provided by the model for intermediate process streams. The compositional information can be used to assess potential operational problems (e.g., corrosion, plugging). Also, assumed unit operation operating characteristics can be compared with vendor specifications of performance that can be achieved and sustained. Feasibility of providing the required feed and energy flows to/from the process can be assessed relative to program constraints (economic, infrastructure, material handling, etc.).

Current Focus

For the current phase of the SBW project, primary interest is in estimating product stream flow rates and compositions for various process configurations. Also of interest are the required feed inputs. Process energy inputs and operational feasibility are of secondary concern. The current steady-state simulation reflects these priorities, and higher-fidelity physical properties methods which require more computational effort are only used in key unit operations where streams are either combined or separated (i.e., where phase separation and/or chemical reaction of process stream components occur) and which strongly influence the characteristics of the final process streams. An offgas scrubber is considered such a key operation because it mixes the offgas stream with scrubbing solution and separates and speciates various components. A heater or cooler, on the other hand, merely changes the temperature of the stream, and a high-fidelity physical property method is not required and can be forgone in order to increase the speed of computation since energy flows are not a concern at this point.

Determinants of Simulation Accuracy

The simulation is confined within the structure of the ASPEN Plus system. This means that mathematical models have been pre-defined for most unit operations, and they generally assume thermodynamic equilibrium is achieved. Thus, finite rate processes (e.g., heat and mass transport) and physical processes (e.g., filtration and cyclonic separation) are not mechanistically represented. Consequently, the ASPEN Plus simulation represents predicted process performance based only on attainment of thermodynamic limits in partitioning and speciating the components of the input streams for each unit operation.

There are two standards by which the fidelity of model predictions might be judged given this simulation environment: (1) They could be compared with measured parameters from tests on a real process, or (2) They could be compared with "true" thermodynamic limits obtained from theoretical calculations based on exact thermodynamic relationships and reliable thermodynamic data. "Reliable thermodynamic data" are precise measurements of thermodynamic variables obtained from carefully controlled and equilibrated experiments. Standard (1) is the one by which the utility of the model will ultimately be determined since it addresses the overall fidelity of the model. However, as noted above, ASPEN does not attempt to account for inefficiencies due to finite rate processes limited by factors other than thermodynamic considerations. Poor comparisons using standard (1) could result from its disregard for these inefficiencies. However, they could also result from poor representations of the thermodynamics of the system. Our focus at this stage is on assessing the latter source of error in ASPEN's predictions.

Given this focus, there are four principal elements of the model that determine its thermodynamic fidelity - the species set, reaction set, physical properties methods, and calculational sequence.

Species Set

Chemical partitioning of the elemental components entering a unit operation will proceed in such a way that the total Gibbs free energy of the effluent stream(s) is minimized (assuming each unit operation is at a fixed pressure and temperature). That is, in the real process the elemental building blocks spontaneously arrange themselves (over time) into whatever array of molecular, ionic, gaseous, liquid, and solid forms minimizes the free energy. The representation of this natural process in ASPEN Plus relies on a correct identification (by the user) of the complete set of chemical species that will be present after the natural equilibration process. ASPEN then calculates the *quantities* of each species that will (a) conserve the total molar quantities of each element present in the input streams, and (b) minimize the total free energy of the output streams. The result of the ASPEN calculation depends on the user-specified set of chemical species. Thus, different species sets result in different predicted compositions and flow rates of the output streams from the unit operations, and thus directly impacts the product stream compositions, which is the current focus in using the model (per above comments).

Reaction Set

As suggested in the foregoing paragraph, nature "arranges" the element species into different chemical and phasic forms so as to minimize free energy. In ASPEN Plus this "arranging" process is performed computationally in one of two ways: (a) According to an explicit set of reaction equations which are, again, specified by the user, or (b) By directly partitioning all elemental species into a set of user-specified products so as to minimize free energy. Method (a) must be used whenever electrolytes are present. When electrolytes are not present method (b) may be used, provided each specie which may be present in multiple phases is explicitly represented in the species list with a different entry for each phase.

When method (a) is used, the free energy minimization is performed using equilibrium constants to describe each reaction. The final equilibrium composition will contain errors if the reaction set is incomplete, or if the equilibrium constants are inaccurate. By the same token, method (b) may produce inaccurate predictions if the species list does not include all possible products that can be formed from the elemental constituents of the process streams.

Physical Properties Method(s)

Physical properties methods are mathematical models used to relate thermodynamic variables. Examples include equations of state (which provide quantitative relationships between pressure, specific volume, and temperature), activity coefficient models (which provide correction factors to

account for non-idealities in mixtures), and transport property methods (which provide estimates of transport properties such as viscosity, thermal conductivity, etc.). The latter methods are not integral to ASPEN's thermodynamic calculations and are not considered further. Equations of state are currently used exclusively for the gas phase only and are deemed accurate since pressures in the system are generally around 1 atm (or lower). Thus, the focus of this discussion is on activity coefficient models.

In an ideal solution the activity coefficients of all species are 1.0, indicating zero departure from ideality. It is not uncommon in solutions of moderate ionic strength to measure activity coefficients which differ from 1.0 by one or more orders of magnitude (both higher and lower). Since the activity coefficients act as correction factors to species concentrations, this suggests that improper accounting for solution non-ideality can result in order-of-magnitude errors in predicted concentrations and phase partitioning of chemical species.

Calculational Sequencing

The architecture of the ASPEN Plus simulation is set up to do either gas phase equilibrium chemistry or aqueous phase electrolyte chemistry, but not both in a given computational block. If conditions in a block are conducive to transfer of reactive species between liquid and gas phases, then it is likely that the equilibrium composition of each phase will shift as a result of intra-phase chemistry. If the block is set up to do aqueous phase electrolyte chemistry then the gas will not be re-equilibrated until it reaches a block which performs gas phase equilibrium calculations (e.g., the 'RGIBBS' does gas phase chemical equilibration through free energy minimization). This may be acceptable, provided a proper phase and chemical equilibration is performed before the stream is again partitioned into two or more separate streams. If such is not the case, the stream components may not be correctly partitioned between the exit streams and thus the final product stream compositions and flow rates will be inaccurate.

Baseline Model

Species and Chemistry

The list of species included in the baseline model is presented in Table 2, and the electrolyte reaction set is shown in Table 3. Table 4 provides information about species and physical/chemical processes expected in steam reforming process streams, based on the information in Nichols & Taylor (2002, App. A), Barnes (2001), Patterson (1999), and Christian (2001). Column 1 of Table 4 lists the chemical species that could be present in one or more process streams. The entries in column 3 indicate the chemical transformations that are expected for each species, as follows:

- 'E-aq' indicates partial dissociation of an ionic substance in an aqueous solution (governed in the ASPEN Plus simulation by a finite equilibrium constant)
- 'E-gas' indicates chemical equilibrium of a molecular specie in a gas mixture (governed in the ASPEN Plus simulation by an overall minimization of Gibbs free energy in the gas phase)
- 'E-het' indicates chemical equilibrium between gas and pure solid in a unit operation where both phases are present

  Column 5 entries indicate the types of phase transformations expected, as follows:

- 'SL' indicates a dissolution of a pure solid (or other non-aqueous pure phase) into component fragments (governed in ASPEN Plus by a solubility product)

- 'VL' indicates equilibration between gaseous and aqueous forms of a specie (governed by equality of the specie fugacities in the two phases).

Finally, column 7 gives the reason that the behavior of the corresponding specie is considered important.

