

Semi-Continuous Evaporation Model for Leachate Treatment Process Evaluation

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The use of evaporation for treatment of landfill leachate may be effective at removing contaminants in one principal unit operation. A semi-continuous evaporation treatment process model, Reaction EQUilibrium Evaporation Model (REQEM), was developed for engineering assessment to: i) simulate different batch flash vaporization processes, ii) predict the effluent stream compositions and quantities, and iii) compute the energy requirements. The model integrates previously separate features into a composite chemical equilibrium and dynamic process simulation model.

Simulations have shown that multi-stage flash with recirculation and condensation heat recovery maximizes the amount of evaporate produced and minimizes the steam and pumping energy requirements. Leachate with low volatile organic acids may need only acidic evaporation to efficiently treat the leachate. Leachate with high concentrations of both ammonia and volatile organic acids may require a two-step, pH-adjustment evaporation process. If nonionic volatile organic compounds are present in leachate, then pretreatment such as air stripping may be necessary to obtain adequate evaporate quality. Adjustments of the initial leachate pH value will have no direct effect on the product-to-feed ratio, the performance ratio, or the evaporate quality with respect to nonvolatile compounds such as metals. Landfill gas may provide sufficient energy for leachate vaporization in many instances for modern landfills, and semi-continuous operations may be the most practical treatment mode.

INTRODUCTION

Leachate is formed from water that infiltrates through a landfill. As leachate migrates through the refuse, it accumulates soluble contaminants present in the solid waste and soluble products from anaerobic decomposition reactions. The landfill may be lined with plastic, compacted clay, or other

relatively impermeable materials to prevent the movement of leachate into the soil beneath the landfill (Reindl, 1981). A drainage system with collection pipes is installed over such liners to convey leachate by gravity to a sump or storage tank from which leachate is periodically removed for treatment and disposal. The quality of leachate can be highly variable and depends on several characteristics of the landfill, including its

Table 1 Characteristics of Landfill Leachate

Parameters (mg/L except pH)	Range of Values Reported for Leachate (Pfeffer, 1992)	Swiss Facility Leachate, Yearly Averages (Hofstetter <i>et al.</i> , 1991)	Delaware Solid Waste Authority Leachate, Yearly Averages (1990)	Western PA Leachate, Typical Values
pH	3.7-8.5	N/A	6.2	N/A
BOD	40-90,000	305	N/A	N/A
COD	81-33,000	4057	8795	954
NH ₃ -N	0-1100	2000	578	357
Alkalinity (CaCO ₃)	240-21,000	N/A	N/A	N/A
Hardness (CaCO ₃)	540-23,000	N/A	N/A	N/A
Calcium	60-7200	N/A	778	200*
Magnesium	17-16,000	N/A	306	60
Sodium	34-7700	N/A	1375	N/A
Potassium	28-3800	N/A	N/A	N/A
Chloride	5-2500	N/A	1482	193
NO ₂ /NO ₃ -N	0-10	N/A	1.0	0.05
Sulfate	1-1600	N/A	243	290
Total Carbonate	N/A	N/A	1321*	3900*
Total P	0-130	N/A	N/A	N/A
Dissolved solids	600-45,000	N/A	N/A	N/A
Suspended solids	10-700	N/A	N/A	N/A
Toluene	N/A	N/A	0.55	0.25
Phenol	N/A	N/A	8.0	0.036

*estimate

age, biological activity, infiltration rate, and refuse type. The literature contains numerous reports on the characteristics of leachate from sanitary landfills. A typical range of leachate characteristics that have been reported are presented in column one of Table 1 (Pfeffer, 1992). Contaminants in leachate include organic compounds that exert a biochemical oxygen demand (BOD); high-molecular-weight nonbiodegradable organic compounds that contribute to chemical oxygen demand (COD); suspended solids, soluble metals and salts; and volatile inorganic and organic compounds such as ammonia and acetic acid, respectively.

Conventional treatment of landfill leachate may require several unit operations to remove the various contaminants to acceptable levels. A typical treatment train may include: i) aerobic or anaerobic biological processes to stabilize biodegradable organic components and ammonia; ii) adsorption, air stripping, or chemical oxidation to remove nonbiodegradable organic compounds; and iii) chemical precipitation to remove heavy metals. As effluent discharge quality standards become more stringent, it is apparent that landfill leachate treatment systems and residuals management are becoming increasingly more complex operations.

Leachate treatment by evaporation may offer the advantage of attaining acceptable discharge limits for various types of contaminants by employing fewer unit operations than a treatment train composed of several sequential unit operations. Evaporative leachate treatment may also produce fewer and more concentrated residual streams than conventional operations. Limited information on the evaporation or distillation of landfill leachate has been published. A process model is needed to assess the effects of influent conditions and process configurations on effluent quality for comparison of process alternatives. An evaporation treatment process model, Reaction Equilibrium Evaporation Model (REQEM), was developed for engineering assessment of landfill leachate evaporation. REQEM was designed to: i) simulate different flash vaporization processes, ii) predict effluent composition and quantities, and iii) compute energy requirements. The model simulates flash vaporization given the initial feed composition and any of the following: i) temperature and pressure, ii) pressure and vaporized fraction, or iii) pressure and heat duty.

BENEFITS OF TREATMENT BY EVAPORATION

Leachate treatment by evaporation allows separation of volatile from nonvolatile components. Solids and metals are not volatile, while the major volatile pollutants in leachate, ammonia and organic acids, can be transformed into nonvolatile ions by adjusting the pH of the solution. A common type of evaporation process is single-stage flash vaporization illustrated in Figure 1, in which the liquid mixture is heated and enters into a flash chamber at a reduced pressure. The mixture partially vaporizes, and the vapors come to equilibrium with the residual liquid at the new lower pressure and temperature. In this paper, the resulting liquid product of Figure 1 is referred to as the concentrate, while the resulting vapor product that becomes a liquid upon condensation is referred to as the evaporate. The evaporate will be mostly water, and it may be high quality and easier to dispose than effluent streams produced by conventional treatment processes. The resulting concentrate will contain most of the contaminants and will be a small fraction of the original leachate volume. Depending on its final composition, the resulting concentrate may be classified a hazardous waste, as is the case with some residuals from conventional leachate treatment processes.

