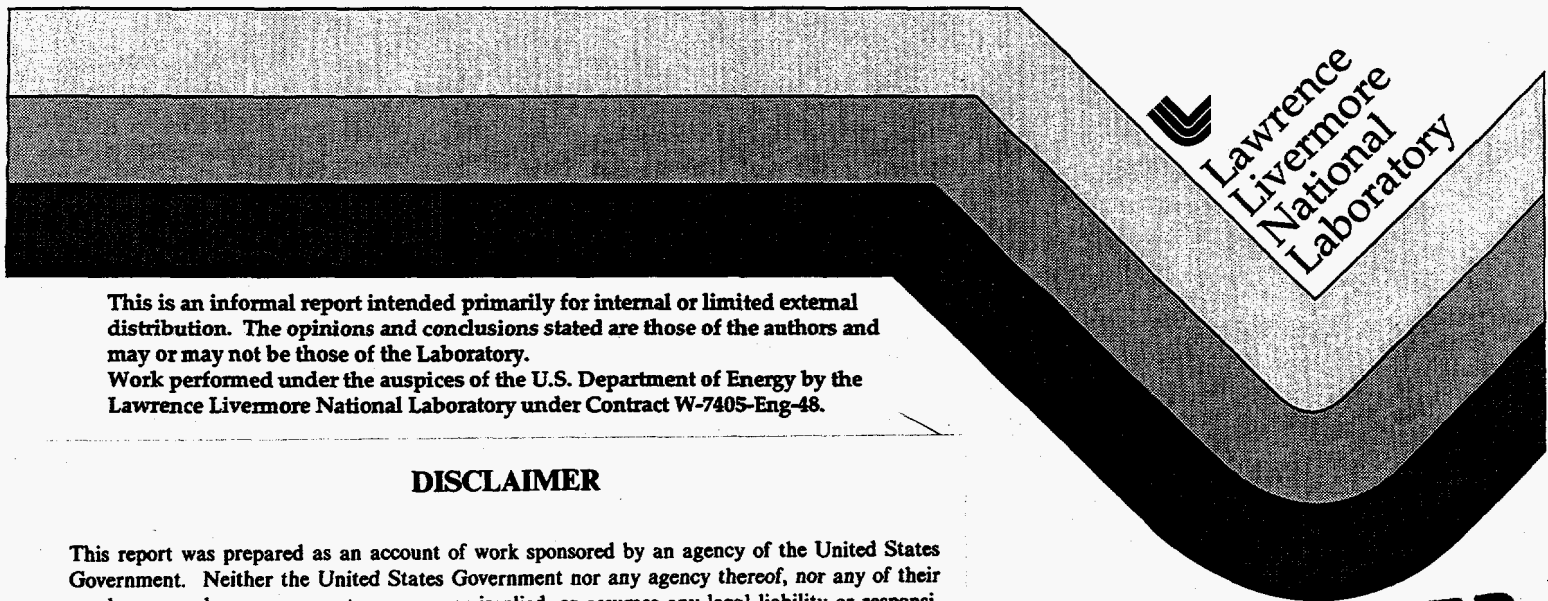# ASPEN Computer Simulations of the
Mixed Waste Treatment Project
Baseline Flowsheet

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Preface

The computer simulations of integrated flowsheets documented in this report were completed with support and guidance provided by the Mixed Waste Treatment Project (MWTP). The project was established by the Department of Energy (DOE) Office of Waste Operations (EM-30) to define and analyze alternative, low-level mixed-waste (LLMW) treatment requirements. The MWTP's goal is to support implementation of treatment capability throughout the DOE complex. The MWTP team is a collaborative effort involving resources from Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory, and Pacific Northwest Laboratory (PNL). Principal members are B. C. Musgrave, leader (LLNL); L. C. Borduin (Los Alamos); and W. A. Ross (PNL). The DOE Headquarters manager for the project during the completion of this initial task was Jo-Ann Bassi. The work was completed by LLNL and Los Alamos authors and T. K. Thompson, Inc., under contract to Los Alamos.

The intended use of these simulations and other models currently being developed is to assess the relative process effectiveness of alternative flowsheets and technologies. Also, use of this software to develop life-cycle costs is planned. Results of these cost and effectiveness assessments can be used by the DOE and its stakeholders to support decision-making related to compliance with the Federal Facility Compliance Act (P.L. 102-386, October 6, 1992).

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1. Introduction

The treatment and disposal of mixed waste (i.e., waste containing both hazardous and radioactive components) is a challenging waste-management problem of particular concern to Department of Energy (DOE) sites throughout the United States. Traditional technologies used for destroying hazardous wastes must be re-evaluated for their ability to handle mixed wastes, and, in some cases, new technologies must be developed.

The Mixed Waste Treatment Project (MWTP), a collaborative effort between Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory, and Pacific North-west Laboratory (PNL), was established by the DOE's Waste Operations Program (EM-30) to develop and analyze alternative mixed waste treatment approaches. One of the MWTP's initiatives, and the objective of this study, was to develop flowsheets for prototype, integrated, mixed-waste treatment facilities that can serve as models for sites developing their own treatment strategies. Evaluation of these flowsheets is being facilitated through the use of computer modeling. The objectives of the flowsheet simulations are to compare process effectiveness and costs of alternative flowsheets and to determine if commercial process-simulation software could be used on the large, complex process of an integrated mixed waste processing facility.

Flowsheet modeling is needed to evaluate many aspects of proposed flowsheet designs. A major advantage of modeling the complete flowsheet is the ability to define the internal recycle streams, thereby making it possible to evaluate the impact of one operation on the whole plant. Many effects that can be seen only in this way—for example, one can evaluate how the offgas levels from one operation affect offgas treatment equipment size farther downstream, or how much the blowdown generated in the offgas treatment section affects the throughput of the aqueous liquids treatment section of the plant. Modeling also can be used to evaluate sensitivity and range of operating conditions, radioactive criticality, and relative costs of different flowsheet designs. Further, the modeled flowsheets must be easily modified so that one can examine how alternative technologies and varying feed streams affect the overall integrated process.

A. Background

The first MWTP generated flowsheet (Fig. 1) was developed by B. Musgrave (LLNL), L. Borduin (Los Alamos), and W. Ross (PNL) and was referred to as the "baseline" flowsheet. This flowsheet provided the basis for the MWTP *Functional and Operational Requirements for an Integrated Facility*[1] (F&OR) study and document developed by T. K. Thompson of T. K. Thompson, Inc., under contract to Los Alamos. Processing rates for the several categories of mixed waste, which collectively served as the F&OR design

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basis, were selected to represent median values for the seven major DOE sites that generate mixed waste. These sites were the Idaho National Engineering Laboratory, K-25, Portsmouth Gaseous Diffusion Plant, Richland Site, Rocky Flats Plant, Savannah River Site, and Y-12. The F&OR flowsheet was predicated on a prototype integrated facility that could process all types of mixed waste. It is extensively interconnected, and all recycle streams are defined and quantified.

The F&OR study was based on the use of existing and proven technology wherever possible and addressed process description; assumptions; process boundaries; flow diagram; mass balance; unit-operation capacities; equipment layout; and the functional, operational, and interface requirements for each processing line. The waste-processing lines treated aqueous liquids, organic liquids, wet solids, homogeneous dry solids, and heterogeneous dry solids external waste streams. Additional treatment lines included thermal treatment, final waste forms, and support operations that provided utility functions to the integrated plant. Figure 2 is the F&OR overall flowsheet.

These processing lines were highly integrated. The feedstream definitions were generic, leading to categories of wastes (gas, liquid, and solid) rather than specifying individual components. Liquids were further divided into organic and aqueous waste streams. Solids were, at times, divided into heavy and light combustibles, nonmetals (inerts), magnetic metals, and nonmagnetic metals. In performing the F&OR mass balances, assumed splits and conversions were entered into an Excel spreadsheet.

An associated flowsheet design was prepared by Bechtel under contract to LLNL using the baseline flowsheet and F&OR as its basis. This *MWTP Process Systems and Facilities Design Study and Cost Estimates*[2] (a.k.a. the Bechtel Design Study) contains more detailed subsystem process flow diagrams, equipment design, and sizing and cost information. The feed definitions were those defined in the F&OR document.

B. Modeling Approach

Several commercial software packages can model steady-state chemical processes. They perform complex mass and energy balances using thermodynamic equilibrium algorithms and can handle multiple recycle streams. They contain built-in codes that simulate typical processing equipment such as distillation columns, heaters, reactors, pumps, and filters. Most can access user-generated FORTRAN codes. The individual pieces of equipment are "piped" together to create the overall flowsheet. Modifications can be made by changing equipment blocks, redefining feed streams, and repiping the connecting streams. One advantage of these commercial software packages is the large chemical property data base supplied with them (typically containing over 2000 components). The user usually can supply data for components not in the data base.

The tool used for flowsheet modeling in this study, ASPEN PLUS[X] (hereafter called ASPEN), is a software package that simulates chemical processes. Its primary function is to perform mass- and energy-balance calculations over typical unit operations in chemical engineering processes. To perform these calculations, it accesses extensive data banks containing component physical and thermodynamic properties and applies them in physical property models selected by the user. Although originally developed for petroleum-industry calculations, ASPEN now includes specialized electrolyte- and solids-handling routines to increase its modeling capabilities.

In addition to mass and energy balances, ASPEN has other modeling and analysis capabilities. These include case-study and sensitivity analysis routines, calculation sequencing and convergence routines (automatic and user-specified), and feedforward- and feedback-loop modeling. The controller-like feedforward and feedback capabilities are handled through specialized convergence blocks. A feedback loop is modeled by a design specification in which an upstream quantity is varied to produce the specified downstream quantity. A feedforward loop is modeled by an inline FORTRAN block in which the downstream quantity is calculated directly from an upstream quantity. Inline FORTRAN also can be used to perform other calculations, call subroutines, and handle input/output (I/O). A package to perform costing calculations is also available. It should be noted that ASPEN is essentially a steady-state simulator, although it does have some kinetic reaction modeling capability.

A chemical-process model is developed in a graphical fashion by connecting unit operation blocks with streams. Then, feeds and block

operation and property models are specified. In many cases, unit operations may be performed on several levels of detail. For example, if component chemical formulas are known, a separation of organic and aqueous liquids may be modeled as a decanter, in which ASPEN calculates the separation using component physical properties contained in the data banks. If the component formulas are not known, the operation may be modeled as a black-box separation unit, in which the user specifies the split of each component between the two phases.

A team approach was taken in using ASPEN to model the first flowsheet. The team consisted of John A. Pendergrass and T. K. Thompson, representing Los Alamos, and Laura J. Dietsche and Ravindra S. Upadhye from LLNL. The first step was to model the F&OR flowsheet independently at each site and then compare the models and results. This allowed the team members to become well acquainted with the ASPEN modeling capabilities and provided a cross-check of our understanding of the processes and underlying assumptions for this baseline flowsheet. The second step would be to combine the best features from both of the site models into a single baseline model. This report summarizes the modeling work conducted at both LLNL and Los Alamos, compares the individual model results, and presents conclusions and recommendations resulting from the joint studies.

2. Flowsheet Modeling at LLNL

A. Introduction

Creating an ASPEN model requires a number of steps. The chemical components involved must be specified, and, in some cases, new components must be added to the data base. For each actual unit operation, the chemical or physical process involved must be evaluated, and a suitable ASPEN unit operation model (or models) must be chosen. The ASPEN unit models (also called blocks) are then connected, feed-stream flows and compositions are defined, and operating conditions are specified. Control or design specifications can be made by using the ASPEN design specification calculation (for feedback control) and FORTRAN statements (for feedforward control). The thermodynamic models to be used for each block or set of blocks must be specified, and the appropriate component properties must be supplied (if they are not already available in the ASPEN data base). Design specification and tear (recycle) stream conversion parameters also can be chosen, although ASPEN's default parameters are often appropriate.

B. Methodology

One goal of the Livermore ASPEN model of the MWTP baseline flowsheet was to model everything in as much detail as possible, including any necessary assumptions.

To fully use ASPEN's thermodynamic capabilities, including calculations of fluid-phase equilibria, the stream compositions must be well defined. Unfortunately, most mixed-waste streams are not well defined. They include an array of radioactive and nonradioactive components and can vary significantly from site to site. This is part of the reason why the MWTP baseline flowsheet and the F&OR deal with categories of wastes rather than with specific components.