Physical Property Methods

The two physical property methods used are the IDEAL and the Electrolyte Non-Random Two-Liquid (ENRTL) model (Chen et al., 1982). When ENTRL is used it predicts activity coefficients for the liquid phase, and vapor phase fugacities are modeled using the Redlich-Kwong equation of state (EOS) (Aspen Technology, 2001). Some of the gaseous species are represented by Henry's law. When the IDEAL property method is selected the ideal gas law is used for the gas phase and the liquid phase solutions are assumed to be ideal (both Raoult's and Henry's laws are valid).

Table 5 shows the ASPEN Plus computational blocks and the corresponding thermodynamic property methods used in the baseline simulation. Only about 1/3 of the components use the ENRTL model. On the surface this suggests that non-ideality is poorly accounted. However, as suggested by the discussion under "Calculational Sequencing," accurate phase and chemical equilibrium calculations are only critical (for the purpose of the present steady state simulation) in blocks where process streams are split into two or more outlet streams *and* where phase and chemical equilibrium dictates the manner in which stream components are partitioned. Examination of Figure 3 indicates that the key species-partitioning unit operations for which the simulation is *expected* to provide mechanistic predictions [as discussed in Taylor & Nichols (2002)] are the QUENCH, SCRUBBER, and HEME. According to Table 5, the ENRTL method is used in all these blocks (as well as some others). Thus, the fidelity of the model to a large degree will be determined by the extent that ENRTL provides accurate accounting of non-ideality.
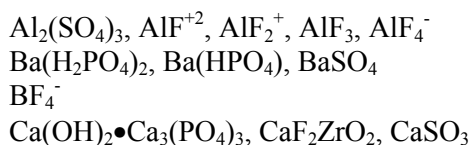
Calculational Sequencing

According to the brief description above, calculational sequencing should only be consequential in blocks representing unit operations where inlet streams are chemically or phasically partitioned among two or more outlet streams. In the baseline configuration of Figure 3 this occurs in the QUENCH, SCRUBBER, and HEME blocks. Ideally, to improve the fidelity of the downstream partitioning, each of these three FLASH2 blocks should be used in combination with a corresponding RGIBBS block in order to approximate simultaneous chemical and phase equilibria.

Analysis of Fidelity Gaps in Baseline Model

Species and Chemistry

The fidelity of the baseline model with respect to its species and chemistry lists was assessed by comparing entries from Table 2 and Table 3 with those in Table 4. A check ($\sqrt{}$) in column 2 of Table 4 indicates the corresponding specie is included in the model. Similarly, a check in columns 4 or 6 indicates the corresponding chemical or phase transformation is represented in the model. Perusal of the table shows that the following species (and their corresponding chemical and phase transformations) are missing in the model:

$Al_2(SO_4)_3$, AlF^{+2}, AlF_2^{+}, AlF_3, AlF_4^{-}
$Ba(H_2PO_4)_2$, $Ba(HPO_4)$, $BaSO_4$
BF_4^{-}
$Ca(OH)_2 \bullet Ca_3(PO_4)_3$, CaF_2ZrO_2, $CaSO_3$

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Cl_2
FeF^{+2}, FeF_2^+, FeF_3, $FePO_4$
H_3BO_3, $H_3BO_3F^-$, $H_2BO_2F_2^-$, H_2BOF_3, HBF_4, $HBOF_3^-$
$HgCl_3^-$, $HgCl_4^{-2}$, $HgCl^+$, $HgCl$
K_2AlCl_9, $K_3H_6Al_5(PO_4)_8 \bullet 18H_2O$
SO_3
ZrF_3^+, ZrF_2^{+2}, ZrF_3^+, ZrF_4, ZrF_5^-, ZrF_6^{-2}

The table also shows that the following key species are present in the model but that complete representation of desired chemical and phase transformations is deficient:

$Al(NO_3)_3$	missing E-het[a]
Al_2O_3	missing SL
$AlPO_4$	missing SL
CaO	missing SL
Fe_2O_3	missing SL
Hg	missing E-aq, VL, SL[b]
Na_2O	missing SL
SiO_2	missing SL

Gas phase chemical equilibration is not present in all pertinent computational blocks, and this may affect the partitioning of species which are reactive in the gas phase and are also involved with significant phase partitioning, such as NO_2 and $HgCl_2$. This condition of incomplete accounting for chemical equilibria in the gas phase is indicated by an asterick in the fourth column of Table 4.

It is noted that the baseline model species list excludes a number of minor species known to be present in the SBW feed in the interest of reducing model complexity and computer run time requirements. In order to account for the aggregate contribution of these species to the mass balance they were lumped together on the basis of valence into "pseudo" components whose chemical and physical behaviors mimic those of major species (e.g., $NaNO_3$ for +1 cations, $Ca(NO_3)_2$ for +2 cations, $Al(NO_3)_3$ for +3 cations, and HCl for -1 anions). Then the ASPEN Plus output streams were "post processed" and the pseudo species separated back into individual components. This approach is reasonable provided none of the minor components so-represented are key species whose fate must be accurately predicted (for regulatory purposes, for example).

Physical Property Methods

As previously noted, the baseline model uses the ENRTL physical property method in key computational blocks and thus nominally addresses the issue of non-ideality in the aqueous phase chemistry. In order to assess the impact of the *choice* of physical property method on the fidelity of the process simulation, and thus establish a basis for examining *alternative* electrolyte models, a simple sensitivity analysis was performed. The blocks in the model which use ENRTL were changed to use the IDEAL method instead, and the ASPEN Plus model was rerun.

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[a] It is unclear whether or not heterogeneous denitration of solid $Al(NO_3)_3$ to form Al_2O_3 is properly accounted for in ASPEN Plus; for purposes of the present assessment it is conservatively assumed that it is not until the contrary is established.

[b] The reader may note that Hg is formally represented in one reaction involving Hg^{+2} and Hg_2^+ in Table 2. However, neither of these species is linked with any of the chloride complexes of Hg, and thus the entire chemistry of Hg/Cl is omitted from the model. In addition, elemental Hg exists primarily as a separate pure liquid phase (with very little dissolved in the aqueous phase), and it is not clear if and how Aspen Plus accounts for the partitioning of elemental Hg between vapor, pure liquid, and liquid aqueous phases. For these reasons it is asserted that mechanistic modeling of chemical and phase transformations of Hg are *not* represented in the current model.

Table 6 provides a comparison of the stream properties and compositions for three product streams (labelled "PRODUCT", "HG-GAC", and "STACKGAS" in Figure 3) as predicted from the ENRTL and the IDEAL simulations. The table indicates that the predicted "PRODUCT" stream composition is impacted the most by the choice of property method (the average deviation is ±18%, and seven components have deviations greater than ±50%), and the "HG-GAC" stream is impacted the least (only three species above ±5%, and all below ±10%). The predicted levels of hydrofluoric acid in the final solid waste and in that sent to the stack ("PRODUCT" and "STACKGAS" streams, respectively) are appreciably different for the two property methods. Interestingly, the predicted thermodynamic properties of the streams are affected relatively little by the choice of property method, most deviations being less than ±10%.

Comparison for all species in the model are provided in Table 7. Almost half of the species in the simulation component list are not predicted to be present in the three selected output streams; i.e., they either experience complete chemical transformations or leave the system via the other secondary product streams. Their respective cells in Table 7 are blank because the percent deviation calculation would involve division by zero. Interestingly, the distribution of calculated deviations for the remaining species appears to be bimodal. Using the mole or mass flow basis and the "PRODUCT" stream, the majority (39 species) are in the primary group (0-10% range), and a few (7) are in the second group encompassing the >50% range. Only one specie falls between the two distribution humps, Na_2CO_3 at ±17.5%.

