MIXED WASTE TREATMENT PROJECT: LLNL AND LANL COMPUTER SIMULATIONS OF INTEGRATED FLOWSHEETS

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ABSTRACT

Computer simulations of mixed waste processing flowsheets using ASPEN PLUS process simulation software were completed by a joint Lawrence Livermore National Laboratory/Los Alamos National Laboratory (LLNL/LANL) effort for the US Department of Energy Mixed Waste Treatment Project. The LLNL model used relatively detailed synthesized chemical "cocktails" to simulate waste streams. The LANL approach used less detail but made extensive use of simple stream splitters and thermodynamic coal models for combustible waste compositions. The two modeling approaches agreed within 16% for the product streams and within 25% for the auxiliary fuel rate. The discrepancy between the auxiliary fuel rates was traced to different methods of handling organics in lab packs and scintillation vials within the process models. The ASPEN models are valuable tools for evaluating waste processing flowsheets.

INTRODUCTION

The treatment and disposal of mixed waste, that is, 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 the destruction of hazardous wastes need to be reevaluated for their ability to handle mixed wastes, and new technologies need to be developed in some cases.

The Mixed Waste Treatment Project (MWTP), a collaborative Lawrence Livermore National Laboratory (LLNL), Los Alamos National Laboratory (LANL), and Pacific Northwest Laboratory (PNL) effort, was established by DOE's Waste Operations Program (EM-30) to develop and analyze alternative mixed waste treatment approaches. One of MWTP's initiatives, and the objective of this study, was to develop flowsheets for integrated mixed waste treatment facilities that can serve as models for sites developing their own treatment strategies. Computer models are facilitating the evaluation of these flowsheets. The objective of the flowsheet simulations is to compare the process effectiveness and costs of alternative flowsheets. Another objective was to determine if commercially available process simulation software could be used on a large complex process such as an integrated mixed waste processing facility.

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 being able to evaluate the effect of individual operations on the whole plant. Modeling also can be used to evaluate the sensitivity and range of operating conditions, radioactive criticality, and relative costs of different flowsheet designs. The modeled flowsheets also need to be easily modified to examine how alternative technologies and varying feed streams affect the overall integrated process.

Background

The first MWTP-generated flowsheet was developed by Musgrave, Borduin, and Ross and was referred to as the "baseline" flowsheet. This flowsheet provided the basis for the "Functional and Operational Requirements" (F&OR) study and document developed by T. K. Thompson of T. K. Thompson, Inc. (1). Mixed waste processing rates, which served as the F&OR design basis, were selected to represent a median value for the seven major DOE mixed waste generating sites. These sites were the Idaho National Engineering Laboratory, Oak Ridge K-25, the Portsmouth Gaseous Diffusion Plant, the Hanford Site, the Rocky Flats Plant, the Savannah River Site, and Oak Ridge Y-12. The F&OR flowsheet was developed assuming an integrated facility that could process all types of mixed waste. The flowsheet is extensively interconnected, and all recycle streams are defined and quantified.

The F&OR study was based on using existing, proven technology wherever possible and addressed the following.

- Process description
- Assumptions
- Process boundaries
- Flow diagram
- Mass balance
- Unit operation capacities
- Equipment layout
- Functional, operational, and interface requirements for each processing line

The waste processing lines treated aqueous liquid, organic liquid, wet solid, homogeneous dry solid, and heterogeneous dry solid external waste streams. Additional treatment lines included final waste forms and support operations, which provided utility functions to the integrated plant. The F&OR flowsheet is shown in Fig. 1.

The processing lines were highly integrated. The feedstream definitions were generic + identifying categories of wastes rather than specifying individual components. Liquids were divided into organic and aqueous waste streams. Solids were divided into heavy and light combustibles, nonmetals (inerts), magnetic metals, and nonmagnetic metals. The F&OR mass balances were calculated using an EXCEL spreadsheet by entering assumed splits and conversions.