Recent investigations suggest that landfill gas produced by the decomposition of landfill refuse may be used as an energy source for the evaporation of leachate (Birchler *et al.*, 1994;

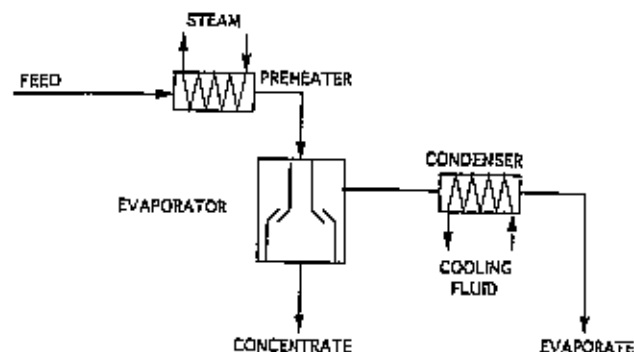


FIGURE 1. Single-stage flash evaporation schematic.

Hofstetter *et al.*, 1991). A Monte Carlo parametric analysis has shown that it is conceptually feasible to evaporate leachate with energy from landfill gas for typical, modern landfill conditions (Birchler *et al.*, 1994). Thus, two by-products from landfill operation, leachate and gas, may be used strategically in a vaporization treatment process.

Current Leachate Evaporation Processes

Only limited information has been published on evaporation or distillation of landfill leachate. Essentially all published available data on leachate evaporation is derived from the experiences of two groups, one in Germany and one in Switzerland. In Bavaria, Germany, laboratory distillation tests have been performed using a two-step evaporation process on mixed-waste landfill leachate of different strengths. A two-step evaporation process is illustrated in Figure 2, where the evaporate from the first step is used as the feed into the next flash chamber. An adjustment of pH can be made prior to either of the flash steps. A two-step, acid/base leachate distillation process in series with pH adjustments between the first and second step was tested at pilot scale (Steinmetzer, 1987). The leachate was first made acidic to separate ammonia and then basic to separate volatile organic acids from the resulting evaporate. A second type of process was evaluated at the pilot scale in which ammonia was first removed by a basic steam stripping pretreatment process, and the basic residual liquid was flash evaporated in a two-stage flash process. The second process was chosen for operational reasons for full-scale evaluation and removed 92 percent of the COD and 94 percent of the ammonia (Steinmetzer, 1987; Tiefel, 1989). Several operational problems were encountered at the full-scale facility, including foaming and scaling problems due to precipitated carbonates (Amsoncit, 1985; Tiefel, 1989). The treatment capacity of the plant was about 3.6 m³ leachate/hr (950 gal/hr) or 10,000 m³/year (2.8 × 10⁶ gal/year) (Amsoncit, 1985). Tiefel (1989) reports that over a seven month period in 1988, the energy requirements of the facility were 0.74 mton steam/mton leachate, 31.3 kWhr electricity/mton leachate, and 0.11 m³ fresh water/mton leachate.

The Hofstetter Company has installed in Uttigen, Switzerland a full-scale, 20 m³/d, semi-continuous batch, sanitary landfill leachate multi-stage evaporation process with recirculation of the concentrate (Buhler, 1991). The leachate is adjusted to pH 4 and is sent through a four-stage flash evaporator as shown in Figure 3. A fraction of the concentrate is continuously recycled until the evaporate volume attains the desired amount. The evaporation process is performed under

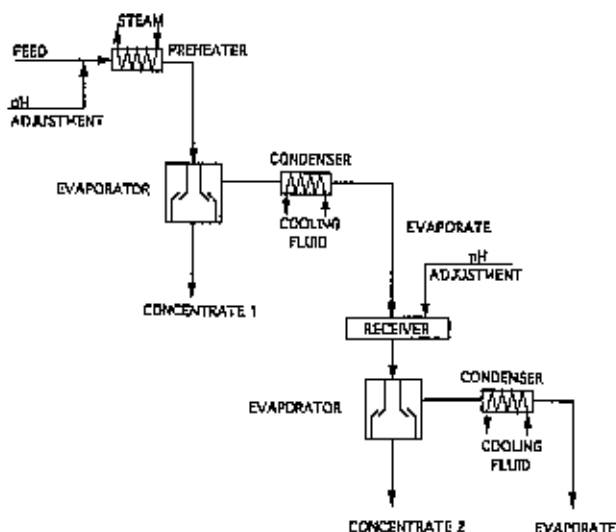


FIGURE 2. Two-step flash evaporation schematic.

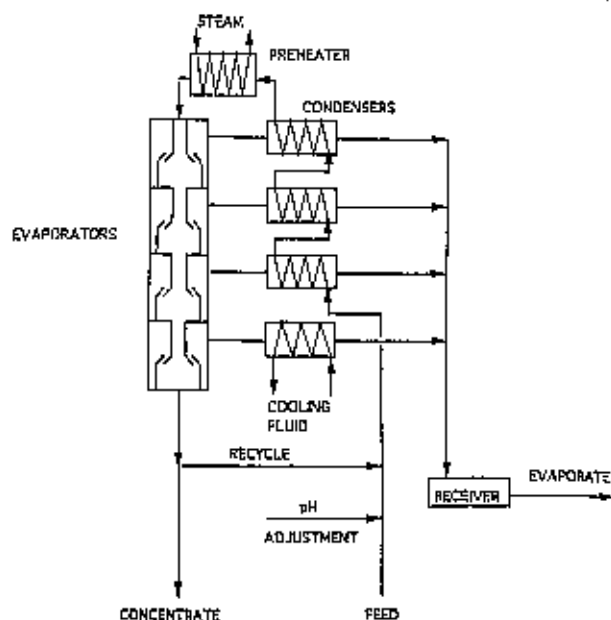


FIGURE 3. Four-stage flash evaporation with recirculation schematic.

vacuum with the heat from vapor condensation being used to preheat the feed leachate. The liquid in the final stage boils at approximately 30 C, at a pressure of 7.6 mm Hg (Hofstetter *et al.*, 1991). Air stripping pre-treatment may be employed to remove carbon dioxide and volatile organic compounds. The energy for evaporation at this facility is supplied indirectly by combustion of landfill gas for electricity generation. Heat recovery in the evaporator is about 60-70 percent (Hofstetter *et al.*, 1991). The evaporate volume is 95 percent of the original leachate volume with 98.5 percent removal of the COD, ammonia, and conductivity (Buhler, 1991; Hofstetter *et al.*, 1991). The manufacturer states that no serious operational problems have been encountered at the Uttigen facility.