The fact that 15% [7/(39+7+1)] of the species present in the solid waste form ("PRODUCT" stream) lie in the high impact group, suggests that use of a mechanistic activity coefficient model rather than assuming ideality is worthwhile. Moreover, it implies that use of a model which provides poor estimates of activity coefficients will likely impact significantly some simulation predictions of key interest (e.g., fate of HF). This observation, together will previously-published comparisons of ENTRL with the Pitzer activity coefficient model (Nichols & Taylor, 2002) illustrating deficiencies of the former, suggest that use of ENRTL should be phased out as a properties model for the simulation of SBW treatment as Pitzer parameter data become available to support full use of the Pitzer model.

Calculational Sequencing

The impact of the calculational sequencing gap discussed above has not yet been assessed. Prior to finalization of the next version of the model, it is anticipated that sensitivity calculations will be performed by inserting RGIBBS blocks after each significant stream partitioning block (principally the FLASH2 blocks in the model) and comparing the resulting product stream compositions (and flow rates) with those obtained without inserting the RGIBBS blocks.

CONCLUSIONS

The current baseline simulation provides a good start for estimating a mass balance. It includes chemical and phase transformations for several key species, such as nitrates, carbonates, and key acids (HNO_3, H_2SO_4, and HCl). It uses a mechanistic electrolyte model, ENRTL, where appropriate. All the key unit operations are included to provide a means to perform integrated process optimization.

The simulation can be improved to enhance its predictive fidelity. Chemical and phase transformations for key mercury, boric, aluminum, zirconium, barium, and iron species are absent and need to be added. Chemical equilibrium in the gas phase is not accounted for in the off-gas treatment train (downstream of the reformer), which may decrease the accuracy of the phase partitioning predicted in the scrubber, quench, and mist eliminator unit operations.

Appreciable benefit is derived from using an activity coefficient model for electrolyte solution thermodynamics rather than assuming ideality. The concentrations of fifteen percent of the species present in the primary output stream are changed by more than 50% when the ENRTL activity coefficient model is used in place of thermodynamic calculations assuming solution ideality.

Path Forward

Nichols and Taylor (2002) demonstrated the superiority of the Pitzer ion-interaction model over ENRTL to predict electrolyte solution thermodynamics. Given the impact of accounting for non-ideal behavior documented here, demonstrated by comparing the ENRTL and IDEAL scenarios, it is recommended that current efforts to determine Pitzer parameters for key species be continued and that the Pitzer model replace ENRTL in SBW simulations. In addition, chemical and phase transformations for key mercury, boric, aluminum, zirconium, barium, and iron species should be added to the model. Finally, it is recommended that RGIBBS blocks be combined with the current scrubber, quench and mist eliminator FLASH2 blocks in the off-gas treatment train in order to simulate simultaneous phase and chemical equilibria.

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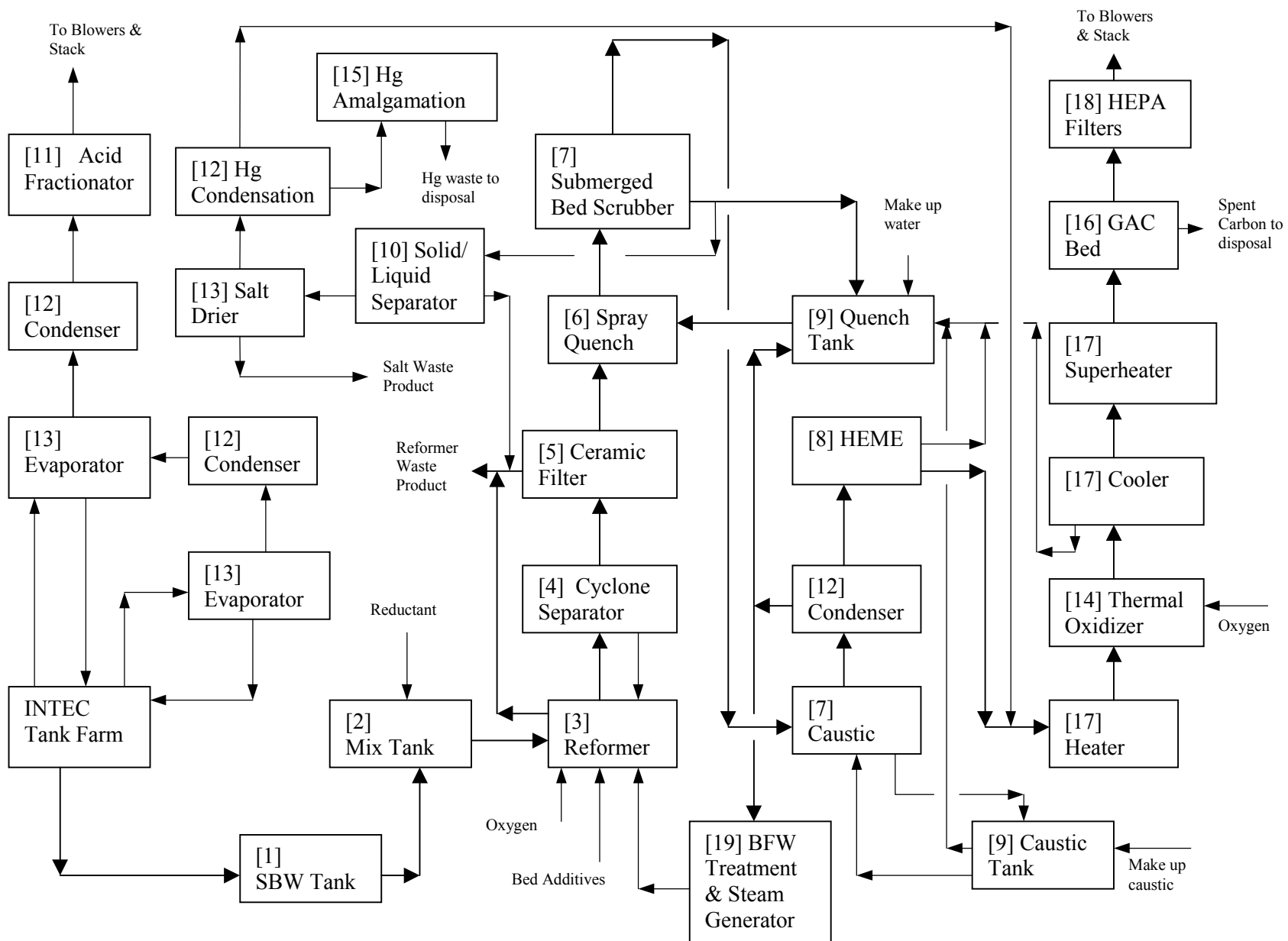
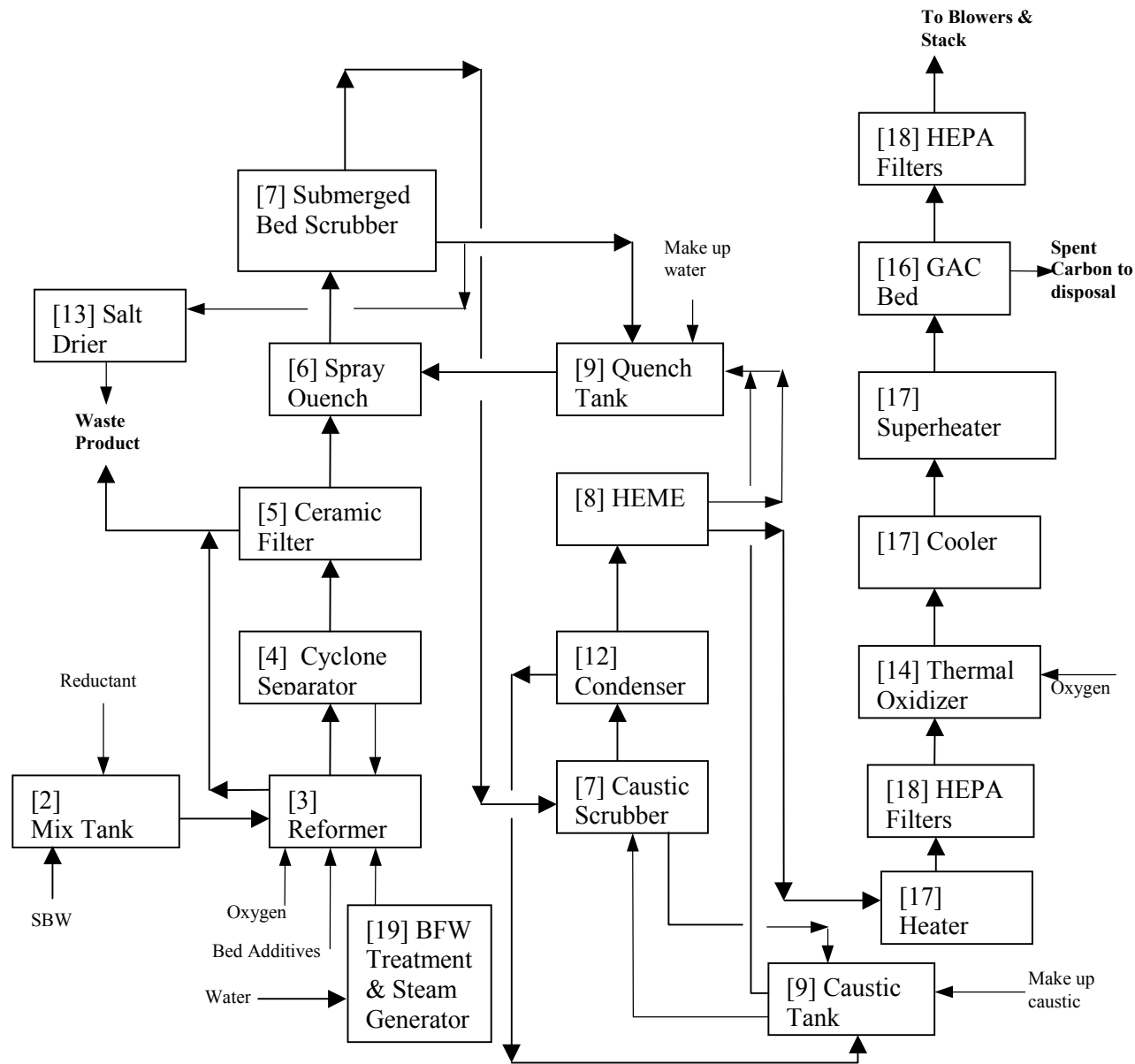Figure 1. Original Steam Reforming Process Configuration [from Taylor et al. (2002)].