An associated flowsheet design was prepared by Bechtel using the F&OR as its basis. The Bechtel "Design Study and Cost Estimates" contain a more detailed equipment design

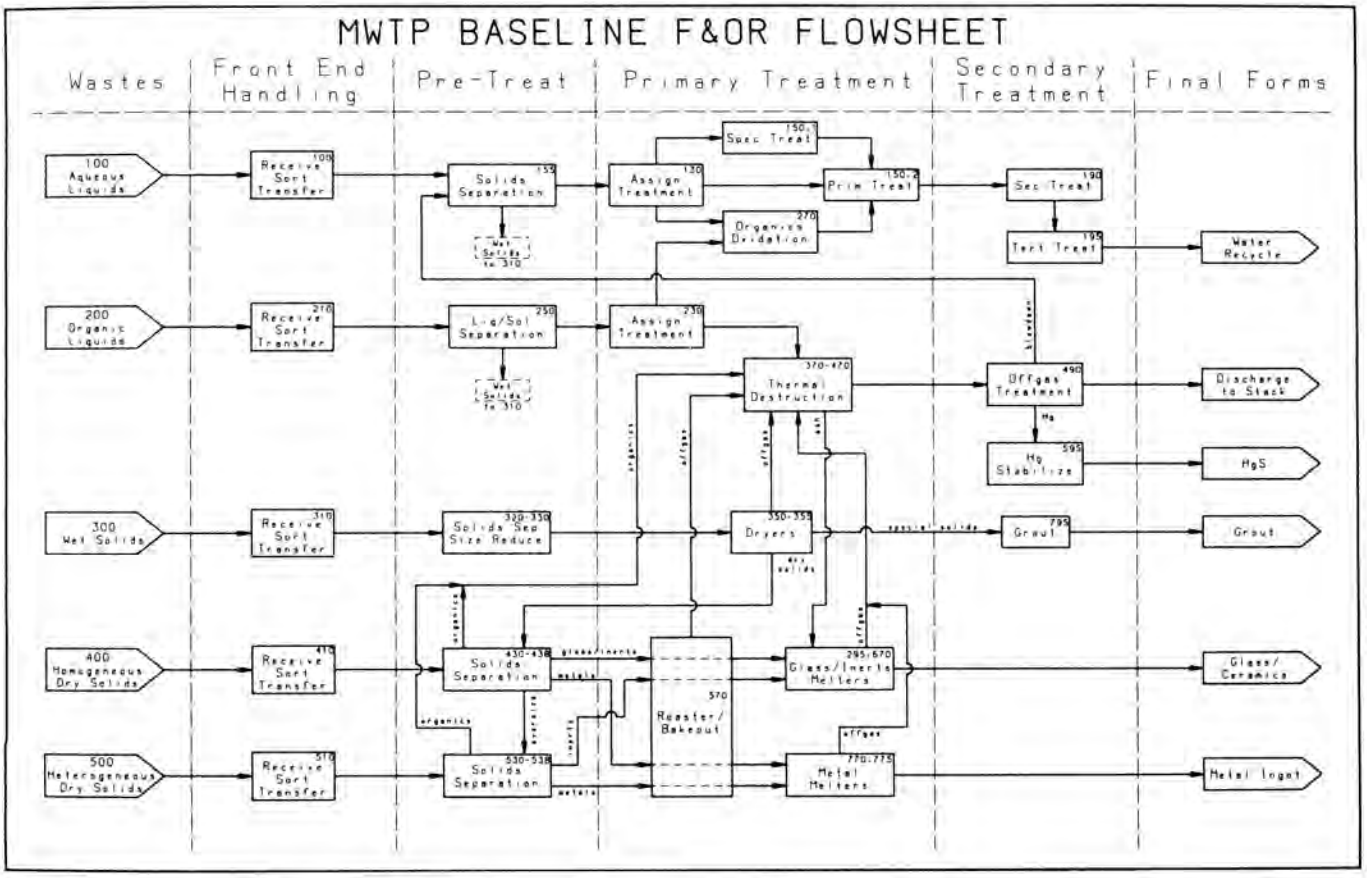

Fig. 1. Overall MWTP F&OR Basecase Flow Diagram.

(but not more detailed feed definitions) and sizing and cost information (2).

Modeling Approach

The computer code used for flowsheet modeling in this study, ASPEN PLUS (hereafter referred to as ASPEN), is a chemical process simulation software package. Its primary function is to perform mass and energy balance calculations over typical unit operations in chemical engineering processes. To perform these calculations, the software 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 modeling 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 in-line FORTRAN block in which the downstream quantity is calculated directly from an upstream quantity. In-line FORTRAN also can be used to perform other calculations, call subroutines, and handle input/output. 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. Feeds and block operations then are specified along with property models. 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 from 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 used to model the first flowsheet using ASPEN. The team consisted of John A. Pendergrass and T. K. Thompson of TK Thompson, Inc., representing LANL, and Laura J. Dietsche and Ravindra S. Upadhye from LLNL. This effort focused on modeling the F&OR flowsheet independently at each site and then comparing 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 basecase flowsheet. This report summarizes the modeling work conducted at both LLNL and LANL, compares the individual model results, and presents conclusions resulting from the joint studies.