EVAPORATION PROCESS MODEL

A process simulation model, Reaction Equilibrium Evaporation Model (REQEM), was developed to aid the engineering assessment of leachate evaporation treatment processes. The model was configured to: i) simulate different flash vaporization processes, ii) predict effluent composition and quantities, and iii) compute energy requirements. This model has been designed to simulate evaporation processes from an environmental engineering perspective and contains a combination of capabilities for simulating the vaporization of fluids with complex composition, such as leachate or other wastewaters.

Requirements of a Leachate Vaporization Process Model

The requirements of a leachate vaporization model are a consequence of the characteristics of the feed and product being modeled. A wide range of inlet concentrations needs to be considered for the evaluation of leachate evaporation, since leachate composition will change over time, and will vary from landfill to landfill. Also, since leachate is a multi-component aqueous solution of strong and weak electrolytes, including volatile and nonvolatile compounds, the process model must incorporate the requisite chemical equilibria to accurately predict the speciation of electrolytes, complexes, and solids that may exist in the aqueous solution and the corresponding equi-

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In summa: process mode the behavior ii) a simulat multi-stage fl to handle bat to handle bo ation and ad separate opti dynamic pro

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The physic of the REQE The majority heat of form were obtaine (ACAPP) da vapor param- vapor pressu ities for com- ley (1981) a: separation d: binary par: REQEM con in Table 2, i plexes and th model does r for all comp. Nonetheless, ative compo semi-volatile organic com: and principa etc.) and diss methane).

Model Algo

REQEM i: reaction equi

Environmen

equilibrium gas phase composition. Because of the various process configurations of flash evaporation, the model should be able to simulate single- or multi-stage flash vaporization with and without recirculation, and multi-effect multi-stage flash vaporization with and without recirculation.

Modern landfills produce a comparatively small leachate flow rate, which will fluctuate depending on the age of the landfill, recent precipitation, and type of refuse in the landfill. Thus, batch or semi-continuous operations, not steady-state processes, may represent the most practical leachate vaporization treatment mode. The concentration of important contaminants in leachate can range from parts per million to parts per thousand. The effluent quality may have to be compared with regulatory discharge limits that are in the sub-parts per million concentrations. Thus, the model must be able to accurately predict both high and low aqueous concentrations.

A pH adjustment feature is necessary for prediction of vapor and liquid equilibrium in flash vaporization. The phase separation of ammonia, chemical oxygen demand (COD), and volatile organic acids depends primarily on the initial pH value and the extent to which the COD is composed of volatile organic acids (VOAs) (Birchler *et al.*, 1994). Since ions of ammonia and VOAs are not volatile, the model must account for the pH change that may occur during evaporation to accurately predict vapor and liquid compositions. A pH adjustment feature also will permit the evaluation of influent pH operational control on the effluent compositions.

In summary, the requirements for a leachate vaporization process model are: i) an equilibrium chemical model to predict the behavior of electrolytes, volatile components, and solids; ii) a simulator for single-stage, multi-stage, or multi-effect multi-stage flash vaporization with recirculation; iii) the ability to handle batch/semi-continuous operations; iv) the capability to handle both high and low concentrations; and v) pH variation and adjustment features. REQEM integrates previously separate options into a composite chemical equilibrium and dynamic process simulation model.

Physical/Chemical Properties

The physical and chemical properties used in the calculations of the REQEM process model were obtained from four sources. The majority of the aqueous chemical equilibrium constants, heat of formation values, liquid heat capacities, and densities were obtained from Aqueous Chemical and Physical Properties (ACAPP) data bank (Radian Corporation, 1991). Most of the vapor parameters, such as Antoine coefficients for determining vapor pressure, and heat of formation values and heat capacities for computing vapor enthalpies, were obtained from Henley (1981) and Reid *et al.* (1987). The vapor/liquid phase separation data for validation of this model, and the Wilson binary parameters, were obtained from Gmehling (1977). REQEM contains thirty-four independent components, listed in Table 2, that can be transformed into seventy-eight complexes and thirty-eight solids species. In its present form, the model does not contain the physical and chemical parameters for all components that might be present in landfill leachate. Nonetheless, parameters are included for principal representative compounds such as: volatile organic acids (acetic acid); semi-volatile organic compounds (phenol and cresol); volatile organic compounds (e.g., toluene and methyl-ethyl ketone); and principal inorganic compounds (e.g., ammonia, calcium, etc.) and dissolved gases (carbon dioxide, hydrogen sulfide and methane).

Model Algorithms and Theory

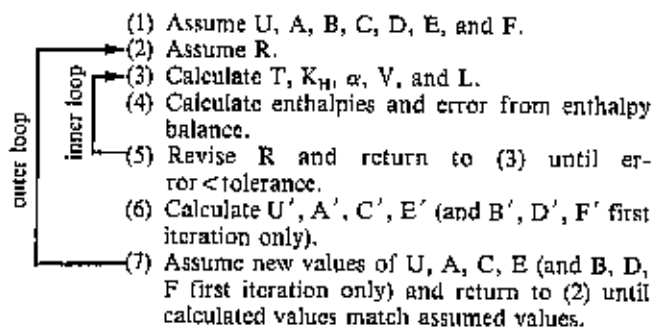
REQEM is comprised of a flash vaporization module, a reaction equilibrium module, and a pH control module.