Figure 2. Revised Steam Reforming Process Configuration.

SBW Steam Reforming Simulation
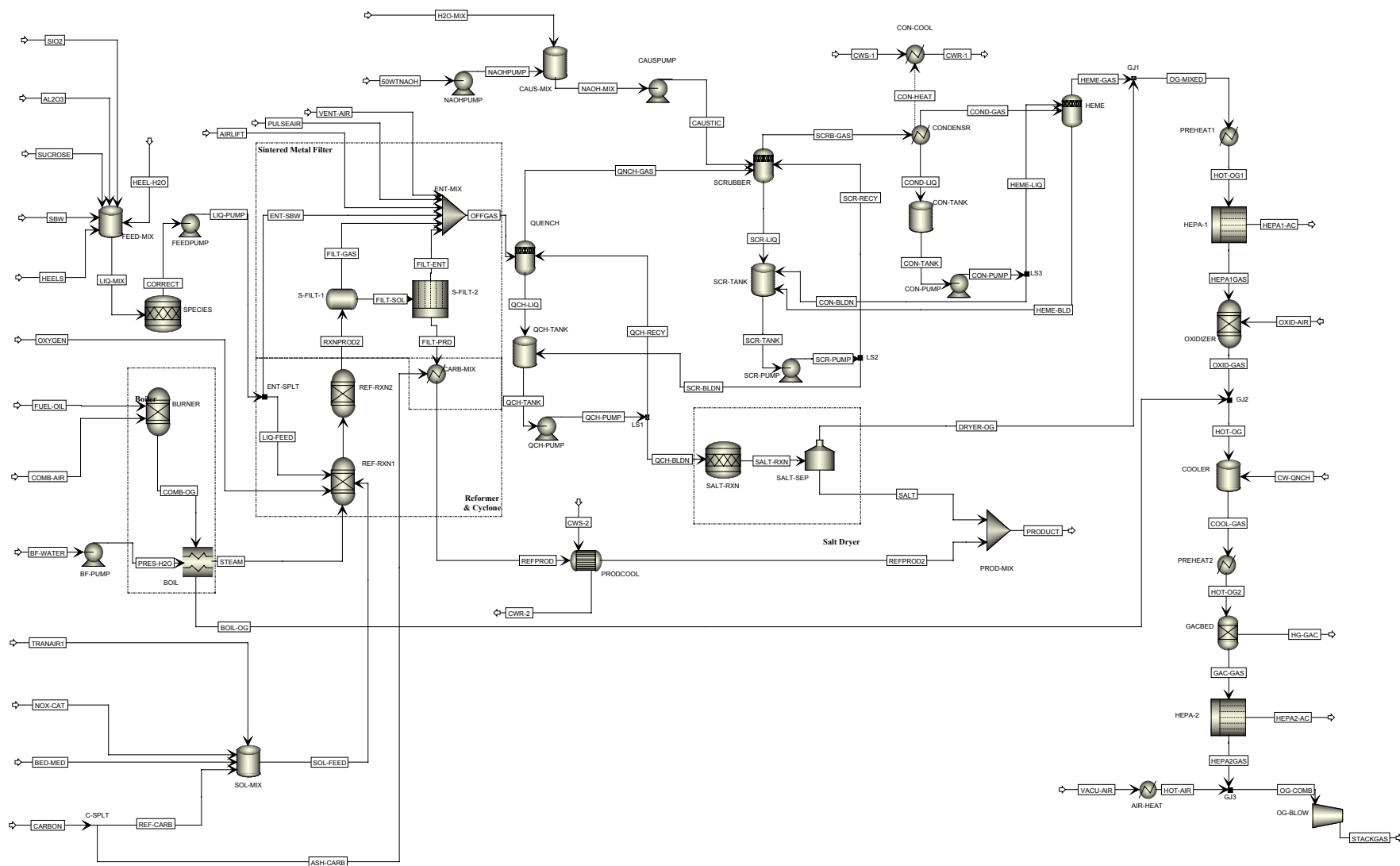
Figure 3. ASPEN Plus Process Flow Diagram.

Table 1. Process Configuration/ASPEN PFD Matrix.