Therefore, several assumptions are included in the components and feed stream definitions used in the ASPEN model of the MWTP baseline flowsheet. The aqueous portion of the feed streams is defined as water, and the liquid organic portion is a "cocktail" of common organics. The ultimate analyses of the combustibles in the streams entering the incinerators (provided in the F&OR) were used to estimate the composition of these cocktails. This is addressed in detail in the next section, Assumptions, of this chapter. Heavy combustible solids were modeled as wood, and light combustibles as paper. Because neither of these are in the ASPEN data base, appropriate thermodynamic properties had to be entered. These combustible solids were first reacted to an ultimate analysis product before being further reacted to a final combustion product using a Gibbs free energy minimization reaction. The combustion products were assumed and included in the component list. Nonmetallic solids were modeled as glass (SiO_2), magnetic metals as iron, and nonmagnetic metals as chromium and nickel. Other components were added as appropriate, such as polyethylene to represent the additive to the polymer final forms and $CaCO_3$ as the additive to the grout final forms.

The Livermore model also used ASPEN's ability to do electrolyte chemistry when modeling the aqueous streams. This included the reaction of CO_2 with water to form carbonic acid (and its associated ions) and the scrubbing of HCl with both water and NaOH. The formation of solid NaCl was also considered. The downside of going to this level of detail is having to deal with more difficult convergences and longer simulation times.

Converting the F&OR flowsheet operational blocks into an ASPEN model required breaking down the blocks into more fundamental unit operations. The Bechtel Design Study often was used to provide details missing in the F&OR. The method was essentially the same for each operational block.

One example of converting an F&OR block to an ASPEN model is the "Offgas Treatment" block found on the F&OR thermal treatment flowsheet shown in Fig. 3. The flowrates in and out are provided in the stream table at the bottom of Fig. 3. The F&OR text provides additional information as to what operations typically are involved in the further treatment of offgas, but it neither gives any details as to how this equipment is piped together nor supplies any operation specifications.

The Bechtel Design Study provides a possible piping scheme and some temperature, heat, and flowrate specifications, as seen in Fig. 4.

Figure 1. Original Mixed Waste Treatment Project baseline flowsheet.

Figure 2. Overall MWTP F&OR flow diagram.

Figure 3. Thermal and off-gas treatment flowsheet from the F&OR.

Stream Number	904T	829	828	827	826	825	824	823	822	821	820	819	818	817	816	815	814	813	812	811	810	809	808	807	806	805	804	803	802	801	311T	213T	211T
Temperature (°C)	1600	25	25	25	25	164	360	1475	1498	25	1600	575	25	49	49	49	100	1200	120	900	900	650	25	25	25	25	25	38	25	25	25	25	25
Pressure (psia)	14.0	14.7	14.7	14.7	14.7	14.7	20.0	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	11.0	14.0	13.5	14.0	14.0	14.0	14.0	14.0	14.7	14.7	14.7	14.7	14.7	14.5	14.7	14.7	14.7
Solids (kg/wk)	1.1	0	0	0	0	0	1324	50.0	1878	1086	77.9	1934	22638	0.2	445	0.4	445	395	48.3	19.6	70.9	4.6	70.7	72.7	2005	1995	25687	2533	1216	256	121	3.8	14.7
Liquids (kg/wk)	0	0	0	0	11700	0	0	0	0	0	0	0	0	0	0	0	0	8460	8469	0	0	0	0	0	1.5	0	6.1	0	6.1	0	6.1	463	819
Liquid Organics (kg/wk)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	463	819
Liquid H2O (kg/wk)	0	0	0	0	11700	0	0	0	0	0	0	0	0	0	0	0	0	8460	8460	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Liquids (kg/wk)	3490	10470	0	0	0	287	45532	0	0	0	0	0	0	0	0	0	0	92670	10470	75470	7966	15335	12167	3608	0	1995	2005	25687	2533	1216	23912	0	0
Liquids (kg/wk)	3491	10470	0	50.0	50.0	11700	287	45532	1324	50.0	1878	1086	77.9	1934	22638	10.5	8905	8041	75865	10519	9267	15335	12238	3613	74.2	1999	2005	25687	2533	1222	24168	584	823

Column stream descriptions (left to right): Final Forms Off-gas, Inleakage Air, Auxiliary Fuel, Misc. Trash, Makeup Water, Atomizing Steam, Combustion Air, Ferrous to Lead Solids Treatment, Nonferrous to Hetero Cleaned to Final Forms, Bottom Ash, Slag, Ferrous to Final Forms, Inerts to Final Forms, Mercury to Recovery, Aqueous Treat. Blowdown to, Separate Hg Scrb Soln. to, Off-gas to Atm. Protection, Hg Condensation Off-gas, Second Chamb. Off-gas, Nonmetallics Off-gas, Low-Residue Off-gas, High-Residue Off-gas, Heavy Organics Off-gas, Mercury Wastes, Nonferrous Metals, Ferrous Metals, Nonmetallic Solids, Light Combustibles, Off-gas from Heavy Combustibles, Wet Solids Off-gas, Heavy Organics, Concentrated Organics.

Figure 4. Process flow diagram for thermal treatment secondary combustion and off-gas.

Figure 5. Thermal off-gas treatment flowsheet from the LLNL ASPEN Model..
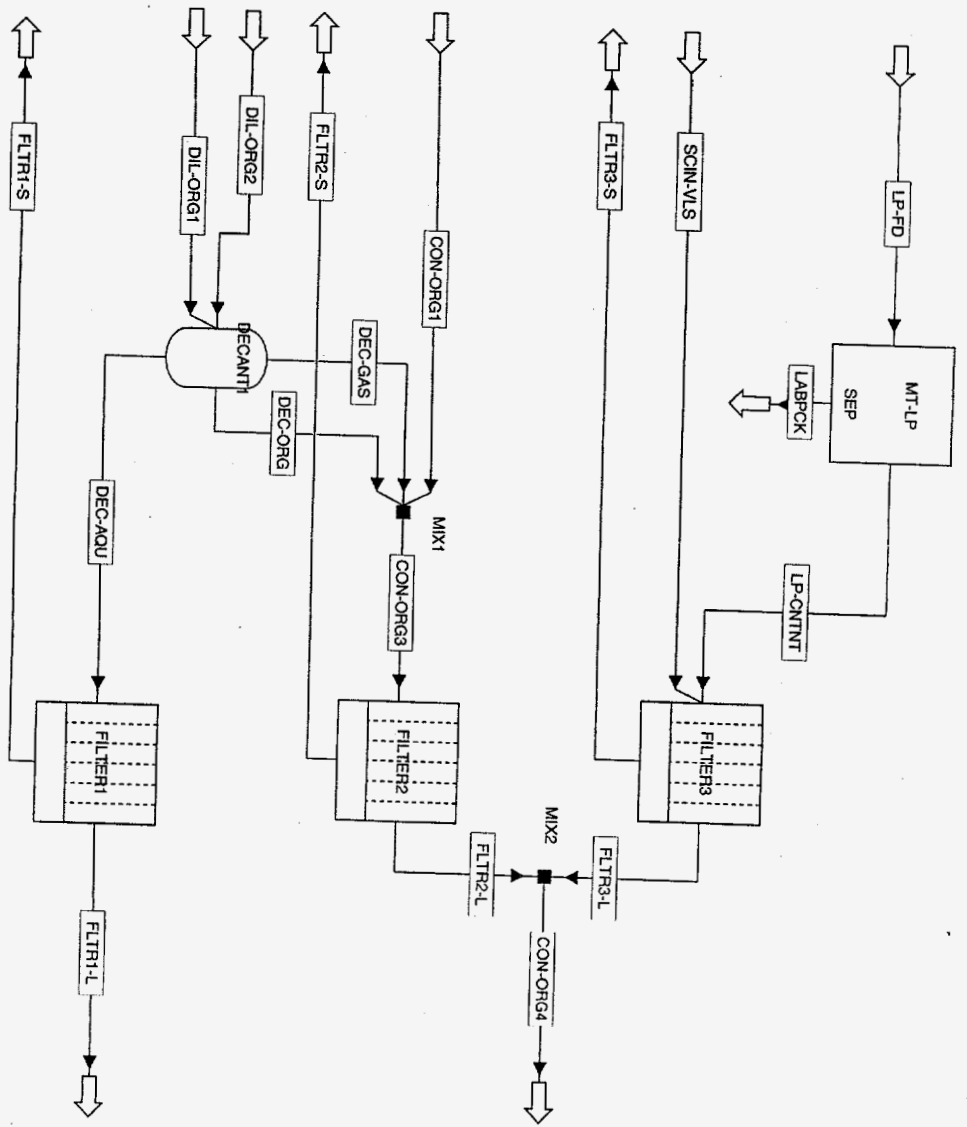
Figure 6. Organic feed preparation flowsheet from the LLNL ASPEN Model.

Figure 7. Organic thermal processing flowsheet from the LLNL ASPEN Model.

Figure 8. Thermal and system offgas treatment flowsheet from the LLNL ASPEN Model.

Figure 9. Aqueous feed treatment flowsheet from the LLNL ASPEN Model, Version 1.

Figure 10. Aqueous feed treatment flowsheet from the LLNL ASPEN Model, Version 2.

Information from both of these reports was used to create the ASPEN flowsheet shown in Fig. 5.

The offgases from the secondary combustion chamber, the final forms mixers, and the solids melters first are sent through a quench column, then through a venturi scrubber, and finally through an aqueous absorber column. "Fresh" water (recycled from the aqueous treatment system) is fed to the absorber column, the bottoms stream from the absorber is used as the quench column makeup water, the aqueous purge from the quench column is sent to the venturi scrubber and finally back to the aqueous treatment system.

The quench column was modeled as a simple FLASH2 (two-phase flash) block, where the heat from the incoming offgas is transferred to the cooling water. A certain fraction of the solids is assumed to be entrained in the vapor outlet stream. The temperatures of the quench outlet streams and the cold recycled water stream were taken from the Bechtel Design Study report. The amount of recycled water is determined by a design specification that makes the quench column adiabatic; i.e., the actual heat removal occurs in the quench recycle stream heat exchanger.

The venturi scrubber is also modeled as a FLASH2 unit to remove most of the remaining solids from the vapor stream. ASPEN has a more detailed venturi model available, but it requires information about the particle size distribution of the solids that was not readily available. This is one of the many refinements that could eventually be made to this model. The solids are filtered out of the aqueous outlet stream from the venturi with a SEP (component separation) block, and part of the stream is recycled back to the venturi. The amount of recycle is again determined by a design specification to obtain a typical venturi water-to-gas ratio.