Table 2 Independent Components Available in REQEM

Neutral	Cations	Anions
methane	Al ³⁺	CH ₃ CO ₂ ⁻
ethane	Ca ²⁺	Cl ⁻
propane	K ⁺	CNS ⁻
toluene	Mg ²⁺	CO ₃ ²⁻
n-decane	Na ⁺	F ⁻
H ₂ O	NH ₄ ⁺	NO ₃ ⁻
H ₂ BO ₃	NH ₄ ⁺	o-Cresol ⁻
H ₄ SiO ₄		phenolate
diethanolamine		PO ₄ ³⁻
monoethanolamine		S ²⁻
methyl-ethyl ketone		S ₂ O ₃ ²⁻
		S ₂ O ₆ ²⁻
		SO ₃ ²⁻
		SO ₄ ²⁻
		hydroxylamine
		disulfonate ⁻

Flash Vaporization Module

The flash vaporization simulator is based on the "inside-out" algorithm (Boston and Britt, 1978). Boston and Britt redefine the typically-used iteration variables: temperature (T), pressure (P), vapor and liquid (V and L) fraction, heat duty (Q), Henry's constant (K_H), and mole fractions of the feed, liquid and vapor (α) of the system and replace them with a new set of variables: U, R, A, B, C, D, E, and F. The steps in the adiabatic flash algorithm are:



Each time flash vaporization is simulated, initial values of U, R, A, B, C, D, E, and F are estimated. In the inside loop, R is varied until the enthalpy balance is satisfied within a prescribed tolerance for assumed values of parameters U, and A through F. Using the resulting R value, calculated values of U', and A' through F' are computed. Completed solution is achieved when the assumed values of the outer loop variables (U, A through F) match the calculated values (U', A' through F') within the tolerance limit. The main reason for redefining the traditional iteration variables is to choose new variables which have minimum dependence upon temperature and pressure. This stabilizes convergence behavior without the need for user manipulation of convergence parameters. The advantage of this algorithm is that the user is not required to furnish initial estimates of vapor and liquid composition, which would be inefficient for batch and multi-stage flash configurations.

Reaction Equilibrium Module

The following three submodules are used in the reaction equilibrium module to calculate the equilibrium concentration of liquid, gas, and solid species: i) an initial value estimator, ii) a mass and equilibrium calculation submodule, and iii) a nonlinear convergence algorithm submodule.

Each time the equilibrium concentration for the aqueous solution is calculated, the initial value estimator computes a first guess approximation of the extent of each reaction and the mole fraction of each equilibrium constituent. The computation of the first trial chemical equilibrium composition values is based on a procedure used by Cavallotti *et al.* (1980), which estimates the extent of each reaction from a system of non-linear chemical equilibrium equations. The chemical equilibrium equations are linearized for all reactions so that the extents of reaction can be calculated directly. The assumptions used to linearize the chemical equilibrium equations are based on a set of independent components which must be chosen from the possible equilibrium species. To produce the most accurate first guess of reaction extents, species present in the greatest quantity at equilibrium should be chosen as the independent components set (Stadler and Scriven, 1973). This choice is determined by the user of the program as an internal parameter input. The extents of the reactions are calculated assuming the reactions occur independently of each other.

The final equilibrium composition is solved iteratively. Mass balance and chemical equilibrium equations and their remainders are calculated using the extents and the liquid mole fraction values provided by the initial guess estimator submodule. As the estimation value of the extent of the reactions approaches its true value, the remainders values approach zero in the equations. Convergence is achieved when the sum of the squares of the remainders in the mass balance and chemical equilibrium equations are below a prescribed tolerance. If convergence has not been achieved, new extents and mole fractions are generated using a non-linear parameter algorithm based on a combination of the Taylor series method and the steepest-descent or gradient method (Marquardt, 1963). The user is often interested in small concentrations in environmental assessment applications. Hence, numerical errors can significantly affect the results. The numerical error can be decreased by varying the degree in which the two methods are combined. The accuracy of the equilibrium program is determined by the sum of the square of mass balance and chemical equilibrium remainders. For the numerical error to be insignificant, the sum of the square value should be less than the smallest concentration of interest squared.

pH Control Module

An external differential control loop is used to estimate the amount of acid or base required to adjust the pH in the aqueous

solution to achieve the desired pH value. The user enters an initial guess of the amount of acid or base to be added to achieve the desired pH level. REQEM calculates the resulting pH value and a second pH value assuming 90 percent of the initial acid/base amount was added. The model computes the amount of acid/base required to achieve the desired pH value through extrapolation using the two pH values. REQEM uses the new guess to revise the amount of acid/base that is added until the calculated pH value is within a prescribed tolerance of the desired pH value. The default acid and base used to adjust pH value are hydrochloric acid and sodium hydroxide, respectively.

MODEL VERIFICATION

The reaction equilibrium module and the flash vaporization module in REQEM are calibrated separately. It is assumed that the resulting combination of the two will provide a reliable simulation of flash evaporation of landfill leachate.

Reaction Equilibrium Module

The predicted equilibrium results of the REQEM model have been compared to the predicted results from Aqueous Chemical and Physical Properties (ACAPP) equilibrium model (Radian, 1991). Table 3 lists for six systems the initial feed species, the final equilibrium species formed, and whether pH adjustment was specified. These cases and others were used to validate the model's pH adjustment feature and the computed equilibrium concentrations for electrolytes, complexes and solids. In cases 5 and 6, solid formation was possible. For case 5, solids were allowed to precipitate; for case 6, supersaturation was assumed.

The predicted REQEM equilibrium concentrations were compared with ACAPP's predicted concentrations. Results in Table 4, for example, show good agreement for case 5 between the two models' predicted equilibrium concentrations. The pH values for the six cases using REQEM and the ACAPP models range from 4 to 13 and agree within 0.1 units. Results in Table 4, and other results not shown, indicate that the predicted equilibrium concentrations of the model are good. Part of the close agreement between the two models results from both models accessing the same data bank containing the equilibrium constant coefficients.