Process Configuration[a]		ASPEN Plus PFD[b]
Type ID	Name	
[2]	Mix Tank	FEEDMIX SPECIES
[3]	Reformer	REF-RXN2 REF-RXN2
[4]	Cyclone Separator	S-FILT-1
[5]	Ceramic Filter	S-FILT-2
[6]	Spray Quench	QUENCH‡
[7]	Submerged Bed Scrubber	QUENCH‡
[7]	Caustic Scrubber	SCRUBBER
[8]	HEME	HEME
[9]	Quench Tank	QCH-TANK
[9]	Caustic Tank	SCR-TANK
[12]	Condenser (Offgas)	CONDENSR
[13]	Salt Dryer	SALT-RXN SALT-SEP
[14]	Thermal Oxidizer	OXIDIZER
[16]	GAC Bed	GACBED
[17]	Heater	PREHEAT1
[17]	Cooler	COOLER
[17]	Superheater	PREHEAT2
[18]	HEPA Filters (Top)	HEPA-2
[18]	HEPA Filters (Bottom)	HEPA-1
[19]	BFW Treatment & Steam Generator	BURNER BOIL

[a] From Figure 2. [b] From Figure 3. ‡The baseline model does not yet incorporate a separate aerosol stream with a particle size distribution; therefore, the Quench and Submerged Bed Scrubber are regarded as equivalent unit operations and their overall effect is represented with the single QUENCH block. Once the model is refined to reflect the effects of particle size on separation efficiencies these two operations will be split into two blocks.

Table 2. List Of Species In Baseline ASPEN Plus Model.

ASPEN Component ID	ASPEN Type	ASPEN Component name	Formula
AL(NO3)3	CONV	ALUMINUM NITRATE NONAHYDRATE	ALN3O9*9W
AL+++	CONV	AL+++	AL+3
AL2O3	SOLID	ALUMINIUM-OXIDE-ALPHA-CORUNDUM	AL2O3
ALNO3(S)	SOLID	ALUMINUM-NITRATE-NONAHYDRATE	ALN3O9*9W
ALPO4	SOLID	ALUMINIUM-PHOSPHATE-ORTHO	ALPO4-O
C2H6	CONV	ETHANE	C2H6
C3H8	CONV	PROPANE	C3H8
CA(NO3)2	CONV	CALCIUM-NITRATE	CA(NO3)2
CA++	CONV	CA++	CA+2
CACL2(S)	SOLID	CALCIUM-CHLORIDE	CACL2
CACO3	SOLID	CALCIUM-CARBONATE	CACO3
CAF2	SOLID	CALCIUM-FLUORIDE	CAF2
CANO3(S)	SOLID	CALCIUM-NITRATE	CA(NO3)2
CAO	SOLID	CALCIUM-OXIDE	CAO
CAOH+	CONV	CAOH+	CAOH+
CARBON	SOLID	CARBON(GRAPHITE)	C
CASO4(S)	SOLID	CALCIUM-SULFATE	CASO4
CH4	CONV	METHANE	CH4
CL-	CONV	CL-	CL-
CO	CONV	CARBON-MONOXIDE	CO
CO2	CONV	CARBON-DIOXIDE	CO2
CO3--	CONV	CO3--	CO3-2
F-	CONV	F-	F-
FE2O3	SOLID	FERRIC-OXIDE	FE2O3
H2	CONV	HYDROGEN	H2
H2O	CONV	WATER	H2O
H2S	CONV	HYDROGEN-SULFIDE	H2S
H2SO4	CONV	SULFURIC-ACID	H2SO4
H3O+	CONV	H3O+	H3O+
HCL	CONV	HYDROGEN-CHLORIDE	HCL
HCO3-	CONV	HCO3-	HCO3-
HF	CONV	HYDROGEN-FLUORIDE	HF
HG	CONV	MERCURY	HG
HG(OH)2	CONV	MERCURY-DIHYDROXIDE	HG(OH)2
HG++	CONV	HG++	HG+2
HG2++	CONV	HG2++	HG2+2
HGCL2	CONV	MERCURY-DICHLORIDE	HGCL2
HGOH+	CONV	HGOH+	HGOH+
HNO3	CONV	NITRIC-ACID	HNO3
HS-	CONV	HS-	HS-
HSO3-	CONV	HSO3-	HSO3-
HSO4-	CONV	HSO4-	HSO4-
K+	CONV	K+	K+
K2CO3	SOLID	POTASSIUM-CARBONATE	K2CO3
K2O	SOLID	POTASSIUM-OXIDE	K2O
K2SO4	SOLID	POTASSIUM-SULFATE	K2SO4
K3PO4	SOLID	POTASSIUM-PHOSPHATE	K3PO4
KCL	SOLID	POTASSIUM-CHLORIDE	KCL

ASPEN Component ID	ASPEN Type	ASPEN Component name	Formula
KHCO3	SOLID	POTASSIUM-BICARBONATE	KHCO3
KHSO4	SOLID	KHSO4	KHSO4
KNO3	CONV	POTASSIUM-NITRATE	KNO3
KNO3(S)	SOLID	POTASSIUM-NITRATE	KNO3
KOH(S)	SOLID	POTASSIUM-HYDROXIDE	KOH
MINUS1	CONV	HYDROGEN-CHLORIDE	HCL
N2	CONV	NITROGEN	N2
NA+	CONV	NA+	NA+
NA2CO3	SOLID	SODIUM-CARBONATE	NA2CO3
NA2O	SOLID	SODIUM-OXIDE	NA2O
NA2S	SOLID	SODIUM-SULFIDE	NA2S
NA2SO3	SOLID	SODIUM-SULFITE	NA2SO3
NA2SO4	SOLID	SODIUM-SULFATE	NA2SO4
NA3PO4	CONV	TRISODIUM-PHOSPHATE	NA3PO4
NA3PO4(S	SOLID	TRISODIUM-PHOSPHATE	NA3PO4
NAALO2	SOLID	NAALO2	NAALO2
NACL	SOLID	SODIUM-CHLORIDE	NACL
NAF	SOLID	NAF	NAF
NAHCO3	SOLID	SODIUM-HYDROGEN-CARBONATE	NAHCO3
NAHS	CONV	NAHS	NAHS
NAHS(S)	SOLID	NAHS	NAHS
NAHSO4	SOLID	SODIUM-BISULFATE	NAHSO4
NANO3	CONV	SODIUM-NITRATE	NANO3
NANO3(S)	SOLID	SODIUM-NITRATE	NANO3
NAOH	CONV	NAOH	NAOH
NAOH(S)	SOLID	SODIUM-HYDROXIDE	NAOH
N-HEX-01	CONV	N-HEXADECANE	C16H34
NO	CONV	NITRIC-OXIDE	NO
NO2	CONV	NITROGEN-DIOXIDE	NO2
NO3-	CONV	NO3-	NO3-
O2	CONV	OXYGEN	O2
OH-	CONV	OH-	OH-
PLUS1	SOLID	SODIUM-NITRATE	NANO3
PLUS2	SOLID	CALCIUM-NITRATE	CA(NO3)2
PLUS3	SOLID	ALUMINUM-NITRATE-NONAHYDRATE	ALN3O9*9W
PLUS4	SOLID	ZIRCONIUM-DIOXIDE	ZRO2
PLUS5	SOLID	DIVANADIUM-PENTAOXIDE	V2O5
PLUS6	SOLID	MOLYBDENUM-TRIOXIDE	MOO3
S--	CONV	S--	S-2
SIO2	SOLID	SILICON-DIOXIDE	SIO2
SO2	CONV	SULFUR-DIOXIDE	O2S
SO3--	CONV	SO3--	SO3-2
SO4--	CONV	SO4--	SO4-2
SUCROSE	SOLID	SUCROSE	C12H22O11

Table 3. List Of Reactions In Baseline ASPEN Plus Electrolyte Chemistry.