The absorber is modeled by a RADFRAC (rigorous multistage distillation column) block with no reboiler or condenser. The number of stages is only estimated at this point and could be refined later. The recycle stream around the absorber column is held constant at a rate estimated from the pump capacity in the Bechtel report. The amount of "fresh" water added to the absorber is determined from a design specification to control the amount of HCl in the final offgas. Several process specifications that were not available in either the F&OR or the Bechtel Design Study reports had to be estimated.
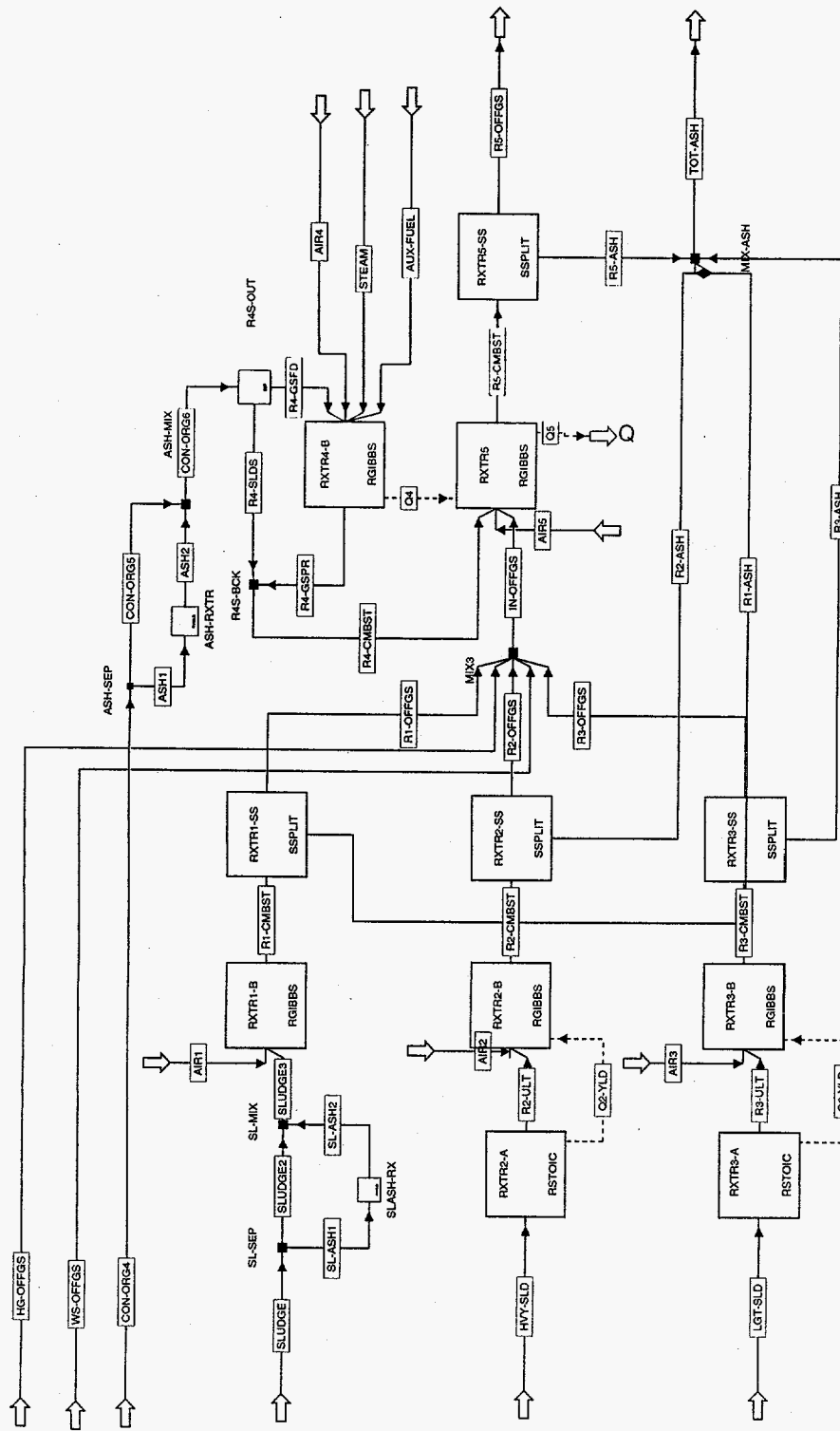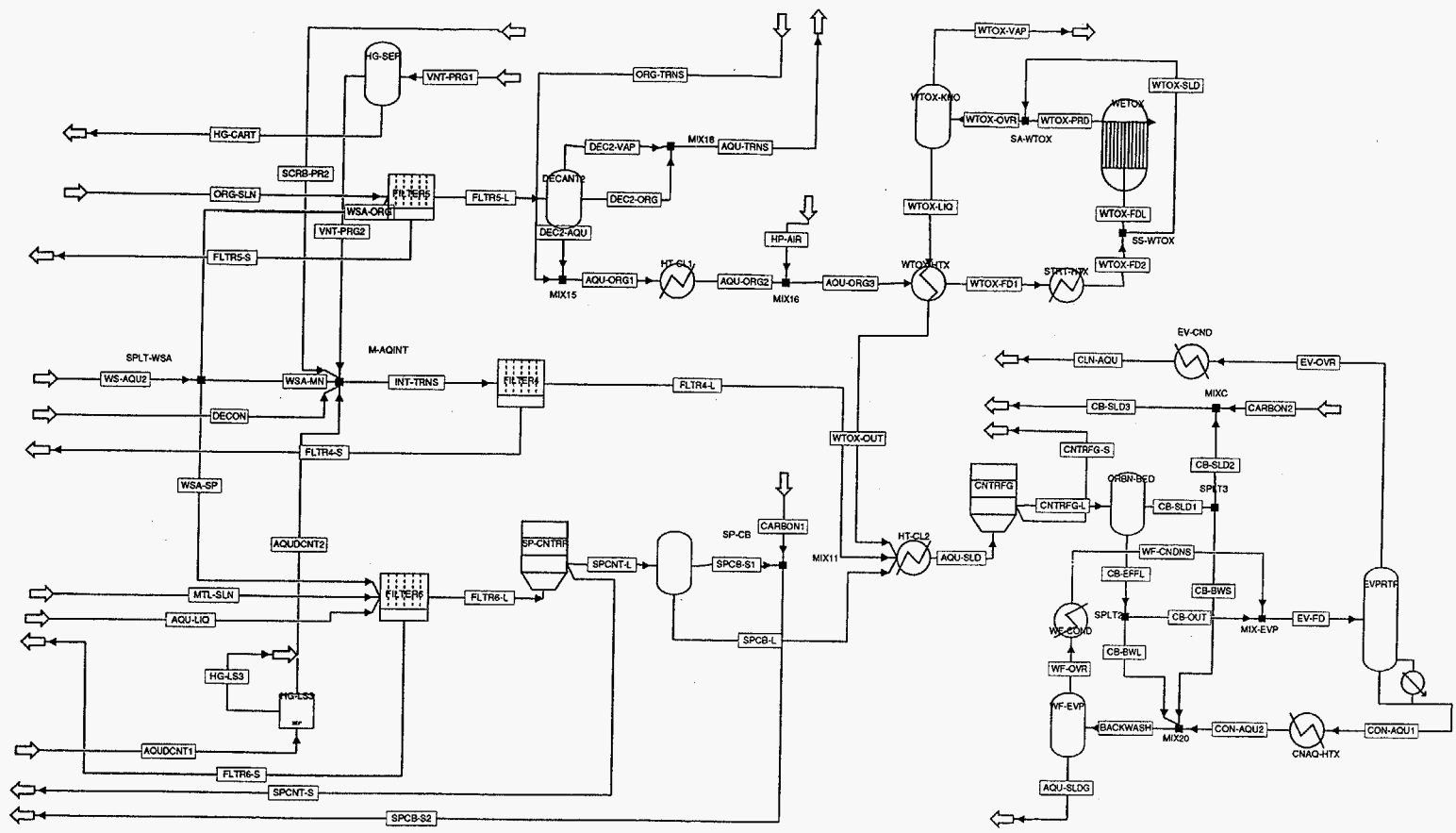
The ASPEN model was initially created in sections, which were then linked to form the overall MWTP baseline model. Figures 6 through 12 show flowsheets for the individual sections. The organic feed preparation blocks formed one section, and the organic incinerators formed a second section. The offgas treatment system for both the thermal offgas and the offgas going to the final atmospheric protection system made up a third section. These three sections were initially linked and modified to obtain convergence. The aqueous feed treatment system was created next and added on. Two different versions of the aqueous flowsheet were created. One uses the secondary polishing method suggested in the F&OR: ion exchange. The other uses an evaporator for secondary polishing, as indicated in the Bechtel Design Study. The overall flowsheet contains the ion-exchange version for now. The fifth section to be modeled combined the solids thermal treatment and final forms processing equipment. The sixth and final section for the ASPEN model included equipment for drying the wet solids.

A few of the connecting tear (recycle) streams between sections and one of the recycle streams within the offgas treatment section were left unconnected during most of the development to avoid convergence problems and long (e.g., 24-hr) simulation times. These included the streams going from the wet solids drying section to the aqueous processing section; the incinerator; the final atmospheric protection system's scrubber bottoms stream, which was recycled back to the aqueous treatment section; and the purge stream from the thermal offgas absorber, which became makeup to the quench column. Feed streams were created that approximated the composition and flowrate of the connecting stream.

C. Assumptions

The MWTP baseline flowsheet is still in a preliminary design stage requiring numerous assumptions to be made when defining feeds and determining the specs in the ASPEN model. Most of the assumptions are based on information contained in the F&OR or Bechtel Design Study reports, but many of the assumptions are based on "engineering judgment" or intuition. The ASPEN program input file contains numerous comment statements that specify most of the

assumptions made. This section outlines the assumptions that required significant leaps from the F&OR or extensive calculations.

The F&OR states flowrates on a per-week basis (using a 60% on-stream factor) to allow flexibility in operation scheduling. The ASPEN model has been converted to an hourly basis assuming a 168-hr/wk (24-hr/day, 7-day/wk) operating schedule. This can be easily modified by placing an ASPEN multiplier block in each of the feed streams using the same multiplication factor, or by using the report scaling option to scale all of the streams in the report to a specified stream and flowrate.

This brings up an important point about ASPEN modeling in general. ASPEN is a continuous-process modeling program. It does not model batch processes except for batch reactors (given reaction-rate data) with surge tanks on either side connecting it to continuous equipment. Because of the small size of many of the mixed-waste streams, some of the mixed-waste treatment units may be run either batch or in a "batch-continuous" (campaigned) mode. The batch-continuous equipment can be modeled by running different cases with the campaigned flows either "on" or "off."

ASPEN cannot model truly batch equipment. As a case in point, the sludge (or heavy organics) incinerator is specified to be run batchwise with a slowly increasing temperature profile and a changing air flowrate. This will volatilize and oxidize the organics first in increasing molecular weight, then oxidize the steel drums at a higher temperature. The ASPEN model treats this as a continuous process using an average temperature given in the stream table in Fig. 3.

As already mentioned, the liquid organic stream compositions were based on the ultimate analysis information given in the F&OR for the combustible portion of the incinerator feed streams. Common organic compounds were formulated into a "cocktail" to simulate the F&OR organic feed streams. Nitrogen was obtained from acetonitrile (C_2H_3N), sulfur from methyl mercaptan (CH_4S), and chlorine from carbon tetrachloride (CCl_4). Oxygen came from ethanol (C_2H_6O), methylethylketone (C_4H_8O), or glycerol ($C_3H_8O_3$). Benzene (C_6H_6) and N-octane (C_8H_{18}) were used to complete the carbon and hydrogen balances.

For the sludge feed stream (F&OR stream #213, Heavy Organics) this was a fairly straight-forward exercise. In this case, glycerol was used to supply the oxygen in an attempt to create a more viscous (supposedly unpumpable) stream, but the resulting cocktail was not extremely viscous. SiO_2 was added to the organics to represent the solid inerts, and 0.5% of the total mass was specified to be mercury. Iron and chromium were added to represent the drums, which were incinerated along with their contents.

For the liquid organic stream entering RXTR4B, the concentrated organics burner (F&OR stream #211, Concentrated Organics), the creation of the appropriate organic cocktail was a little more involved because this stream is a combination of a number of streams coming from filters and decanters, including recycle streams from other sections of the flowsheet. In this case, the desired composition of the burner feed cocktail could be determined, and estimates of the contributing feed-stream organic compositions could be made to obtain this cocktail while maintaining the organic flowrates of the contributing streams found in the F&OR. Several iterations and modifications were required to get close to the desired final cocktail composition.

One stream that contributed to the organic burner stream, the labpack and scintillation vial streams (F&OR #202, concentrated organics to solids separator), required additional assumptions because of missing information in the F&OR. Apparently, the flows reported in the stream table did not account for the labpacks, absorbents, vials, etc., resulting in a low solids-phase flowrate.

In this case, the Livermore ASPEN model assumes that the liquid organic flowrate given in the F&OR stream table is correct as 240 kg/wk. The labpack waste stream was specified in the F&OR to be 3.5 wt% of the total drummed organics, giving a labpack stream a net weight of 49.4 kg/wk. From a surrogate waste-stream definition given in a Mixed Waste Integrated Program (MWIP) document,[3] the labpack contents were assumed to be (by weight) 60% organics, 20% bottles, 16% absorbent, and 4% other solids (e.g., Pb, Cr, Fe, and Hg). Assuming that the labpacks themselves are 10% of the total labpack stream weight. This allows one to determine the labpack stream composition. The remaining organics in F&OR stream #202 are assumed to be contained in the scintillation vial stream. The F&OR specifies that the scintillation vial drums are 75% full (total drum volume is $0.208 \, m^3$) with a net weight of 125 kg/drum. The

occupied volume is 50% vials and 50% liquid (assumed to contain 5% dissolved or suspended solids with an overall density of 0.9 g/mL). These assumptions allowed the determination of a scintillation vial stream composition.