Table 4 Concentrations from

Species
H
NH ₄
NH ₄ OH
Acetate
Acetic A
Cl
OH
NO ₃
SO ₄
Ca
CaCO ₃
CaHCO ₃
CaNO ₃
CaOH
CaSO ₄
Mg
MgCO ₃
MgHCO ₃
MgOH
MgSO ₄
Na
NaCO ₃
NaHCO ₃
NaN ₃
NaOH
NaSO ₄
NH ₄ CO ₂
NH ₄ CO ₃
NH ₄ HCC
NH ₄ HSO
NH ₄ SO ₄
H ₂ CO ₃
HCO ₃
CO ₂
CO ₃
HNO ₃
HSO ₄
Solids
CaCO ₃ (2)
Mg(OH) ₂
MgCO ₃ (6)

Table 3 Representative Validation Cases for the Reaction Equilibrium Module of REQEM

Systems	Feed	Species Formed	pH Adjustment	Solids
Case 1	H ₂ O, NH ₄ OH, CH ₃ CO ₂ H	H ⁺ , OH ⁻ , H ₂ O, NH ₄ OH, NH ₄ ⁺ , CH ₃ CO ₂ H, CH ₃ CO ₂ ⁻	No	N/A
Case 2	H ₂ O, NH ₄ OH, CH ₃ CO ₂ H	H ⁺ , OH ⁻ , H ₂ O, NH ₄ OH, NH ₄ ⁺ , CH ₃ CO ₂ H, CH ₃ CO ₂ ⁻	Yes, pH = 4	N/A
Case 3	H ₂ O, NH ₄ OH, CH ₃ CO ₂ H	H ⁺ , OH ⁻ , H ₂ O, NH ₄ OH, NH ₄ ⁺ , CH ₃ CO ₂ H, CH ₃ CO ₂ ⁻	Yes, pH = 10	N/A
Case 4	H ₂ O, NH ₄ OH, CH ₃ CO ₂ H, CO ₂ , C ₆ H ₅ OH	H ⁺ , OH ⁻ , H ₂ O, NH ₄ ⁺ , NH ₄ OH, NH ₄ CO ₃ ⁻ , NH ₄ HCO ₃ , NH ₄ CO ₂ ⁻ , CH ₃ CO ₂ H, CH ₃ CO ₂ ⁻ , H ₂ CO ₃ , HCO ₃ ⁻ , CO ₂ , CO ₃ ²⁻ , C ₆ H ₅ O ⁻ , C ₆ H ₅ OH	No	N/A
Case 5	H ₂ O, NH ₄ OH, CH ₃ CO ₂ H, CO ₂ , Ca, Mg, Na, Cl, SO ₄ , NO ₃	39 Species (see Table 4)	No	Yes (10 solids possible)
Case 6	H ₂ O, NH ₄ OH, CH ₃ CO ₂ H, CO ₂ , Ca, Mg, Na, Cl, SO ₄ , NO ₃	39 Species	No	Supersaturated

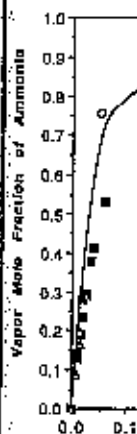


FIGURE 4. / mole fraction

Table 4 Comparison of Predicted Equilibrium Concentrations from REQEM and ACAPP (Radian, 1991) at 40C

Species	Initial Molarity	REQEM Activity	ACAPP Activity
H	0.0E+00	1.6E-09	1.4E-09
NH ₃	0.0E+00	4.2E-02	3.1E-02
NH ₄ OH	7.8E-02	3.0E-02	3.4E-02
Acetate	0.0E+00	4.8E-01	3.8E-01
Acetic Acid	5.2E-01	2.6E-05	3.2E-05
Cl	2.7E-02	2.5E-02	1.8E-02
OH	0.0E+00	2.7E-05	2.1E-05
NO ₃	7.4E-04	6.8E-04	4.7E-04
SO ₄	1.6E-02	7.3E-03	1.3E-03
Ca	1.8E-01	1.5E-05	3.8E-06
CaCO ₃	0.0E+00	4.2E-06	5.0E-06
CaHCO ₃	0.0E+00	1.4E-06	1.2E-06
CaNO ₃	0.0E+00	6.7E-09	5.7E-09
CaOH	0.0E+00	2.4E-09	2.0E-09
CaSO ₄	0.0E+00	9.7E-07	1.2E-06
Mg	6.4E-01	8.9E-02	1.2E-02
MgCO ₃	0.0E+00	4.2E-02	5.0E-02
MgHCO ₃	0.0E+00	4.4E-03	3.8E-03
MgOH	0.0E+00	2.7E-04	2.3E-04
MgSO ₄	0.0E+00	4.8E-03	5.8E-03
Na	3.3E-01	3.0E-01	2.3E-01
NaCO ₃	0.0E+00	1.5E-09	1.0E-09
NaHCO ₃	0.0E+00	3.5E-03	4.0E-03
NaNO ₃	0.0E+00	8.9E-26	1.1E-25
NaOH	0.0E+00	1.1E-06	1.3E-06
NaSO ₄	0.0E+00	1.0E-03	7.3E-04
NH ₄ CO ₂	0.0E+00	2.3E-06	1.6E-06
NH ₄ CO ₃	0.0E+00	9.8E-04	6.8E-04
NH ₄ HCO ₃	0.0E+00	4.3E-05	4.0E-05
NH ₄ HSO ₄	0.0E+00	4.3E-11	5.1E-11
NH ₄ SO ₄	0.0E+00	7.1E-04	5.0E-04
H ₂ CO ₃	0.0E+00	5.6E-08	6.5E-08
HCO ₃	0.0E+00	2.3E-02	1.6E-02
CO ₂	5.0E-01	3.8E-05	4.5E-05
CO ₃	0.0E+00	3.7E-03	7.0E-04
HNO ₃	0.0E+00	3.0E-14	3.6E-14
HSO ₄	0.0E+00	3.7E-10	2.6E-10
Solids			
CaCO ₃ (s)	0.0E+00	1.7E-01	1.8E-01
Mg(OH) ₂ (s)	0.0E+00	2.3E-01	2.4E-01
MgCO ₃ (s)	0.0E+00	2.3E-01	2.4E-01