FLOWSHEET MODELING AT LLNL

Methodology

One of the goals of the LLNL ASPEN model of the MWTP baseline flowsheet was to model everything in as much detail as possible, making any necessary assumptions. To fully use ASPEN's thermodynamic capabilities, including fluid-phase equilibria calculations, the stream compositions need to 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 specific components. Therefore, a number of assumptions have gone into the component 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. Heavy combustible solids were modeled as wood, and light combustibles were modeled as paper. Neither of these are in the ASPEN database, so appropriate thermodynamic properties needed to be entered. These combustible solids were reacted first to an ultimate analysis product before being reacted further 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 were modeled as iron, and nonmagnetic metals were modeled as chrome 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 capability to simulate 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 also was considered. The disadvantage of going to this level of detail is dealing with more difficult convergences and longer simulation times.

The ASPEN model initially was created in sections that then were joined to form the overall MWTP base-case model. 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 initially were joined and modified to obtain convergence. The aqueous feed treatment system was created next and added. 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 the drying of 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-h) simulation times. These included the streams going from the wet solids drying section to both the aqueous processing section and to the incinerator, the final atmospheric protection system's scrubber bottoms stream that was recycled back to the aqueous treatment section, and the purge stream from the thermal offgas absorber that became makeup to the quench column. Feedstreams were created that approximated the composition and flow rate of the connecting stream.

The MWTP baseline flowsheet is still in a preliminary design stage and requires that numerous assumptions be made when defining feeds and determining the specifications in the ASPEN model. Most of the assumptions are based on information contained in the F&OR or Bechtel Design Study reports, but some assumptions are simply "engineering judgment" or intuition. The ASPEN program input file contains numerous comment statements that specify most of the assumptions made. They will not all be repeated here. Assumptions that required significant extrapolations from the F&OR or extensive calculations are outlined below.

The F&OR states flow rates 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 h/wk (24-h/day, 7-day/wk) operating schedule. This can be modified easily 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 the streams in the report to a specified stream and flow rate.

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". Truly batch equipment cannot be modeled in detail using ASPEN. 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 airflow rate. 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 on the F&OR flowsheet.

As previously 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 chrome were added to represent the drums that were incinerated along with their contents.

The F&OR stated oxygen requirements for the incinerators in terms of percentage 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 0.01 of that entering the incinerator. This allows for 102% of stoichiometric air because 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.

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 to perform Vapor Liquid Equilibrium (VLE) calculations. As most of these organics are not very soluble in water, it is very difficult (or impossible) to find values for the Henry's Law constants (or the associated VLE data) in the open literature. 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.

The electrolyte calculation package seemed to have real trouble handling liquid mercury in the aqueous stream. Therefore, the mercury in streams entering an aqueous section of the flowsheet (Aqueous Treatment, Offgas Treatment, and Wet Solids Drying) was first moved to the conventional solids phase or substream and 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 mercuric chloride) should be considered in future models. When mercury vapor-liquid or liquid-liquid equilibrium calculations were required (in the non-aqueous section of the flowsheet), the mercury was moved back to the "mixed" substream.

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 report 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.

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 allowed for 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/h was calculated, compared with a flow rate of 5 kg/h for the concentrated organics. Thus, the auxiliary fuel requirements are significant.

The wet-oxidation reactor also requires some additional heat input. 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 no other heat input is 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, 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 the model organics described above.

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 also is 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/h out of 935 kg/h total coming from the ion exchange column) that could potentially 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 have to be evaluated.

FLOWSHEET MODELING AT LANL

Methodology

The guiding philosophy in development of the LANL MWTP model was to produce a flexible, easily usable model that could become more detailed as understanding of mixed waste processes increased. The modeling approach taken was somewhat different than LLNLs and provided a good test for comparison. The LANL approach was to start at a low level of detail using the split assumptions given in the F&OR, then to increase the complexity as more detailed information was made available. Information from the Bechtel Design Study was not used. The LANL model includes extensive front-end solids sorting and uses mostly "black box" separators with assumed separations. The LANL 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 are first converted to an ultimate analysis product before being further reacted to the final combustion products using a Gibbs Free Energy minimization reaction.

The F&ORs are written at a low level of detail, reflecting the lack of knowledge of mixed waste composition and treatment processes. Because 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. There are many "black box" operations, where 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 without intimate knowledge of its design required. 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 to facilitate changes to alternative flowsheet designs.