The F&OR stated oxygen requirements for the incinerators in terms of percent of that required for total combustion. These requirements were translated as design specification in the ASPEN model. When a specification of 100% of stoichiometric air was made, the design specification was set up to adjust the incoming air so that the flow of O_2 out equaled 1% of that entering the incinerator. This allows for 102% of stoichiometric air, since 100% would result in no O_2 exiting, which would be satisfied by any amount of air less than or equal to the stoichiometric amount. When 200% of stoichiometric air was specified, the design specification required that the flow of O_2 exiting the incinerator be half of that entering. The design specification became a little more complicated when 50% of stoichiometric air was required. In this case, one would expect to see essentially no oxygen in the exiting gas stream but would expect substantial amounts of CO and only a small amount of CO_2. We assume that most of the oxygen is being used to oxidize carbon and hydrogen, which will, of course, depend on the composition of the organics being oxidized, but which should be the case for the ultimate analyses provided in the F&OR. The carbon reaction can then be represented by

$$nC + fnO_2 \rightarrow xCO_2 + (n - x)\, CO , \qquad (1)$$
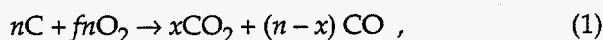
where f is the fraction of oxygen that would be needed for the complete combustion of carbon to carbon dioxide, which is being consumed by this reaction. An oxygen atom balance for this reaction gives

$$x + (n - x)/2 = fn . \qquad (2)$$

Similarly for hydrogen, we have

$$mH_2 + gm/2\, O_2 = gmH_2O + (m - gm)H_2 . \qquad (3)$$
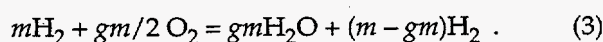
where g is the fraction of oxygen that would be needed for the complete combustion of hydrogen to water, which is being consumed by this second reaction. The oxygen atom balance for this reaction does not provide any new information. The total oxygen consumption can be represented by

$$fn + gm/2 = F(n + m/2), \qquad (4)$$

where F is the fraction of oxygen that would be needed for the total combustion of both carbon and hydrogen, which is being consumed by both reactions. Equations (2) and (4) can be combined and rearranged to give

$$x = \frac{(2F - 1)(n - x)}{2(F - 1)} + \frac{F(m - gm)}{2(F - 1)} - \frac{gm}{2} . \qquad (5)$$

From these reactions, it can be seen that x will equal the CO_2 concentration in the incinerator offgas, $(n - x)$ will equal the CO concentration, $(m - gm)$ the H_2 concentration, and gm the H_2O concentration. When $F = 0.55$ (55% of stoichiometric air required), we obtain the design specification equation

$$[CO_2] = 0.11[CO] + 0.61[H_2] + 0.5[H_2O] . \qquad (6)$$

This equation was used for the sludge (heavy organics) incineration in RXTR1. Although not exact, it should provide an amount of air close to that desired.

The ASPEN electrolyte thermodynamic package uses Henry's law to determine the vapor composition in equilibrium with the aqueous liquid. When soluble or entrained organics are present in the aqueous stream (even in very minute amounts), Henry's-law constants must be provided for these organics in order to perform vapor–liquid equilibrium (VLE) calculations. Since most of these organics are not very soluble in water, it is difficult (or impossible) to find published values for the Henry's law constants (or the associated VLE data).

To provide some data, we assumed that the water would not have a strong influence on the organics and therefore that the mole fraction of the organics in the vapor would equal that in the liquid; i.e., we assumed that the Henry's law constant was equal to the vapor pressure of the organics.

ASPEN requires that the Henry's law constant H be given in the form $\ln H = a + b/T + c\ln T + dT$, where T is the absolute temperature and a, b, c, and d are empirical constants. It was assumed that c and d were zero, and the values of a and b were correlated with vapor pressure data found in the *Handbook of Chemistry and Physics*.[4] Table 1 gives the results.

Table 1. Assumed Henry's law empirical constants a and b for various organics.[a]

Organic	a	b (K^{-1})	r^2 [b]
Carbon tetrachloride	10.61	–3738.8	–0.9996
Octane	11.33	–4541.7	0.9995
Dodecane	12.70	–6187.8	–0.9999
Methyl mercaptan	10.52	–2938.4	–0.9999
Acetonitrile	11.14	–3953.5	–1.0000
Benzene	10.85	–3849.2	–0.9997
Ethanol	13.52	–4779.5	–0.9995
MEK	11.17	–3936.7	–1.0000

[a] The Henry's law equation is $\ln H = a + b/T$), where H is in atmospheres and T in kelvins. The correlation assumes that the Henry's law constant H approximately equals the pure component vapor pressure.
[b] Statistical fit to the vapor pressure data found in Ref. 4.

Table 2. VLE data[5] and corresponding Henry's law constants for ethanol in water.[a,b]

T (K)	x	y	P (kPa)	$H = yp/x$ (atm)
303.15	0.05	0.478	10.46	0.1
323.15	0.05	0.505	29.53	0.3
343.15	0.05	0.522	72.53	0.8
363.15	0.05	0.531	158.65	1.7

[a] The empirical constants for the Henry's law equation, $\ln H = a + b/T$, are also given, where H is in atmospheres and T is in kelvins.
[b] $a = 14.86$, $b = –5198.4$, $r^2 = –0.9999$.

This approach will most likely be in error for highly soluble organics. For the organics we are using, the most soluble are ethanol and methylethylketone (MEK). Table 2 gives solubility and VLE data on ethanol[5] and the calculated Henry's law constants as functions of temperature. The mole fractions of ethanol in the liquid and vapor phases are very close, as was assumed in using the vapor pressure approach to evaluating the Henry's law constant. Indeed, the values of a and b are very close for the two approaches. This was very encouraging. However, VLE data for MEK in water[6] given in Table 3 show an order of magnitude difference in the liquid and vapor phase mole fractions of MEK because of hydrogen bonding in the liquid phase. There is not enough data to do an accurate regression on a

Table 3. VLE data[6] and corresponding Henry's law constants for MEK in water.

T (K)	x	y	P (kPa)	$H = yp/x$ (atm)
98.84	0.00175	0.0427	101.325	24.72
99.65	0.00100	0.0142	101.325	14.39

and b from these data, but they could be significantly different from the values determined from the vapor pressure data. For lack of any better VLE data on MEK, we will continue to use the vapor-pressure approach.

The electrolyte calculation package seemed to have considerable trouble handling liquid mercury in the aqueous stream. The mercury in streams entering an aqueous section of the flowsheet (Aqueous Treatment, Offgas Treatment, and Wet Solids Drying) was therefore moved to the conventional solids phase or substream and was thereafter treated as a solid. This seemed at least somewhat reasonable, because mercury should sink to the bottom of any aqueous stream, although the possibility of reactions to form soluble salts containing mercury (such as HgCl) should be considered in future models. When mercury vapor–liquid or liquid–liquid equilibrium calculations were required (in the nonaqueous section of the flowsheet), the mercury was moved back to the "mixed" substream.

One of the systems that differed between the F&OR and the Bechtel Design Study was the mercury removal and cleanup system. In both cases, the aqueous letdown from the thermal offgas treatment system passes through a mercury separation unit before being recycled to the aqueous treatment section. The spent cartridges contaminated with mercury are sent, along with any solid inert or metallic wastes known to contain mercury, to a mercury bakeout furnace. The offgases from this furnace go through a condenser and knockout pot to condense out the mercury.

The F&OR condenser operates at 120°C, allowing water and some mercury vapor to return to the secondary combustion chamber and offgas treatment system. The condensed mercury is distilled to recover a reusable mercury stream overhead. The still bottoms are reacted with sulfur to produce cinnabar, which is then encapsulated into a final form. The Bechtel process
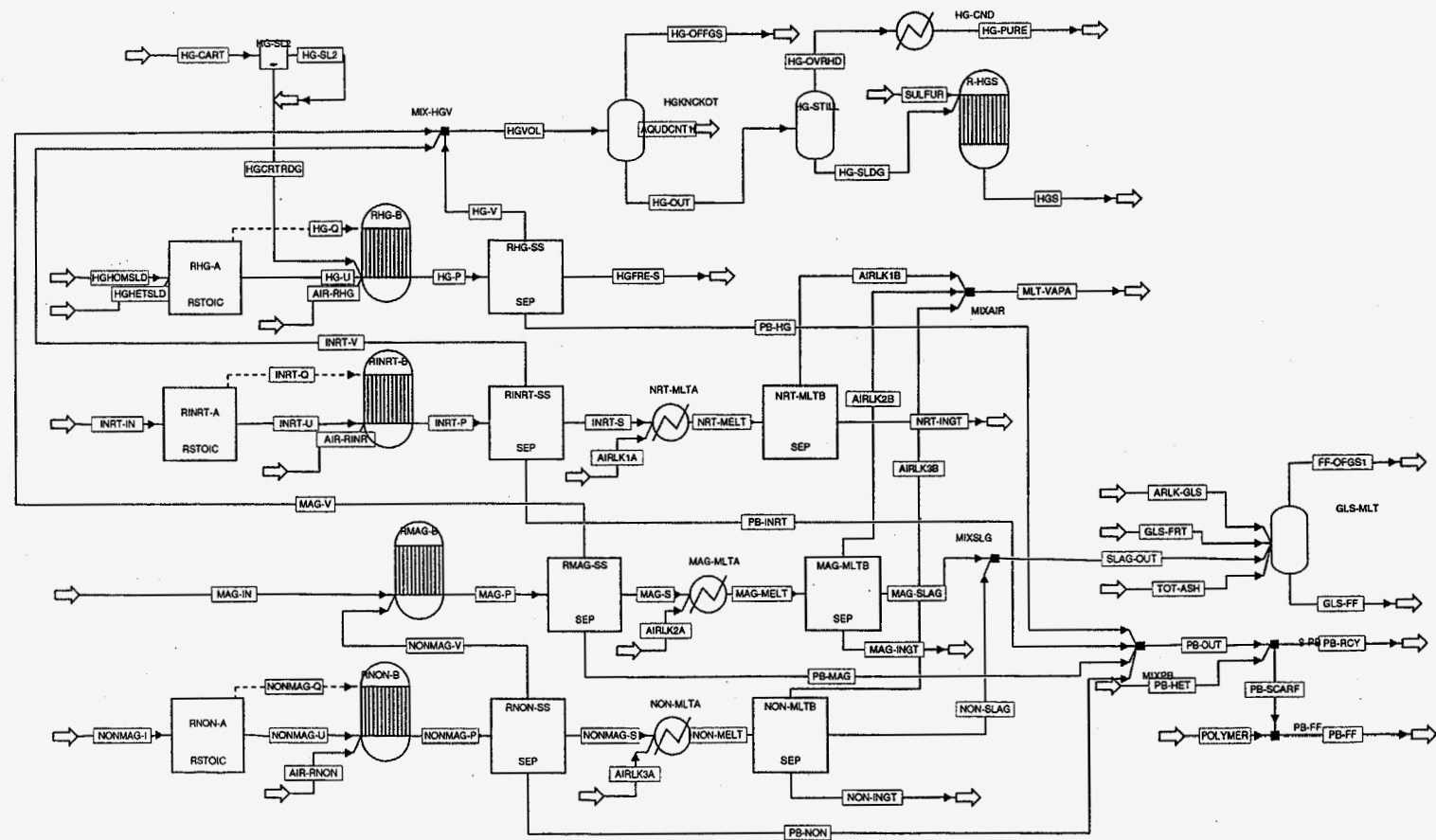
Figure 11. Nonorganic solids thermal treatment and final forms flowsheet from the LLNL ASPEN Model.

Figure 12. Wet-solids drying flowsheet from the LLNL ASPEN Model.

operates the condenser at 10°C, removing most of the water and mercury from the offgas stream. The water forms a liquid layer on top of the mercury and is decanted and sent to the aqueous treatment section. If the mercury layer is pure enough, it is recycled as is; otherwise, it is further distilled, with the bottoms reacted to cinnabar (without further encapsulation).

The offgas from the condenser is sent through a Boliden/Norzink processing system to remove any remaining mercury before going to the secondary combustion chamber. This patented process involves scrubbing the offgas with a mercuric chloride ($HgCl_2$) solution to form mercurous chloride (Hg_2Cl_2), which precipitates. Part of the mercurous chloride is treated with chlorine to form more mercuric chloride, which is then recycled back to the scrubber. The rest is removed as a sludge.