Flash Vaporization Module

The validity of the flash vaporization calculations of REQEM has been tested by comparing the REQEM model predictions with experimental results for binary vapor/liquid equilibrium mole fractions. Four binary cases were studied. In each of the binary systems examined, water was one of the components and the other component was either ammonia, acetic acid, carbon dioxide, or phenol. The liquid and gas mole fractions of the REQEM model were compared with several experimental data sets (Gmehling, 1977). Figure 4 shows a comparison of REQEM's predictions with three experimental results for water and ammonia. The results show that the nonideality of these mixtures is handled adequately by introducing activity coefficients calculated from the Wilson equation (Gmehling, 1977). The Wilson equation with the binary interaction constants fit experimental data well even in dilute regions where variation of the compound's activity coefficient becomes exponential. Good agreement exists between REQEM's predictions and the experimental results for the equilibrium mole fraction of liquid and vapor.

As a result of the separate validation of the aqueous chemical equilibrium module and the liquid/vapor equilibrium module, the resulting combination of these modules will provide simulation of flash vaporization of leachate accounting for both aqueous reactions and vapor/liquid equilibrium.

pH CONTROL AND EVAPORATE QUALITY

The initial pH of leachate can strongly influence the separation of the contaminants in the evaporation processes. In order to evaluate the effect of feed pH on evaporate quality, a single-stage flash evaporation process was simulated using yearly average leachate characterization data from a landfill operated by Delaware Solid Waste Authority (1990). The average leachate quality was NH₃ = 578 mg N/L and COD = 8800 mg/L (as acetic acid equivalent); the other species reported in leachate are listed Table 1. In the simulations, the leachate was preheated to 97 C and flashed with 90 percent vaporization at 80 C with external heat added. Four different cases were simulated. In two cases, the initial pH was adjusted to pH 4 using HCl and H₂SO₄, respectively. In the third case, the influent leachate value of pH remained unchanged from its initial value of 6.2, and in the fourth case, the pH was adjusted to 10 using NaOH. The evaporate concentrations and percent remaining in the evaporate for the different pH adjustments are shown in Figures 5 and 6 for ammonia and acetic acid, respectively.

The following discussion on the effect of pH adjustment on evaporate quality focuses on ammonia and acetic acid, as these two volatile species are a principal concern in leachate treatment. The adjustment of the initial leachate pH value will have no direct effect on the evaporate quality with respect to non-volatile compounds such as metals and simple salts.

Acidic Vaporization

A one-step, acidic evaporation process simulation showed separation of 99 percent of ammonia from the evaporate. By initially adjusting the pH level to 4, the ammonia in the leachate is transformed to ammonium ion and does not vaporize and contaminate the evaporate. However, 75 percent of the original acetic acid is predicted to carry over to the evaporate. Thus, one-step evaporation with acidic pH adjustment may be suitable for producing an evaporate having low concentrations of both ammonia and volatile organic acids (VOAs) only if the leachate contains initially low concentrations of VOAs.

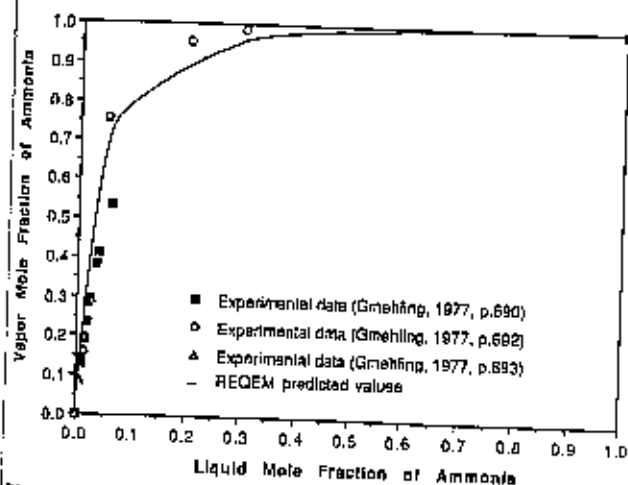


FIGURE 4. Ammonia and water vapor/liquid equilibrium mole fraction comparison for REQEM and experimental data.

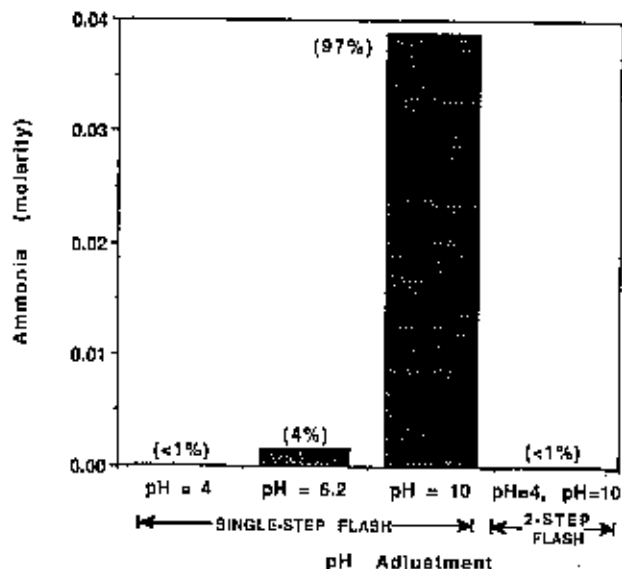


FIGURE 5. Ammonia evaporate concentrations for two-stage flash evaporation processes using DSWA feed leachate with a prescribed 90% vaporization.

Basic Vaporization

A one-step basic evaporation process simulation showed separation of VOAs from the evaporate. With the initial pH at 10, acetic acid is ionic and 99 percent remains in the concentrate, while the majority of the ammonia is transformed to a volatile species and 3 percent remains in the concentrate. Thus, a one-step evaporation with basic pH adjustment may be suitable for producing an evaporate free of both VOAs and ammonia only if low amounts of ammonia are present initially in the leachate.