Reaction	Type	Stoichiometry
1	Equilibrium	2 H2O <--> H3O+ + OH-
2	Equilibrium	H2S + H2O <--> H3O+ + HS-
3	Equilibrium	HS- + H2O <--> H3O+ + S--
4	Equilibrium	CO2 + 2 H2O <--> H3O+ + HCO3-
5	Equilibrium	HCO3- + H2O <--> H3O+ + CO3--
6	Equilibrium	H2SO4 + H2O <--> H3O+ + HSO4-
7	Equilibrium	HSO4- + H2O <--> H3O+ + SO4--
8	Equilibrium	HCL + H2O <--> H3O+ + CL-
9	Equilibrium	HF + H2O <--> H3O+ + F-
10	Equilibrium	HNO3 + H2O <--> H3O+ + NO3-
11	Equilibrium	SO2 + 2 H2O <--> H3O+ + HSO3-
12	Equilibrium	HSO3- + H2O <--> H3O+ + SO3--
13	Equilibrium	HG++ + HG <--> HG2++
14	Equilibrium	HG++ + 2 H2O <--> H3O+ + HGOH+
15	Equilibrium	HGOH+ + 2 H2O <--> H3O+ + HG(OH)2
16	Equilibrium	CAOH+ <--> CA++ + OH-
NACL	Salt	NACL <--> NA+ + CL-
NA2SO4	Salt	NA2SO4 <--> 2 NA+ + SO4--
K2CO3	Salt	K2CO3 <--> 2 K+ + CO3--
KHCO3	Salt	KHCO3 <--> K+ + HCO3-
NAOH(S)	Salt	NAOH(S) <--> NA+ + OH-
KOH(S)	Salt	KOH(S) <--> K+ + OH-
CACL2(S)	Salt	CACL2(S) <--> CA++ + 2 CL-
CANO3(S)	Salt	CANO3(S) <--> CA++ + 2 NO3-
CASO4(S)	Salt	CASO4(S) <--> CA++ + SO4--
CAF2	Salt	CAF2 <--> CA++ + 2 F-
KCL	Salt	KCL <--> K+ + CL-
KHSO4	Salt	KHSO4 <--> K+ + HSO4-
KNO3(S)	Salt	KNO3(S) <--> K+ + NO3-
K2SO4	Salt	K2SO4 <--> 2 K+ + SO4--
NA2CO3	Salt	NA2CO3 <--> 2 NA+ + CO3--
NAF	Salt	NAF <--> NA+ + F-
NAHCO3	Salt	NAHCO3 <--> NA+ + HCO3-
NANO3(S)	Salt	NANO3(S) <--> NA+ + NO3-
NA2S	Salt	NA2S <--> 2 NA+ + S--
NA2SO3	Salt	NA2SO3 <--> 2 NA+ + SO3--
CACO3	Salt	CACO3 <--> CA++ + CO3--
NAHSO4	Salt	NAHSO4 <--> NA+ + HSO4-
NAHS(S)	Salt	NAHS(S) <--> NA+ + HS-
ALNO3(S)	Salt	ALNO3(S) <--> AL+++ + 3. NO3- + 9. H2O
NAOH	Dissociation	NAOH --> NA+ + OH-
CA(NO3)2	Dissociation	CA(NO3)2 --> CA++ + 2 NO3-
KNO3	Dissociation	KNO3 --> K+ + NO3-
NANO3	Dissociation	NANO3 --> NA+ + NO3-

Table 4. Species, Reactions, and Phase Transformations Needed for Simulation.

Specie		Ch Trf. [a]		Ph Trf. [b]		Rationale
Al(NO3)3	√	E-het		SL	√	Al+3 and NO3- are major species in the waste feed and the formation of Al(NO3)3 and its inclusion in solid products is of interest because of its effect on agglomeration behavior during solids transport and handling. (see also comment under 'NaNO3', which may be applicable due to limited solubility of Al(NO3)3)
Al2(SO4)3		E-aq		SL		Due to the abundance of Al in the feed, Al2(SO4)3 may be formed from the sulfate in the reformer. The fate of sulfate is of interest (see 'H2SO4'). (also see comments under 'Ca(OH)2•Ca3(PO4)3')
Al2O3	√			SL		Al is a major component of TDS in waste and Al2O3 will be major contributor to solid product and PM loading in offgas. Its fate will determine equipment sizing. Al2O3 will likely be a major contributor to UDS in scrub solutions, and may determine solid/liquid separation requirements and pumping system requirements for scrub recycle.
AlF+2		E-aq				Aluminum complexes with fluoride impact chemistry of HF (Hammer, 1979). See 'HF'.
AlF2+		E-aq				(see 'AlF+2').
AlF3		E-aq				(see 'AlF+2').
AlF4-		E-aq				(see 'AlF+2').
AlPO4	√	E-aq		SL		(same comment as for 'Ca(OH)2•Ca3(PO4)3')
Ba(H2PO4)2		E-aq		SL		Ba was a significant cation in solids samples from tank farm tank WM-188 (Patterson, 1999) and PO4-3 is a major constituent of solid samples from the tank farm (Barnes, 2001),(Patterson, 1999). Ba+2/PO4-3 salts may account for these facts and should be considered if blended solution stabilities and solids formation are of interest.
Ba(HPO4)		E-aq		SL		(see 'Ba(H2PO4)2')
BaSO4		E-aq		SL		Ba was a significant cation in solids samples from tank farm tank WM-188 (Patterson, 1999). BaSO4 is a sparingly soluble salt that may account for this and should be considered if blended solution stabilities and solids formation are of interest.
BF4-		E-aq				(see 'H3BO3F-')
Ca(OH)2 •Ca3(PO4)3		E-aq		SL		PO4-3 is a major constituent of solid samples from the tank farm (Barnes, 2001), (Patterson, 1999). The species at left has been identified as possible precipitate from tank farm solutions (Christian, 2001) and should be considered if blended solution stabilities and solids formation are of interest.
CaCl2	√			SL	√	Chemistry of CaCl2 impacts fate of Cl-, which impacts fate of HCl and Cl2.
CaCO3	√			SL	√	Ca is a significant cation in the waste feed. CaCO3 will likely be part of the reformer product. It may

Specie		Ch Trf.[a]		Ph Trf.[b]		Rationale
						impact scrub solution pH, UDS concentrations, and handling characteristics of solid waste product.
CaF_2	√			SL	√	Chemistry of CaF_2 impacts fate of F-, which impacts fate of HF (see 'HF'). CaF_2 may contribute significantly to UDS in scrub solutions (see 'Al2O3').
CaF_2ZrO_2				SL		Zr is a major cation in tank farm solids samples (Barnes, 2001), (Patterson, 1999), (Christian, 2001) and calcium fluorozirconate was mentioned as a commonly-encountered solid in tank farm samples (Swenson, 2002)
CaO	√			SL		Hygroscopicity of CaO in reformer product may impact handling characteristics.
$CaSO_3$				SL		(see comments under ' Al2(SO4)3')
$CaSO_4$	√			SL	√	('CaCO3' comments apply)
Cl_2		E-gas	*	VL		Cl2 concentration in offgas regulated by MACT.
CO	√	E-gas E-het	*			CO is an explosion hazard and a MACT-regulated pollutant--concentrations must be known to design required control measures.
CO_2	√	E-gas E-aq	* √	VL	√	CO2 is part of chemistry of CO and of metal carbonates . It will also be a major diluent in offgas if water vapor is removed and will contribute to oxidation chemistry of HCs and CO in thermal oxidizer.
Fe_2O_3	√			SL		Fe2O3 may be a major contributor to UDS in scrub solutions (see 'Al2O3').
FeF^{+2}		E-aq				Iron complexes with fluoride impact chemistry of HF (Hammer, 1979). See 'HF'.
$FeF2+$		E-aq				(see ' FeF+2').
FeF_3		E-aq				(see ' FeF+2').
$FePO_4$		E-aq		SL		(same comment as for 'Ca(OH)2•Ca3(PO4)3')
H_2	√	E-gas	*	VL	√	H2 is an explosion hazard--concentrations must be known to determine required control measures.
$H2BO2F2-$		E-aq				(see 'H3BO3F-')
$H2BOF3$		E-aq				(see 'H3BO3F-')
H_2O	√	E-gas E-aq	* √	VL	√	H2O is part of gas phase chemistry of many other species of interest. It will be the largest single component of offgas and scrub solutions. Its fate will determine equipment sizing.
H_2S	√	E-gas	*	VL	√	H2S is toxic and its concentration will be of interest to regulators.
H_2SO_4	√	E-gas E-aq	* √	VL	√	H2SO4 is part of chemistry of H2S. Also, fate of sulfate may be of interest in case the reformer product is ever vitrified.
H_3BO_3		E-aq				Boric acid participates in borate chemistry (see 'H3BO3F-').
$H3BO3F-$		E-aq				Borates form soluble complexes with F- and thus are an integral part of the chemistry (Hammer, 1979) of HF .
HBF_4		E-aq				(see 'H3BO3F-')
$HBOF3-$		E-aq				(see 'H3BO3F-')