In comparing the F&OR and the Bechtel flowsheets for mercury handling, the ASPEN modeling team felt that purification of the condenser offgas using the Boliden/Norzink process was not warranted, because mercury is also contained in other feed streams to the secondary combustion chamber. However, this process might be useful as a first step in the thermal offgas treatment system.

In order to model the Boliden/Norzink process using ASPEN, more processing information is required than is provided in the Bechtel Design Study. Therefore, a literature search on the process was performed. The results of this search are provided here to allow the Boliden/Norzink process to be included in future MWTP ASPEN models. The patents involved are found in Refs. 7, 8, and 9. Reference 10 is an article on the process development, and Ref. 11 describes an application of the process. References 12, 13, and 14 list properties of mercuric and mercurous chloride. Since the reactions occur in aqueous solutions, the ASPEN electrolyte package probably should be used to model this process.

Another difference between the F&OR and the Bechtel Design Study is the composition of the aqueous stream going to the final atmospheric protection system scrubber. The F&OR uses pure water, whereas the Bechtel Design Study uses a 10% caustic (NaOH) solution. The LLNL ASPEN model uses the Bechtel approach for this system. The amount of caustic added is adjusted so that 30% of the caustic is consumed in scrubbing the acids in the offgas.

D. Results and Observations

The Livermore ASPEN model of the MWTP baseline flowsheet model is completely connected except for the recycle streams coming from the wet solids drying system and going to both the organic thermal section and to the aqueous processing section. When these final two streams were connected, the ASPEN input translator froze, so that the model could not be run. This is a problem that has not yet been solved. Meanwhile, input streams with compositions very close to these recycle streams are being used to approximate closure.

A number of observations can be made from the Livermore ASPEN run results. The F&OR permitted an auxiliary fuel stream to be added to the burner for the secondary combustion chamber to provide additional heating capacity to the concentrated organics stream, so that complete combustion would take place in the combustion chamber. The amount of auxiliary fuel was not calculated, because no energy balances were performed for the F&OR. The ASPEN run was able to determine the auxiliary fuel requirements by using a design specification calculation that required the secondary combustion chamber to be adiabatic (at the temperature specified in the F&OR). An auxiliary fuel rate of 6.5 kg/hr was calculated, compared to a flowrate of 5 kg/hr for the concentrated organics. The auxiliary fuel requirements are thus significant. A sensitivity study was performed that helped to determine one of the major users of the auxiliary fuel's heat input. In this study, the flowrate of the wet solids offgas to the secondary combustion chamber was varied from 20 to 160 kg/hr, and the resulting auxiliary fuel requirements determined. Figure 13 shows the results. The auxiliary fuel requirements varied linearly with the wet solids offgas flowrate, dropping to zero when the wet solids flowrate was less than about 16 kg/hr. Thus, most of the auxiliary fuel is being used to heat this offgas stream, which comes in cold and has very little heating value.

The wet-oxidation reactor is another place where additional heat input is required. Normally one would expect that enough heat is generated in the oxidation reactor to allow the liquid product to be used to preheat the feed, so that no other heat input would be required after startup. However, the current simulation does not yield a large enough combustible fraction of the feed stream to provide all the heat needed,
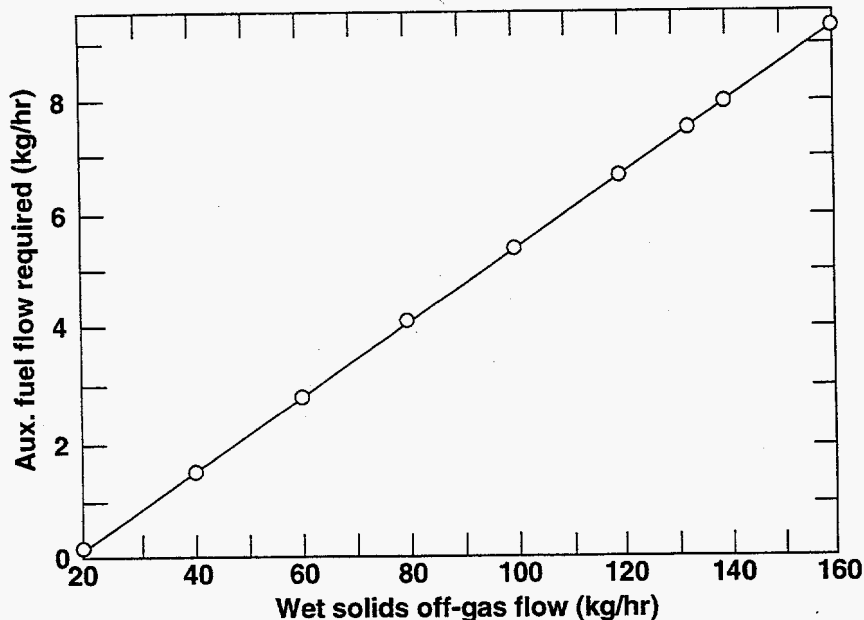
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Figure 13. ASPEN Sensitivity Study results for the auxiliary fuel requirements.

thus requiring a small continuous heat duty from the startup heater. The presence of more water-soluble organics, or less efficient decanters, could easily change this situation. It should be noted that the F&OR assumes a much higher (by an order of magnitude) amount of entrained organics in the aqueous stream out of the aqueous treatment line decanter than is determined by ASPEN using these model organics.

The ultimate goal of a mixed waste treatment facility is to produce environmentally acceptable final waste forms. The solid wastes are encapsulated in various media (polymer matrix, grout, glass, etc.). The acceptability of these waste forms is based on various strength and leaching tests. Two other output streams that can be evaluated for acceptability from the ASPEN results are the stack gases and the aqueous purge stream. The stack gas composition determined from the ASPEN simulation is mostly N_2 and O_2 (as expected), with 830 ppm water, 220 ppm CO_2, 0.9 ppm NO_x (consisting of NO, NO_2, and N_2O), 0.5 ppm SO_2, 20 ppb organics, and trace amounts of CO and H_2. The acceptability of this stream will depend on air-quality regulations.

Most of the organics in the stack gases originate in the water input to the absorber and scrubber. This water is recycled from the aqueous treatment section. Water from this section is also recycled to the wet solids drying system (to aid in removing the wet solids from the drums and

create a slurry). A small purge stream remains (170 kg/hr out of 935 kg/hr total coming from the ion exchange column), and this might be used elsewhere in the plant or be discharged. The composition of this purge stream from the current ASPEN run includes approximately 0.1% dissolved NaCl and 0.8% NaOH. The caustic comes from the scrubber effluent (approximately 13% NaOH), which could be neutralized as it enters the aqueous treatment system, thereby increasing the pH of the downstream aqueous streams. The aqueous purge stream from the ion exchange column also contains some dissolved gases and approximately 15 ppm organics. The need for further treatment to remove some of these components before discharge would need to be evaluated.

As already mentioned, a second aqueous treatment flowsheet was created in which the ion exchange column was replaced by an evaporator to provide secondary polishing of the aqueous stream. The aqueous purge stream from this process is free of NaCl and NaOH, but has a five-fold increase in organics. This is one of the design options that must be evaluated further.

E. Possible Improvements

Several improvements could be made to the Livermore ASPEN model. First of all, more-realistic feed streams definitions would help to

Figure 14. Aqueous liquids treatment from the Los Alamos ASPEN Model.

Figure 15. Organic liquids treatment from the Los Alamos ASPEN Model.
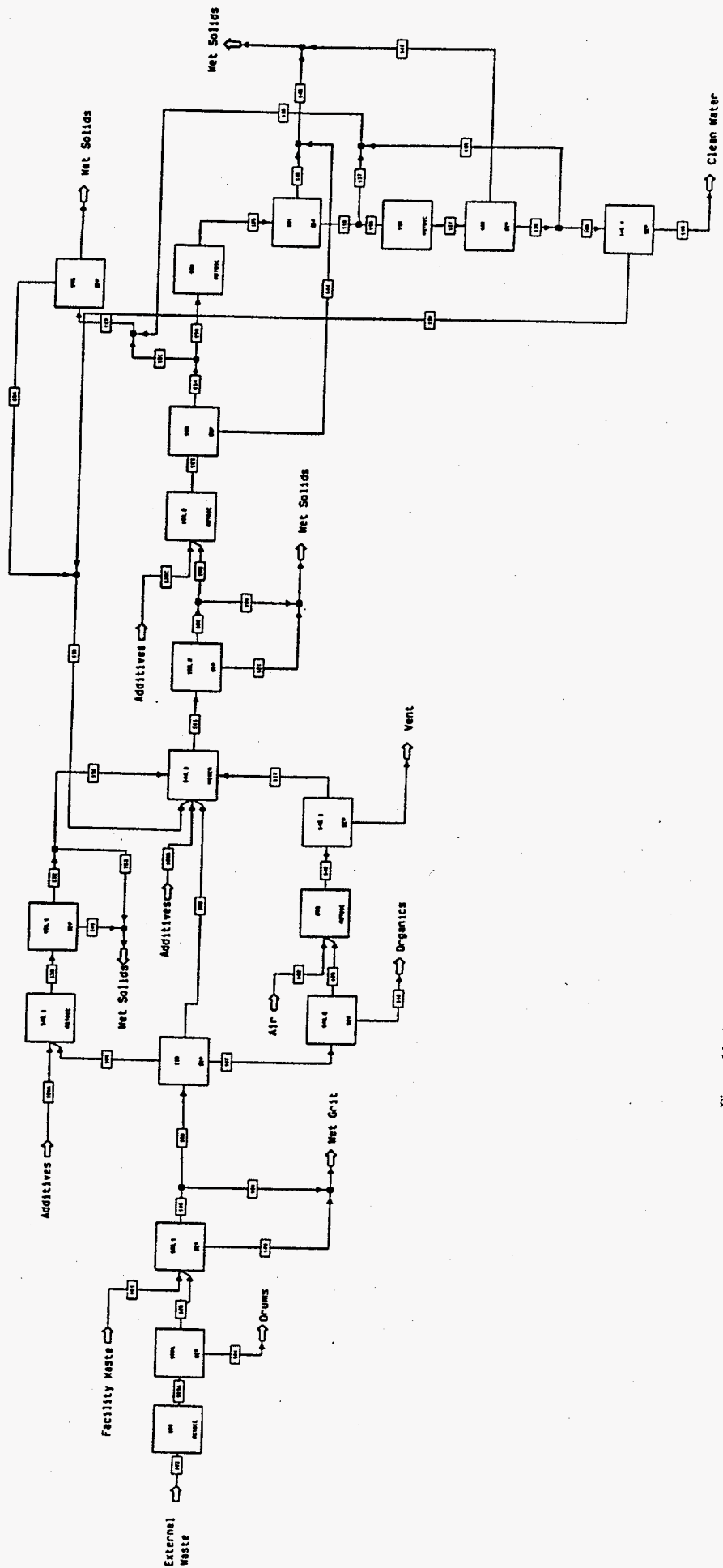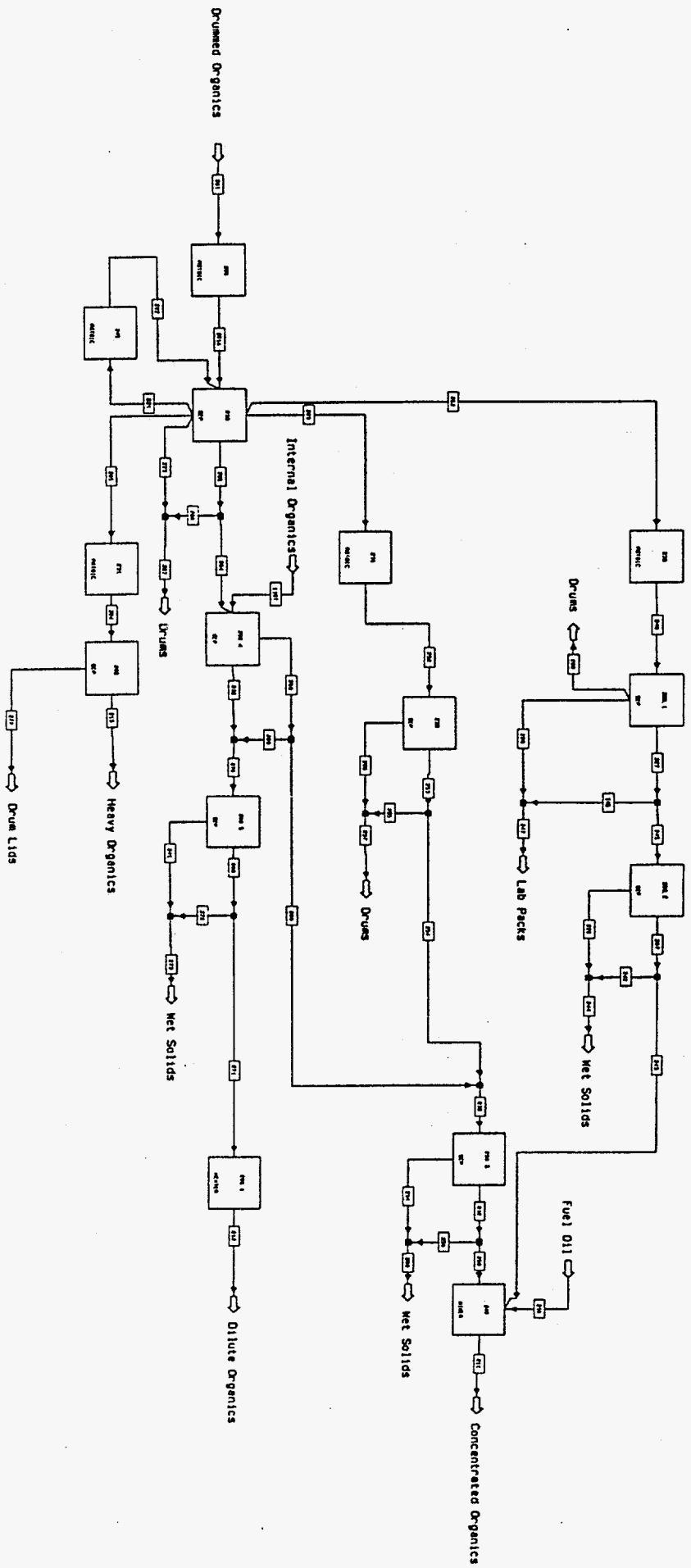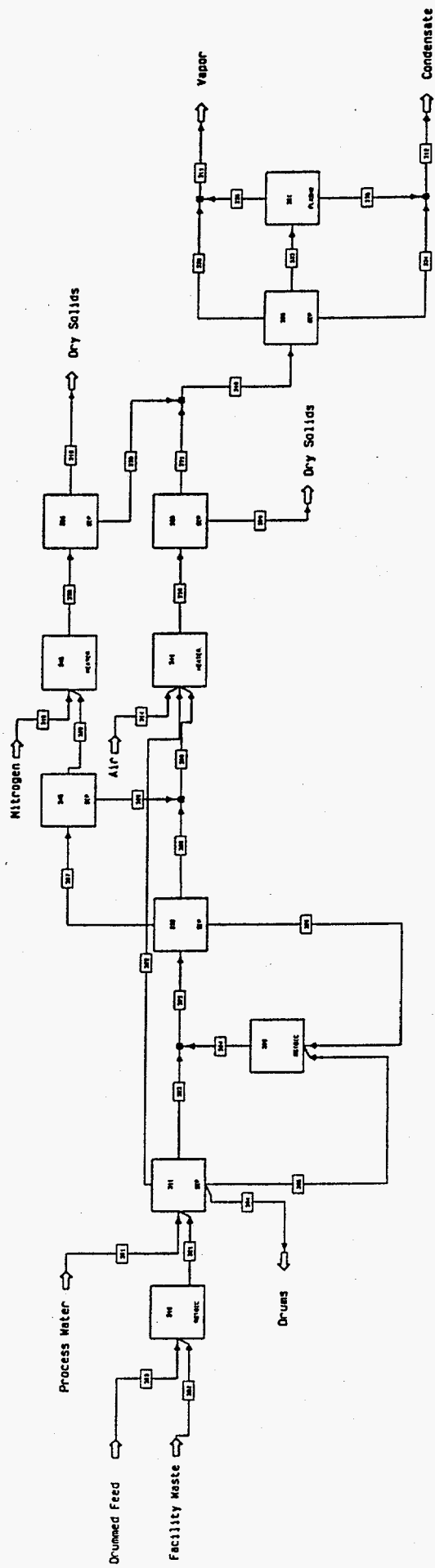
Figure 16. Wet solids treatment from the Los Alamos ASPEN Model.