Two-step pH Adjustment Vaporization

The simulations discussed above, and the results of laboratory tests and field experience with leachate, suggest there is no single pH value where both ammonia and acetic acid can

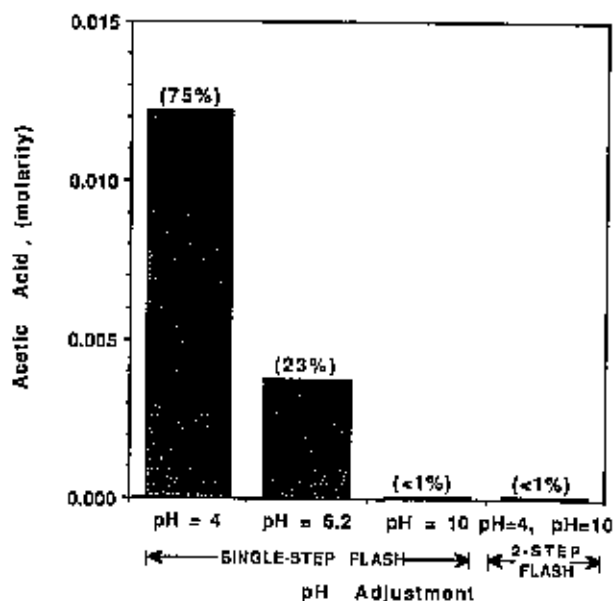


FIGURE 6. Acetic acid evaporate concentrations for two-stage flash evaporation processes using DSWA feed leachate with a prescribed 90% vaporization.

be prevented from vaporizing into the product. For example, flash evaporation simulations with no pH adjustment (pH = 6.2) showed significant amounts of ammonia and acetic acid in the evaporate. This agrees with laboratory tests for pH values ranging from 5 to 7 in which both ammonia and acetic acid are somewhat volatile and carry over into the evaporate (Birchler *et al.*, 1994).

A two-step pH adjustment evaporation process may be required to remove ammonia and VOAs when high levels of both compounds are present in leachate. A two-step acid/base evaporation process was simulated by adjusting pH to 4, preheating the leachate to 97 C, and flashing at 80 C (355 mm Hg); the second step was simulated by condensing the evaporate, adjusting pH to 10, and flashing at 50 C (92.5 mm Hg). The quality of the evaporate is predicted to improve greatly for the two-step process. Figures 5 and 6 illustrate that over 99 percent of both the ammonia and the acetic acid may be retained in the concentrates from a two-step acid/base pH adjustment process. Thus, an acid/base, two-step evaporation process, or an equivalent technology incorporating distillation with evaporation, would be needed to obtain satisfactory evaporate quality for a strong leachate having high levels of both ammonia and VOAs.

Selection of the pH Value

The pH of leachate should be adjusted about 1 pH unit from the pK_a value, towards the ionic constituents, for separation of significant ionizable volatile compounds. The pK_a of ammonia, acetic acid, and phenol at the temperatures of interest are around 8, 5, and 10, respectively. Hence, if the pH of the solution is 10, for example, then the phenol is partially volatile and some will carry over to the evaporate during a basic evaporation step. The pH of leachate with large amounts of phenol should be adjusted to 11 to retain the majority of the phenol in the concentrate. In a two-step acid/base flash evaporation simulation where the first-step pH adjustment was pH 4, and the second-step pH adjustment was pH 10, the percent of phenol that remained in the evaporate was 5 percent of the total phenol concentration. When the second-step pH adjustment was set at pH 11, the resulting percent of phenol in the evaporate was reduced to less than 0.6 percent; almost ten times lower than that at pH 10.

Nonionic, Volatile Organic Compounds in Leachate

Another set of simulations was performed to assess toluene disposition for the case of leachate data reported by the Delaware Solid Waste Authority. Toluene is a nonionic, volatile organic compound. As a result, the concentration of toluene in the evaporate should not vary as a result of pH adjustment. The predicted concentrations of toluene in the evaporate were between 74–76 percent of the total toluene for single-stage flash process simulations with pH adjustment of 4, 6.2, and 10. Thus, if significant amounts of nonionic volatile organic compounds (VOCs) such as toluene are present in the leachate, additional measures may be necessary to obtain adequate evaporate quality. This relates to the Swiss experience which has employed air stripping as a pretreatment to remove VOCs, and the German experience which employed steam stripping with evaporation to achieve removal of total organic carbon.

Potential for Scaling

The process simulation showed that the potential for scaling varies when different acids are used to adjust the pH, and when the order of adding acid and base is altered. For a single-stage flash with leachate composition for the Delaware Solid Waste Authority at a prescribed value of 90 percent vaporized,

$CaSO_4(s)$ was H_2SO_4 was used for the pH adjustment. The evaporate quality was used.

The simulation showed that calcium hydroxide was used as a basic first step, and basic second step. About 90 percent of the calcium and the cation carbonate did not form. The simulation made basic and decreased the likelihood of vacuum during

CONCENTR

The two-step process varies greatly. The fraction of the typical concentration is 10 percent of the total. The second flash evaporation is the first vaporization step. The important constituents in leachate are the metals. This process, if the waste, is a cost of disposal of the concentrate. For purposes of simulation, the equilibrium data for a dilute leachate from Pennsylvania is used to simulate a concentration, i.e., a

PROCESS C

Several process criteria: and the effluent is dimensionless. The evaporate product-to-feed ratio is 0.90 for preheating process. The diagrams of evaporation preheat the waste low oper

CaCO₃) was predicted to precipitate in the concentrate when H₂SO₄ was used to adjust the pH to 4. When HCl was used for the pH adjustment, no solids were predicted to form. The evaporate quality was the same whether H₂SO₄ or HCl was used.