Specie		Ch Trf.[a]		Ph Trf.[b]		Rationale
HCl	√	E-aq E-gas	√ *	VL	√	HCl concentration in offgas regulated by MACT.
HF	√	E-aq	√	VL	√	HF is highly toxic and will be regulated in offgas. HF is corrosive and its concentration is needed for material specifications.
Hg	√	E-aq		VL SL		Hg in stack gas is regulated to a very low concentration under MACT and Hg in solid wastes is indirectly regulated through LDR restrictions on TCLP concentrations. Fate of Hg is needed to design acceptable control measures for stack gas concentrations and to develop suitable measures to tailor solid waste forms to satisfy TCLP limits.
HgCl		E-aq		SL		HgCl (calomel) is part of chemistry of Hg.
HgCl+		E-aq				(see 'HgCl3-')
HgCl2	√	E-aq		VL SL	√ √	HgCl2 is much more soluble than Hg and thus can strongly influence mercury partitioning between liquid and gas phases provided the required redox conditions prevail. (see also 'Hg')
HgCl3-		E-aq				Soluble Hg+2/Cl- complexes are part of chemistry of Hg.
HgCl4-2		E-aq				(see 'HgCl3-')
HNO3	√	E-aq	√	VL	√	NO3- is the largest component of the feed and will result in large quantities of NOx in offgas. Fate of HNO3 and NO2 will impact pH of scrub solutions. NOx emissions will be regulated by state and HNO3 chemistry is part of NO2 chemistry.
K2AlCl9		E-aq		SL		(same comment as for 'Ca(OH)2•Ca3(PO4)3')
K3H6Al5(PO4)8 •18H2O		E-aq		SL		(same comment as for 'Ca(OH)2•Ca3(PO4)3')
KNO3	√			SL	√	KNO3 was identified in solids from tank farm solutions (Christian, 2001) and should be considered if blended solution stabilities and solids formation are of interest.
N2	√	E-gas	*	VL	√	N2 is part of NO2 and HNO3 chemistry
Na2CO3	√			SL	√	('CaCO3' comments apply)
Na2O	√			SL		Na+ is the 2nd most abundant cation (excluding H+) in the feed and will likely be converted to Na2O in the reformer. It will impact pH of scrubber solutions and will likely form submicron aerosols that will penetrate to the HEPA filters and dictate their changeout frequency. Hygroscopicity of Na2O in product may impact handling characteristics.
Na2SO4	√			SL	√	('CaCO3' comments apply)
NaNO3	√			SL	√	Na+ and NO3- were the most abundant cation and anion, respectively identified in tank farm tank WM-180 and it has been inferred that the liquid was supersaturated in NaNO3 (Christian, 2001). NaNO3(s) should thus be considered if blended solution stabilities and solids formation are of

Specie		Ch Trf.[a]		Ph Trf.[b]		Rationale
						interest.
NO	√	E-gas	*			NO is part of the oxidation chemistry of NO2 and N2.
NO2	√	E-gas E-aq	*	VL	√	NO2 concentrations dictate oxidizing potential of offgas and will strongly impact speciation of Hg. (see also 'HNO3')
O2	√	E-gas	*	VL	√	O2 is part of gas phase chemistry of H2, CO, and hydrocarbons (HCs) formed in reformer and will impact their concentrations.
SiO2	√	E-aq		SL		Si has been identified as a significant component of solids in tank farm tank WM-180 (Christian, 2001). (see comment for 'Ca(OH)2•Ca3(PO4)3')
SO2	√	E-gas	*	VL	√	(see comments under 'H2SO4')
SO3		E-gas E-aq	*	VL		(see comments under 'H2SO4')
ZrF+3		E-aq				Zr+4 forms several soluble complexes with F- and thus is an integral part of the chemistry (Hammer, 1979) of HF.
ZrF2+2		E-aq				(see 'ZrF+3')
ZrF3+		E-aq				(see 'ZrF+3')
ZrF4		E-aq				(see 'ZrF+3')
ZrF5-		E-aq				(see 'ZrF+3')
ZrF6-2		E-aq				(see 'ZrF+3')

√ => specie or transformation is present in baseline model. [a] 'E-aq'=partial aqueous dissociation, 'E-gas'=equilibrium gas phase reaction, 'E-het'=equilibrium heterogeneous reaction (gas/solid). [b] 'SL'=solid/liquid phase equilibrium, 'VL'=vapor/liquid phase equilibrium. * See discussion under section **Calculational Sequencing**.

Table 5. Thermodynamic Property Methods Currently Used By Unit Operation Blocks In ASPEN
Plus Baseline Simulation.

| NAME | TYPE | Phase | |
		Liquid	Gas
OG-BLOW	COMPR	IDEAL	-
CONDENSR	FLASH2	ENRTL	ENRTL
HEME	FLASH2	ENRTL	ENRTL
QUENCH	FLASH2	ENRTL	ENRTL
SALT-SEP	FLASH2	IDEAL	IDEAL
SCRUBBER	FLASH2	ENRTL	ENRTL
S-FILT-1	FLASH2	IDEAL	IDEAL
C-SPLT	FSPLIT	IDEAL	IDEAL
LS1	FSPLIT	-	ENRTL
LS2	FSPLIT	ENRTL	-
LS3	FSPLIT	ENRTL	-
AIR-HEAT	HEATER	-	IDEAL
CARB-MIX	HEATER	IDEAL	IDEAL
CON-COOL	HEATER	IDEAL	-
PREHEAT1	HEATER	-	IDEAL
PREHEAT2	HEATER	-	IDEAL
PRODCOOL	HEATX	IDEAL	IDEAL
BOIL	MHEATX	IDEAL	IDEAL
CAUS-MIX	MIXER	ENRTL	-
CON-TANK	MIXER	ENRTL	-
COOLER	MIXER	-	ENRTL
ENT-MIX	MIXER	IDEAL	IDEAL
FEED-MIX	MIXER	IDEAL	-
GJ1	MIXER	IDEAL	IDEAL
GJ2	MIXER	IDEAL	IDEAL
GJ3	MIXER	-	IDEAL
PROD-MIX	MIXER	IDEAL	IDEAL
QCH-TANK	MIXER	ENRTL	-
SCR-TANK	MIXER	ENRTL	-
SOL-MIX	MIXER	IDEAL	IDEAL
BF-PUMP	PUMP	IDEAL	-
CAUSPUMP	PUMP	ENRTL	-
CON-PUMP	PUMP	ENRTL	-
FEEDPUMP	PUMP	-	IDEAL
NAOHPUMP	PUMP	ENRTL	-
QCH-PUMP	PUMP	ENRTL	-
SCR-PUMP	PUMP	ENRTL	-
BURNER	RGIBBS	IDEAL	IDEAL
OXIDIZER	RGIBBS	IDEAL	IDEAL
REF-RXN1	RGIBBS	IDEAL	IDEAL
REF-RXN2	RSTOIC	IDEAL	IDEAL
SALT-RXN	RSTOIC	IDEAL	IDEAL
SPECIES	RSTOIC	IDEAL	-
GACBED	SEP	IDEAL	-
ENT-SPLT	SSPLIT	IDEAL	IDEAL
HEPA-1	SSPLIT	-	IDEAL
HEPA-2	SSPLIT	IDEAL	IDEAL
S-FILT-2	SSPLIT	IDEAL	IDEAL

Table 6. Comparison of ENRTL and IDEAL Property Methods (Summary).