Figure 17. Homogeneous dry solids treatment from the Los Alamos ASPEN Model.
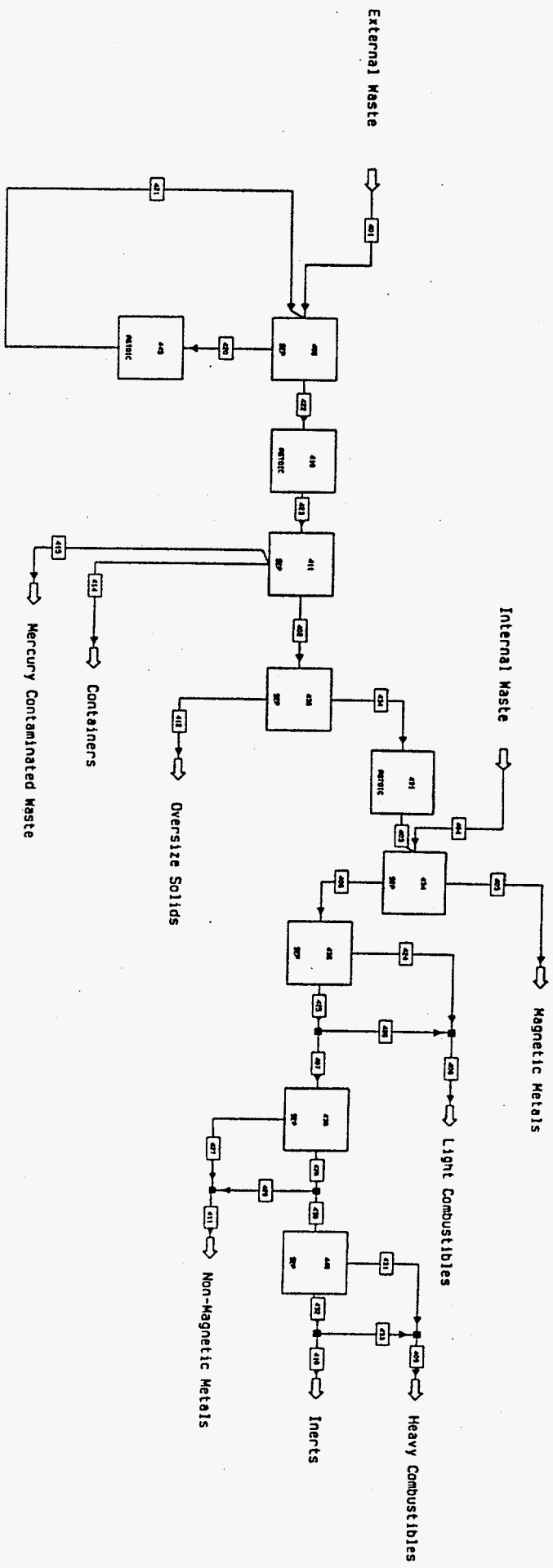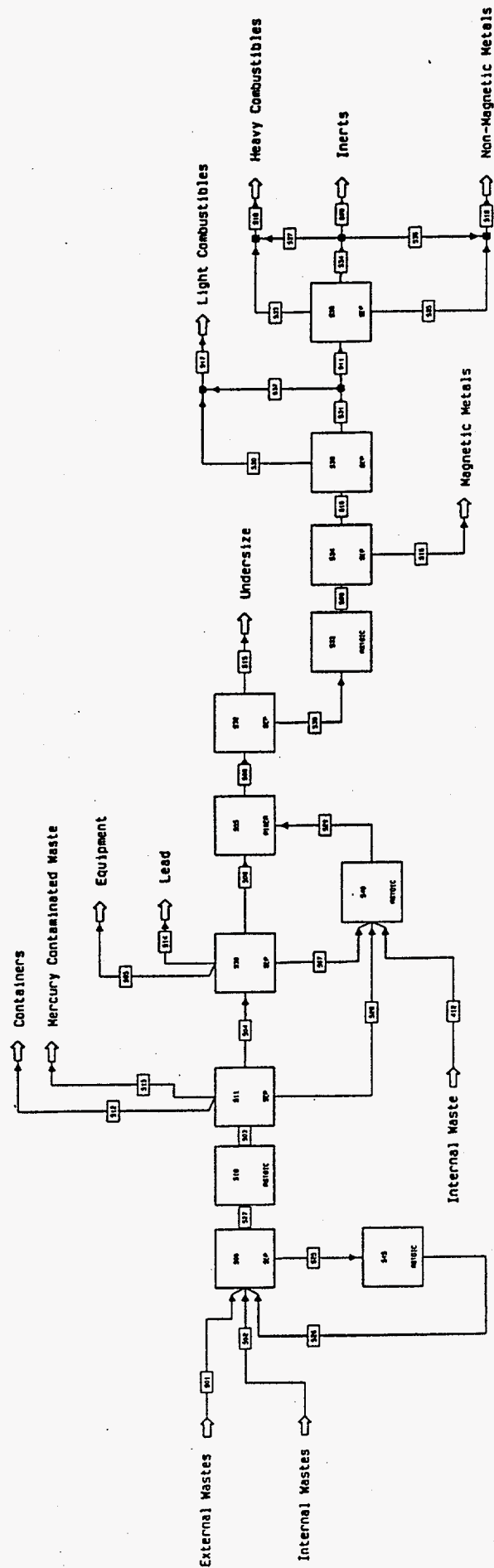
Figure 18. Heterogeneous dry solids section from the Los Alamos ASPEN Model.
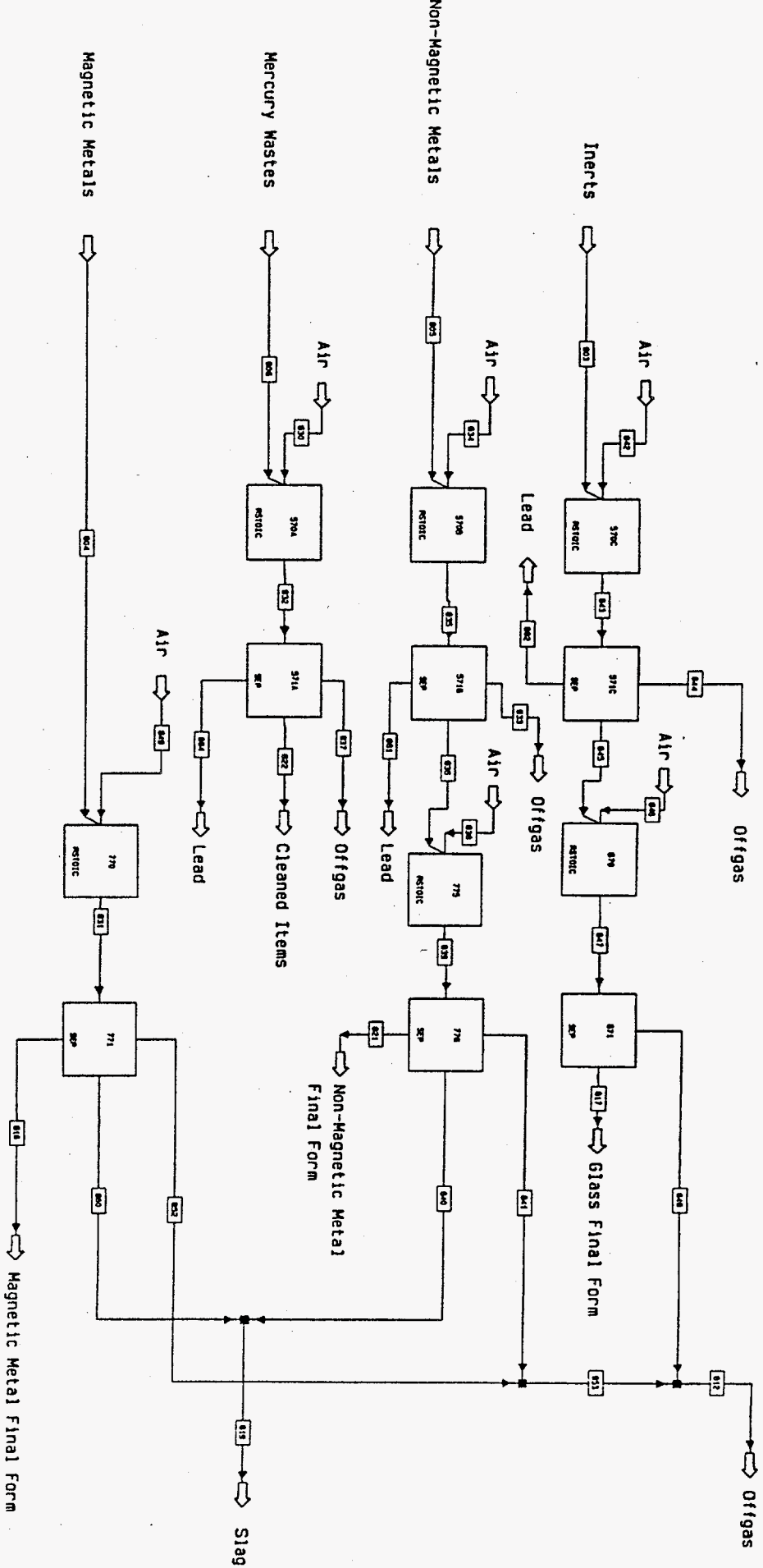
Figure 19. Inorganic solids thermal treatment from the Los Alamos ASPEN Model.