It was necessary first 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 a chemical formulas. However, the feeds to mixed waste treatment processes typically will be heterogeneous and poorly defined with a wide array of substances.

In the ASPEN model, components were 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. This system retains the same component descriptions used in the F&ORs. The types of components were as follows.

1. Gaseous and liquid compounds: N_2, CO_2, H_2O, etc.
2. Electrolytes (Ions?): H^+, Cl^-, HCO_3^-, etc.
3. Organic liquids. These were not assigned chemical formulas; instead, they were entered as nonconventional components and described by an ultimate analysis.
4. Solid compounds: Fe, Hg, Pb, SiO_2, NaCl.
5. Filled containers.
6. 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, the properties of density and heat capacity (necessary for stream and energy calculations) were entered in the database. 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. The 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 in-line 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 are first sorted according to size, passing through a screen with the undersized portion going 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. Subsequently, the heterogeneous waste is sorted by magnetic and density table separation into the five categories addressed by thermal treatment. To change the original waste types into the separation categories, a dummy stoichiometric reactor is inserted into the flowsheet before sorting. An in-line FORTRAN routine uses the composition information to calculate product coefficients.

The organic liquids, wet solids, homogeneous dry solids, and heterogeneous dry solids sections are essentially sorting and separation processes. There were not detailed data available from the F&ORs to rigorously calculate liquid phase separations. In the solids treatment sections and in the filtration and elutriation processes, material splits are dependent 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 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, and 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.

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:

$$\text{Waste} + O_2 = = = > CO_2 + H_2O + N_2 + Cl_2 + SO_2 + \text{Ash}$$

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 above combustion reaction, a partial oxidation was used:

$$\text{Waste} = = = > C + H_2 + N_2 + Cl_2 + S + \text{Ash}$$

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 specified through in-line 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 a source for the LANL 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 then are recombined before further treatment.

Results

The completed baseline LANL 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 was not able to determine a calculation order for the very complexly interconnected complete flowsheet. The model was too large to attempt a manual calculation sequence; this problem was 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.

RESULTS AND CONCLUSIONS

Comparison of Models

On a larger scale, the overall feed and product flow rates of the LANL 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. A comparison summary is given in Table I. The flow rates for all but one of the product streams were within 10% of each other (the exception being within 16%). Another interesting point of comparison was the amount of auxiliary fuel required for the secondary combustion chamber burner. Despite the differences in how the combustibles were defined and in how 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 lab pack and scintillation vial feed streams. The total flow rate of organics being sent to the burner, including auxiliary fuel, is within 8% for the two models.

TABLE I
Comparison of F&OR, LANL, and LLNL Model Flow Rates (kg/day)

Stream	F&OR	LANL Model	LLNL Model
Clean Water	22444	22408	22430
Inerts Final Form	3234	3193	3410
Non-Ferrous Metals Final Form	268	325	271
Ferrous Metals Final Form	276	275	278
Lead Final Form	213	211	214
Recycled Lead	740	735	739
Glass Final Form	332	314	338
Thermal Offgas to Stack	13240	16220	14508
Auxiliary Fuel	–	205	155
Total Organics to Burner	–	303	280

CONCLUSIONS

The initial ASPEN modeling effort at both LLNL and LANL has provided us with some very valuable information on the capabilities and limitations of process simulators like ASPEN in the MWTP flowsheet modeling effort. Overall, we have found that a process simulator can be a very powerful tool to model a flowsheet from a very low level of detail to a great amount of detail. It can perform mass and energy balances on very highly integrated facilities, define recycle streams, and can easily accomplish activities such as determining auxiliary fuel

requirements. It can calculate reactions based on thermodynamic criteria, user-supplied kinetics, or strict stoichiometry. It is flexible enough to allow for minor, or even major changes, to the flowsheet without a tremendous amount of effort. Finally, it may provide some guidance for cost estimation and comparisons. Overall, ASPEN is proving to be a very valuable part of the MWTP modeling effort.

REFERENCES

1. T. K.THOMPSON, "Mixed Waste Treatment Project Functional and Operational Requirements for an Integrated Facility," TK Thompson, Inc. report prepared for Los Alamos National Laboratory under Subcontract 9-XY2-Y9590-1, Task 014 (August 30, 1992).

2. "Mixed Waste Treatment Project Process Systems and Facilities Design Study and Cost Estimates," prepared for Lawrence Livermore National Laboratory (September 1992).