Specie	Per Cent Absolute Deviation[a] of ENRTL from IDEAL > 5%		
	PRODUCT	HG-GAC	STACKGAS
CO2	9.89		0.15
H2O	9.10		3.99
HCL	0.00		8.72
HF	66.23		99.94
HG [b]	0.48	8.62	8.62
NA2CO3	17.49		
NAHSO4	97.03		
NAHS	54.30		
NA2S	99.92		
CARBON [c]	0.97	9.43	
NAHCO3	274.52		
OH-	100.00		
MINUS1 [b]		8.72	
CAOH+	99.97		
Stream Statistics			
Maximum	274.52	8.72	99.94
Minimum	0.00	0.00	0.00
Average	17.65	5.78	9.02
Standard Deviation	48.44	5.01	26.34
Stream Properties			
Total Flow kmol/day	0.89	8.62	2.71
Total Flow kg/hr	0.98	8.62	2.21
Total Flow l/hr	1.02	8.65	2.70
Temperature C	0.00	0.00	0.03
Pressure atm	0.00	0.00	0.00
Enthalpy cal/mol	0.01	3.44	0.71
Enthalpy cal/gm	0.10	3.44	1.20
Enthalpy cal/sec	0.87	11.76	3.45
Entropy cal/mol-K	9.58	1.50	7.23
Entropy cal/gm-K	9.66	1.50	7.76
Density mol/cc	0.13	0.04	0.01
Density gm/cc	0.04	0.03	0.47
Average MW	0.09	0.00	0.48
Liq Vol 60F l/hr		8.62	1.76

[a] Deviations for species are on mole or mass flow rate basis, unless otherwise noted. [b] Less than 5% deviation in mole fraction and mass fraction scales. [c] Values shown pertain to mass fraction scale (carbon had less than 5% deviation in the other scales).

Table 7. Comparison Between ENRTL and IDEAL Property Methods (Complete Specie Data).

SPECIE	PER CENT ABSOLUTE DEVIATION OF ENRTL FROM IDEAL[a]								
	MOLE OR MASS FLOW			MOLE FRACTION			MASS FRACTION		
	PRODUCT	HG-GAC	STACKGAS	PRODUCT	HG-GAC	STACKGAS	PRODUCT	HG-GAC	STACKGAS
H2	0.00		0.00	0.88		2.64	0.97		2.16
CO	0.00		0.00	0.88		2.64	0.97		2.17
CO2	9.89		0.15	10.68		2.79	10.76		2.31
O2	0.00		1.01	0.88		1.66	0.97		1.18
N2	0.00		0.48	0.88		2.17	0.97		1.69
NO			0.00			2.64			2.17
NO2			0.50			3.12			2.65
H2S	0.06			0.82			0.91		
SO2	0.00		0.68	0.88		1.98	0.97		1.51
H2O	9.10		3.99	8.14		1.24	8.05		1.73
HNO3			1.79			4.38			3.92
HCL	0.00		8.72	0.88		11.13	0.97		10.70
HF	66.23		99.94	66.53		99.95	66.56		99.95
H2SO4			0.45			2.20			1.72
HG	0.48	8.62	8.62	0.40	0.00	11.03	0.49	0.00	10.60
HGCL2	0.37			0.51			0.60		
NA2CO3	17.49			18.21			18.29		
K2CO3	0.00			0.88			0.97		
CACO3	0.00			0.88			0.97		
NA2O	0.00			0.88			0.97		
K2O									
CAO	0.00			0.88			0.97		
NAALO2									
AL2O3	0.00			0.88			0.97		
SIO2	0.00			0.88			0.97		
FE2O3	0.00			0.88			0.97		
NACL	0.00			0.88			0.97		
KCL	0.00			0.88			0.97		
CAF2									
NANO3	0.00			0.88			0.97		
NANO3(S)									
KNO3									
KNO3(S)									
CA(NO3)2									
CANO3(S)									
AL(NO3)3	0.00			0.88			0.97		
ALNO3(S)									
NAHSO4	97.03			97.06			97.06		
NA2SO4	0.00			0.88			0.97		
NAHS	54.30			52.94			52.80		
NAHS(S)	0.00			0.88			0.97		
NA2S	99.92			99.92			99.92		

| SPECIE | PER CENT ABSOLUTE DEVIATION OF ENRTL FROM IDEAL[a] | | | | | | | | |
| | MOLE OR MASS FLOW | | | MOLE FRACTION | | | MASS FRACTION | | |
	PRODUCT	HG-GAC	STACKGAS	PRODUCT	HG-GAC	STACKGAS	PRODUCT	HG-GAC	STACKGAS
NAOH	0.22			1.09			1.18		
SUCROSE	0.01			0.87			0.96		
CARBON	0.00	0.00		0.88	9.43		0.97	9.43	
NA2SO3	0.00			0.88			0.97		
NAHCO3	274.52			271.23			270.90		
NAF	0.18			0.70			0.79		
K2SO4	0.00			0.88			0.97		
KHSO4									
KHCO3									
AL+++									
H3O+									
NA+									
K+									
CA++									
HG++									
HSO3-									
NO3-									
F-									
HSO4-									
CL-									
HCO3-									
HS-									
SO3--									
SO4--									
CO3--									
S--									
OH-	100.00			100.00			100.00		
HG2++									
N-HEX-01									
CH4									
C2H6									
C3H8									
NA3PO4									
NA3PO4(S	0.00			0.88			0.97		
K3PO4	0.00			0.88			0.97		
ALPO4	0.00			0.88			0.97		
PLUS1									
PLUS2									
PLUS3									
PLUS4	0.00			0.88			0.97		
PLUS5	0.00			0.88			0.97		
PLUS6	0.00			0.88			0.97		
MINUS1		8.72			0.12			0.12	
CAOH+	99.97			99.97			99.97		
HGOH+									

| | PER CENT ABSOLUTE DEVIATION OF ENRTL FROM IDEAL[a] | | | | | | | | |
| | MOLE OR MASS FLOW | | | MOLE FRACTION | | | MASS FRACTION | | |
SPECIE	PRODUCT	HG-GAC	STACKGAS	PRODUCT	HG-GAC	STACKGAS	PRODUCT	HG-GAC	STACKGAS
HG(OH)2									
CASO4(S)	0.00			0.88			0.97		
CACL2(S)									
KOH(S)	0.00			0.88			0.97		
NAOH(S)	0.00			0.88			0.97		
Maximum	274.52	8.72	99.94	271.23	9.43	99.95	270.90	9.43	99.95
Minimum	0.00	0.00	0.00	0.40	0.00	1.24	0.49	0.00	1.18
Average	17.65	5.78	9.02	18.22	3.18	10.68	18.28	3.18	10.32
Std. Dev.	48.44	5.01	26.34	47.81	5.41	25.89	47.74	5.41	25.99

[a] Blank cell indicates a zero concentration in a stream, which results in division by zero for the calculation of the % deviation.