Figure 20. Organics thermal treatment from the Los Alamos ASPEN Model.

better define the process requirements throughout. A number of components are only very loosely defined at this point, such as the composition of glass, grout, polymer, and ash.

If solids size distribution data were available, ASPEN's solids handling capabilities could be better used. The venturi scrubber in the offgas treatment system could be modeled by ASPEN's VENTURI block rather than by a FLASH2 block, the centrifuges could be modeled by a CENTRI-FUGE block rather than a black box solids separator (SSPLIT), and the filters could all be more precisely modeled. These more-detailed solids blocks also require more-detailed equipment specifications, which would require additional information or assumptions.

The absorber and scrubber columns have not been optimized at this point as to number of stages or recycle flowrates. The mercury still is being modeled as a FLASH2 block because the liquid portion of the feed is already pure mercury. If the impurities in the mercury feed stream were defined, this block could be replaced by a multistage column block (such as RADFRAC).

The wet-oxidation reactor is modeled using only high-pressure air as the oxidizing agent and as a Gibbs-free-energy equilibrium reaction. A considerable amount of research has been conducted on more-effective oxidizing agents with different reaction conditions. This reaction may be kinetically limited, in which case a different ASPEN reactor model may be more appropriate if kinetics or conversions are known.

The ion-exchange column in the aqueous polishing system is modeled as an ion remover rather than as an exchange reaction. It would be better modeled as a reactor with appropriate exchange rates given. As already mentioned, an alternative to the ion-exchange column as the secondary polishing step is an evaporator. This has been modeled successfully in the separate aqueous treatment section flowsheet and could be added to the integrated flowsheet.

One aqueous reaction that has not been taken into account is the very fast reaction of NO_2 with water to form HNO_3 and associated electrolytes. A previous attempt to include this reaction resulted in convergence problems, so that work was dropped for the time being. It would probably be worthwhile to attempt to add this reaction again.

Another change that could be made would be to add the properties of molten metals and glass to the data base in order to more appropriately model the melters. Because the current model has only solid metal and glass properties, the heat of fusion is not included in the energy balance. The melters (currently modeled as a heat exchanger and separator) would need to be replaced by reactors in both the heating and cooling stages to convert the solid to the liquid and vice versa. A three-phase flash could be placed between the reactors to separate the vapor, slag (assuming appropriate slag components are present), and the molten metal. Similarly, if molten lead is added to the data base, the solid lead could be converted to molten lead in the roaster bakeout reactors, then converted back in a separate reactor as the lead is cooled down.

Other pieces of the F&OR flowsheet could also be added to the LLNL ASPEN model, such as the front end solids sorting and drum decontamination processes. Many of these are included in the Los Alamos model and will be part of the combined Los Alamos/LLNL model.

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3. Flowsheet Modeling at Los Alamos

A. Introduction

The modeling approach taken at Los Alamos was somewhat different than LLNL's and provided a good test for comparison. The Los Alamos approach was to start at a low level of detail using the split assumptions given in the F&OR and then increase the complexity as more detailed information became available. Information from the Bechtel Design Study was not used. The Los Alamos model includes extensive front end solids sorting, and uses mostly "black box" separators with assumed separations. This model used a built-in estimation package in ASPEN based on thermodynamic coal models to determine the properties of the combustibles based on their ultimate analyses. These combustibles first are converted to an ultimate analysis product before being further reacted to the final combustion products using a Gibbs-free-energy minimization reaction. The results from the Los Alamos and LLNL models are compared in Sec. 5.

B. Methodology

The guiding principle in the development of the Los Alamos MWTP model was to produce a flexible, easily usable model that could become more detailed as understanding of mixed-waste processes increased.

The F&ORs are written at a low level of detail, reflecting the lack of knowledge of mixed-waste composition and treatment processes. Since the components are not well characterized, it is impossible to describe their behavior in a treatment system with great accuracy. Therefore, many processes such as separations cannot be described rigorously; instead, estimates are made that reflect engineering judgment. This level of detail is retained in the ASPEN model. In many "black box" operations, insufficient characterization of feeds and processes exists to warrant anything more. However, the model framework and the nature of ASPEN make it easy to replace less-detailed operations with more-detailed ones as system understanding increases.

The model also was designed to be accessible to multiple users who had no intimate knowledge of its design. It was constructed with no hardwiring of values within the model; the problem is completely specified by the input, which was designed to be simple and clear. The numbering of the streams and units conforms to the F&ORs, so the model is easy to follow and change. Finally, the model was designed to be flexible so as to facilitate changes to alternative flowsheet designs. Figures 14 through 20 show sections of the Los Alamos model, corresponding to treatment sections in the F&OR.

First, it was necessary to describe the material components within the ASPEN framework. ASPEN was originally developed to simulate chemical industry manufacturing plants, in which components can be described exactly by chemical formulas. However, the feeds to mixed-waste treatment processes typically will be heterogeneous and poorly defined, with a wide array of substances. This is reflected in the F&OR feed descriptions. Feeds to the wet and dry solids treatment sections are described only as categories of solid waste, with no composition information (see Table 4). The only inorganic substances considered specifically are lead and mercury; radioactive species are not included. Liquid organic feeds are divided into six types (see Table 5). Ultimate analyses for streams containing organic components are given at points of entrance to the thermal treatment section (see Table 6), but the organic liquid waste categories are not given specific ultimate analyses. Aqueous feeds are categorized simply as water, organics, dissolved solids, and suspended solids. Farther on in the solids sorting sections, components are broken up into the functional categories of magnetic metals, nonmagnetic metals, nonmetallic inert solids, light combustibles, and heavy combustibles.

In the ASPEN model, components are described as a mixture of specific chemical compounds and less specific substance names. It was attempted to describe components as what the process was actually "seeing" at any given point (see category 5). This system retains the same component descriptions used in the F&ORs. Types of components were as follows:

- Gaseous and liquid compounds: N_2, CO_2, H_2O, etc.
- Electrolytes (ions?): H^+, Cl^-, HCO_3^-, etc.
- Organic liquids (see Table 5). These were not assigned chemical formulas; instead, they

Table 4. Annual stored and newly generated heterogeneous dry solid mixed waste.

Code	Component	Wt%	Gross (kg/yr)	Density (kg/m³)	Gross (m³/yr)	Net (kg/yr)
510	Equipment	0.00	0	3000	0	0
520	Gloveboxes	0.00	0	3000	0	0
530	Construction debris	24.23	149,550	1500	100	135,470
540	Metals, general	0.16	970	3200	<1	920
550	Wood	0.00	0	400	0	0
700	Sortable dry solids	0.05	340	400	1	220
710	Filters	1.94	11,990	400	30	7,750
720	Glass	1.05	6,480	1200	5	5,710
730	Equipment and metals	14.67	90,530	3200	28	86,540
740	Combustibles	3.17	19,560	240	82	8,050
750	Misc. waste/comb.	17.40	107,370	600	179	82,100
760	Ceramics, graphite	10.47	64,620	1600	40	58,920
770	Leaded gloves and aprons	0.01	50	2500	<1	40
780	Lead	26.62	164,250	5000	33	159,610
790	Mercury contaminated	0.23	1,410	800	2	1,170
	Totals/averages	100.00	617,120	1234	500	546,500

Table 5. Annual external organic liquid waste rates.

Code	Category	Density (kg/m³)	Gross kg/yr	Gross m³/yr	Drums/yr
200	Organic liquids	800	3,900	5	24
210	Solvents	800	13,900	17	88
220	Scintillation cocktails	1,000	9,600	10	61
230	Organic sludges	900	24,900	28	140
240	Hg contaminated	900	100	<1	1
250	PCBs	1,250	500	<1	2
	Totals/averages:	882	52,900	60	316

Table 6. Feed compositions (wt%).

	Feed stream	C	H	O	N	S	Cl	Ash	Moisture
211T	Conc. organics	85.5	12.0	0.6	0.5	0.4	0.0	1.0	0.0
213T	Heavy organics	83.0	11.6	1.2	1.7	0.7	0.0	1.8	0.0
801	Heavy combustibles	40.2	5.1	26.2	1.5	0.2	2.6	18.6	5.6
802	Light combustibles	47.0	5.8	25.3	2.1	0.3	4.5	9.9	5.1
803	Inert combustibles	43.5	5.5	25.7	1.8	0.3	3.6	14.3	5.3
804	Magnetic metals	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
805	Nonmagnetic metals	43.5	5.5	25.7	1.8	0.3	3.6	14.3	5.3

were entered as nonconventional components, described by an ultimate analysis adapted from Table 6.

- Solid compounds: Fe, Hg, Pb, SiO_2, and NaCl.

- Filled containers. For example, the component "drhvmet" was used for an unopened drum containing aqueous heavy metal waste.

- Unspecified solid wastes: bricks, cemented sludges, nonmagnetic metals, etc. Solids for which it was not possible to give a chemical formula.

Components without chemical formulas were entered in the ASPEN component list simply by name as conventional inert solids or nonconventional solids. For inorganic solids, density and heat capacity (necessary for stream and energy calculations) were entered in the data base. In a few cases, formulas were assigned to substances when it seemed sensible; for example, the steel drums are entered as pure iron. Values were selected to be somewhat representative of the type of component; for ceramics, SiO_2 properties were used. For organic liquids and solids, the DuLong correlation for coals was used by ASPEN to estimate the substances' thermodynamic properties based on ultimate analysis.

Next, physical property calculation methods were set. The Redlich–Kwong–Soave gas model was used along with the aqueous NRTL models and Henry's law for electrolytes.

Feed enters the plant as mixed waste contained in drums, bins, or boxes. The filled containers pass through an initial sorting unit to the appropriate flowsheet section. Emptying of the containers is simulated by a stoichiometric reactor in ASPEN. The "reaction" that takes place is the conversion of the filled waste container to the empty container plus its contents. Stoichiometric coefficients for the reactions are calculated by an inline FORTRAN subroutine that allows the user to specify mass fractions of each type of waste along with container mass, volume, and fill factor. Thus, feed and container data can be changed easily.

A similar use of stoichiometric reactors to model functional presence of components takes place in the homogeneous dry solids and heterogeneous dry solids sections. For example, the heterogeneous dry solids first are sorted according to size by a screen; the undersized portion goes to the homogeneous dry solids section. The size distribution of the waste at this point is given in the F&ORs by the 17 types of heterogeneous

waste (see Table 4). The heterogeneous waste is sorted later by magnetic and density table separation into the five categories addressed by thermal treatment. In order to change the original waste types into the separation categories, a dummy stoichiometric reactor is inserted to the flowsheet prior to sorting. An inline FORTRAN routine uses the composition information in Table 7 to calculate product coefficients.

The organic liquids, wet solids, homogeneous dry solids, and heterogeneous dry solids sections are essentially sorting and separation processes. The data available from the F&ORs was not detailed enough to rigorously calculate liquid phase separations. In the solids treatment sections and in the filtration and elutriation processes, material splits depend on a number of unknown factors, including solids size, density, chemical characteristics, and homogeneity. Therefore, most splits were modeled as essentially black-box separations, reproducing the engineering assumptions made in the F&ORs. The ASPEN unit-operation models used were SEP, a black-box separator, and FSPLIT, a unit to divide complete streams. For example, filtration is modeled as a two-step process in ASPEN. First, to simulate solids separation, the stream passes through a SEP block in which splits are specified for each solid component. Second, to simulate retention of liquid in the filtrate, the filtered stream passes through an FSPLIT block in which a small percentage of the stream is split off and recombined with the filtrate. To achieve a given mass fraction of liquid in the filtrate, a Design Specification calculation block is used to vary the FSPLIT fractions.

In the thermal treatment section, nonaqueous organic waste is oxidized, lead and mercury are separated from solid wastes, and the inerts, magnetic metals, and nonmagnetic metals wastes are converted to final forms. Light combustibles, heavy combustibles, and organic sludges are oxidized in separate chambers, and the offgas is routed through a secondary combustion chamber heated by the combustion of liquid organic wastes and auxiliary fuel. Inerts, nonmagnetic metals, magnetic metals, and high-mercury wastes pass separately through the roaster-bakeout chamber. Then, the first three streams are melted and converted to final forms, while mercury wastes are recycled to solids sorting. Melted lead is collected from the roaster-bakeout chamber for further processing. Offgas from the chamber is routed to secondary combustion.

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Table 7. External waste size distribution and composition assumptions (wt%).

| | | Size distribution | | Composition breakdowns | | | |
		<2 in.	>2 in.	Combus-tible	Nonmag. metals	Mag. metals	Inerts
Code	Component						
510	Equipment	5.0	95.0	2.0	85.0	10.0	3.0
520	Gloveboxes	5.0	95.0	5.0	80.0	0.0	15.0
530	Construction debris	30.0	70.0	15.0	10.0	10.0	65.0
540	Metals, general	5.0	95.0	2.0	58.0	38.0	2.0
550	Wood	5.0	95.0	95.0	0.0	3.0	2.0
700	Dry solids, sortable	30.0	70.0	50.0	10.0	10.0	30.0
710	Filters	10.0	90.0	15.0	25.0	0.0	60.0
720	Glass	30.0	70.0	2.0	0.0	0.0	98.0
730	Equipment and metals	5.0	95.0	2.0	85.0	10.0	3.0
740	Combustibles	20.0	80.0	95.0	0.0	2.0	3.0
750	Misc. waste w/combustibles	20.0	80.0	40.0	10.0	10.0	40.0
760	Ceramics, graphite	40.0	60.0	20.0	0.0	0.0	80.0
770	Leaded gloves and aprons	5.0	95.0	10.0	80.0	0.0	10.0
780	Lead	5.0	95.0	0.0	100.0	0.0	0.0
790	Mercury contaminated	30.0	70.0	50.0	10.0	10.0	30.0

Combustion chambers are modeled as a multistep process. First, the organic waste is converted to a model set of products in a stoichiometric reactor unit through the reaction

$$\text{Waste} + O_2 \rightarrow CO_2 + H_2O + N_2 + Cl_2 + SO_2 + \text{ash} . \tag{7}$$
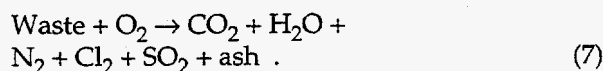
Reaction coefficients are calculated from the ultimate analysis of each waste component. Second, the products pass through an RGIBBS unit operation, which calculates a Gibbs equilibrium mixture for the gaseous products. Additional species considered in equilibrium calculations are CO, C, H_2, N_2O, NO, NO_2, S, SO_3, and HCl. Finally, the equilibrium products pass through a separator that simulates the entrainment of solids in the gaseous product stream. In the pyrolysis chamber, where there was insufficient oxygen for the combustion reaction in Eq. 7, a partial oxidation was used:

$$\text{Waste} \rightarrow C + H_2 + N_2 + Cl_2 + S + \text{ash} . \tag{8}$$
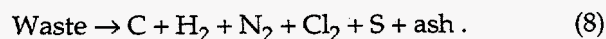
Again, the reaction products were passed through a Gibbs equilibrium unit, with the oxygen present, to calculate final products.

The stoichiometric amount of air required for complete combustion is calculated from the ultimate analysis of the organic wastes and is specified through inline FORTRAN. Limited kinetic modeling of chemical reactions is available in ASPEN; in this model, all combustion reactions are assumed to proceed to equilibrium.

The auxiliary fuel required in the concentrated organics burner is calculated through a design specification loop, in which the amount of auxiliary fuel added is varied to converge on the correct temperature of the secondary chamber offgas. At present, it is assumed that both chambers are adiabatic.

The mercury condenser unit is modeled as a simple splitter, as in the F&ORs. The offgas treatment unit is modeled as a one-stage flash unit, with aqueous blowdown recycled to aqueous treatment and offgas sent through the atmospheric protection section in the support operations system. The Bechtel report, which details a complete offgas treatment system, was not used as a source for the Los Alamos modeling effort.

The roaster bakeout furnace, which is actually a single kiln that receives batch loads of four solid waste streams, is modeled in ASPEN as four separate units treating each solid stream continuously. This approach maintains the separation of the solid waste streams while producing the same outlets; ASPEN is not set up to handle batchwise switching of feed streams to a unit operation. Furnace offgas and lead runoff streams are then recombined before further treatment.

C. Results

The complete baseline Los Alamos model took approximately 25 min to run on a Sun Sparc Station. The model simulated the entire F&OR flowsheet design. Two recycle streams were left unconnected because the automatic sequencer in ASPEN could not determine a calculation order for the very complexly interconnected complete flowsheet. The model is too large to attempt a manual calculation sequence; this problem is being examined at ASPEN Tech headquarters in conjunction with development of a new sequencing package for the next software release. For the current study, the unconnected recycle streams were converged manually with little difficulty.

4. Combined Flowsheet Model

A. Combination of LLNL and Los Alamos Models

Melding of the two models into a single model is an ongoing effort at this time. This will yield a model with the best of both the LLNL and Los Alamos models. To accomplish this, the LLNL model was dissected into smaller sections and sent to Los Alamos, where appropriate pieces are being added to the Los Alamos model (including the liquid organic stream definitions, the offgas treatment system, and the electrolyte chemistry modeling). The resulting model is the largest ever seen by ASPEN technologists. Once this model is completed, it can be modified to look at the effect of alternative treatments or feed-stream compositions. It will also provide the basis for modeling significantly different conceptual flowsheets. Case and sensitivity studies can be performed on the various models to observe the effect of parameter changes and to define operating envelopes. The radioactive components currently are not included in the ASPEN models; these components eventually can be added to the data base and the simulation to enable tracking them to their final output streams. Cost comparisons between the various flowsheets can be made using ASPEN's costing package.

Combining the models was performed at Los Alamos in communication with LLNL. The LLNL model was divided into sections and sent to Los Alamos. The basic framework of the Los Alamos model was used, with many additions from the LLNL model. Major changes to the Los Alamos model were as follows:

- The LLNL offgas section was added in its entirety.
- LLNL solid, organic liquid, and electrolyte components were added, allowing for flexibility in feed specifications.
- LLNL electrolyte chemistry models were added to the aqueous liquids and wet solids treatment sections.
- The LLNL two-stage mercury separation process was added.
- Decanters were added to the aqueous liquids and organic liquids treatment sections, replacing the black-box separations of the F&ORs and the Los Alamos model.
- The LLNL design of a heat exchanger loop around the wet oxidation unit was included.

- Alternative model versions were developed with the LLNL ion exchange and evaporator unit operations in the aqueous liquids treatment section.

B. Improvements to the Baseline Combined Model

Several improvements could be made to the combined baseline flowsheet model. Some are clear and will be addressed as time permits; in other cases, it may not be important to expend significant effort on them, depending on the projected use of the baseline flowsheet model.

- An input file containing all process feed information outside of the ASPEN model should be developed. Feed specifications then could be changed by any user without entering ASPEN, and sets of runs could be stored without storing the whole model.
- Typical radioactive components and their physical properties should be added to the component data base and modeled in the simulation.
- Some electrolyte chemistry should be added, particularly the solubilization of nitrous oxides in offgas treatment aqueous streams.
- Offgas treatment units could be optimized.
- The routing of feed streams could be changed. The operation of some of the feed sorting processes in the F&ORs is unclear.
- The oxidation of iron drums in the organic sludge pyrolysis chamber could be modeled.

Larger efforts would be driven by increasingly detailed knowledge of feed composition and equipment operation. In addition to general increase of the specificity of the model, these efforts could include the following:

- Particle size distribution modeling could be used to determine operation of solids separation units.
- Electrolyte chemistry models could be added to model behavior of additional aqueous liquid section feed components.
- Separation and entrainment fractions could be specified for individual solid components in units such as combustion chambers, dryers, and filters. At present, only general solids splits are used.

5. Results and Conclusions

A. Comparison of Models

At a summary level, the overall feed and product flowrates of the Los Alamos and LLNL ASPEN models agree very well with the F&OR stream table values. Despite the differences between the models, these simulation results were strikingly similar, as summarized in Table 8. The flowrates for all but one of the product streams were within 10% of each other (the exception was within 16%). Another interesting point of comparison was the amount of auxiliary fuel required for the burner in the secondary combustion chamber. Despite the differences in how the combustibles were defined and the reactors were modeled, the auxiliary fuel requirements were within 25% of each other, and most of this difference could be accounted for by a different interpretation of the percentage of organics in labpack and scintillation vial feed streams. The total flowrates of organics being sent to the burner, including auxiliary fuel, are within 8% for the two models.

B. Future Direction

One future effort will be to include a cost package to the flowsheet model. This is important for evaluating relative costs of proposed alternative flowsheet designs, an important decision-making criterion. Under investigation currently are Aspen Tech's own costing package and COST and ICARUS 2000 from Icarus, which is currently developing a direct ASPEN interface for the packages. Another possibility, alone or in conjunction with packages for specialized units, is to include empirical cost models through in-line FORTRAN routines.

Another effort will be to develop models of alternative flowsheet designs. These models will be developed by altering the baseline flowsheet, thus retaining the framework of components, feeds, and common treatment sections. Currently planned are models of debris grouted, debris processed, and no flame flowsheets.

Along the same lines, it will be possible to develop site-specific treatment flowsheets from the baseline flowsheet as needed. Individual site waste mixes could be easily accommodated by changing input waste composition to the ASPEN model.

Finally, the model may be used to analyze the impact of alternative technologies on the complete process, by substituting the unit operations that model the new technology's performance in the baseline flowsheet.

C. Conclusion

ASPEN models (LLNL and Los Alamos) were developed that simulate the MWTP baseline flowsheet for an integrated, full-scope, mixed-waste treatment facility. A combined ASPEN model that combines the best of both models is nearing completion. The model has the scope of

Table 8. F&OR, Los Alamos, and LLNL model flowrates (kg/day).

Stream	F&OR	Los Alamos	LLNL
Clean water	22,444	22,408	22,430
Inerts FF	3,234	3,193	3,410
Nonferrous metals FF	268	325	271
Ferrous metals FF	276	275	278
Lead FF	213	211	214
Recycled lead	740	735	739
Glass FF	332	314	338
Thermal offgas to stack	13,240	16,220	14,508
Auxiliary fuel	—	205	155
Total organics to burner	—	303	280

the complete facility flowsheet and the technically correct details of each unit operation for each subsystem.

The initial ASPEN modeling effort at both LLNL and Los Alamos gave us valuable information on the capabilities and limitations of process simulators such as ASPEN in the MWTP flowsheet modeling effort. Overall, we have found that a process simulator can be a powerful tool for modeling a flowsheet from a overview level to one that contains great amounts of detail. ASPEN can perform mass and energy balances on highly integrated facilities, can define recycle streams, and can easily accomplish activities such as determining auxiliary fuel requirements. It can perform reactions based on thermodynamic criteria, user-supplied kinetics, or strict stoichiometry. It is flexible enough to permit even major changes to the flowsheet without an undue amount of effort. Finally, it may provide some guidance for cost estimation and comparisons. Overall, ASPEN is proving to be a valuable part of the MWTP modeling effort.

The completion of the baseline flowsheet model sets the stage for the most productive use of ASPEN flowsheet modeling: the evaluation of alternatives and "what if's." Alternative treatment technologies can be inserted for comparison and to assess their effects on the rest of the integrated system. Alternative flowsheet designs can be modeled for comparison. Candidate site treatment flowsheets for treatment of specific waste streams from individual sites or combinations of sites can be modeled and assessed. This capability is available to provide a technically sound basis for evaluating site and transportation-treatment options in support of FFCA and WGA activities.

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