The simulations showed that calcium carbonate and magnesium hydroxide solids would form if the leachate was made basic first. When the leachate was made acidic first (using HCl) and basic second, no solids were predicted to form because 58 percent of the carbonate was removed in the acidic evaporation and the cations (Ca, Mg) that may form solids with hydroxide and carbonate remained in the concentrate. As a result, solids did not form in the solution from acidic evaporation when made basic and flashed in the second step. In summary, to decrease the likelihood of scaling during acidic flash evaporation, HCl instead of H₂SO₄ should be used to adjust the pH of leachate. If basic evaporation is necessary to remove VOAs from ammonia, flashing first with acidic leachate and adjusting the resulting evaporate to basic conditions will reduce the likelihood of solids precipitating, as well as help maintain vacuum during the basic evaporation.

CONCENTRATE STREAM QUALITY

The two-step flash evaporation process produces two effluent concentrate streams (Figure 2), and their composition varies greatly. The volume of the concentrate stream is a small fraction of the original feed volume. In these simulations, the typical concentrate stream volume was specified between 5 and 10 percent of the original stream's volume. If a two-step flash vaporization process is required, the concentrate stream from the second flash vaporization will contain only the residual ionic fractions of volatile compounds carried over from the first vaporization. The concentrate stream from the first flash evaporation is predicted to contain essentially all the nonvolatile impurities such as metals, salts and solids. This is an important consideration for evaluating the fate of heavy metal cations in leachate feed streams. The ratio of the feed volume to the concentrate volume gives the concentration factor for the metals. This factor is one of the decision variables for the process. If the concentrate stream is characterized as a hazardous waste, a high concentration factor will help reduce the cost of disposal. In such case, additional drying or crystallization of the concentrate may be warranted.

For purposes of reliable simulations, the concentration factor may be limited by computational algorithms and chemical equilibrium data bases for very high ionic strength solutions. For a dilute leachate, such as that reported for the western Pennsylvania leachate in Table 1, the simulation can accommodate a concentrate stream that is four percent of the feed stream, i.e., a concentration factor of 25.

PROCESS CONFIGURATION EVALUATIONS

Several process configurations were evaluated using the following criteria: product-to-feed ratio, the performance ratio, and the effluent stream quality. The product-to-feed ratio is a dimensionless number that is equivalent to the volume of evaporate produced per initial volume of the feed. A large product-to-feed ratio indicates a small quantity of concentrate to be disposed. The product-to-feed ratio was arbitrarily set at 0.90 for process configuration evaluation. The performance ratio is an important parameter often used to evaluate desalination processes. The performance ratio is the number of kilograms of evaporate produced per kilogram of steam used to preheat the feed leachate. A large performance ratio indicates low operating costs in terms of fuel consumption.

Table 5. Recycle and Once-through Comparison of Performance Ratios for a Single-stage Flash Evaporation

Process Description	Product-to-feed Ratio	Performance Ratio (kg evaporate/kg steam)
Once-through	0.03	0.2
Recirculation	0.90	0.7

Temperature Range of Flash Evaporation

For a given leachate flow rate, the vapor production is determined by the temperature differential between the preheated feed and the final equilibrium flash temperature of the process. The performance of the flash evaporation process can be improved by increasing the temperature differential; however, there are constraints that limit the size of the temperature differential. The first constraint is the boiling point range of leachate which is about 100 C at 760 mm Hg. To prevent boiling in the preheater, the leachate should be below 100 C unless it is pressurized. Steam pressure availability is also a constraint. If the steam pressure is low, an allowance has to be provided for the pressure drops in lines and valves that would lower the condensing temperature of the steam. The minimum flash temperature is limited by the need to condense the resulting flash vapors at a reasonable temperature. Desalination plants usually design the equilibrium flash temperature to be 35-40 C (45-55 mm Hg), so that ambient temperature water or feed can condense the vapors (Kahn, 1986). If preheated temperature is 100 C and the final flash temperature is 35 C, the sensible heat of pure water released due to the pressure drop is about 70 kcal/kg, which is approximately 1/8 of the amount of heat required to vaporize one kg of water. Thus, the best product-to-feed ratio obtainable under these constraints is about 0.12 for flash evaporation; hence, there is the need to recycle the concentrate in the process to attain a large percentage of evaporate relative to feed.

Recirculation of the Concentrate

In order to increase the product-to-feed ratio and improve heat efficiency, the concentrate must be recirculated through the process. A prescribed product-to-feed ratio can be achieved by recycling the concentrate back through the flash chambers until the desired evaporate volume is produced. In this manner, it is possible to achieve 0.90 or more product-to-feed ratios using only flash evaporation. Table 5 lists the product-to-feed ratio and the performance ratio for a once-through and a recirculating single-stage adiabatic flash process using the initial feed leachate composition as reported for the Swiss facility with an assumed value of 90 percent vaporization with leachate recirculation. The simulation was performed for leachate adjusted to pH 4, preheated to 97 C, and flashed at 80 C (355 mm Hg). The performance ratio was approximately three times larger for the process with recirculation than for the process without recirculation. The increase in the performance ratio results from the need to preheat the recycled stream from only 80 C to 97 C instead of 25 C to 97 C, and the need to preheat smaller amounts of the concentrate for each recirculation pass. In this simulation of a single-stage flash vaporization process with recirculation, the concentrate was predicted to recirculate 112 times, and over 35 times the original feed volume was heated to obtain 0.90 product-to-feed ratio. Recirculating the concentrate stream releases less amounts of noncondensable gas that helps maintain vacuum in the flash chamber and good heat transfer in the condenser. Flash evaporation with recirculation also requires additional pumping energy.

Multi-stage Flash with Recirculation

Process simulations showed that multi-stage flash with recycle uses less pumping energy than a single-stage flash with recycle to produce the same amount of evaporate. A four-stage flash evaporation processes with recycle was simulated for an initial leachate composition as reported for the Swiss facility. The simulation was performed for leachate adjusted to pH 4, preheated to 97 C, and flashed in the final stage at 40 C. The performance ratio for a recirculating four-stage flash process with prescribed 90 percent vaporization fraction was predicted to be 0.7 kg evaporate/kg steam. The concentrate was predicted to be recirculated 28 times, and almost 10 times the original feed volume was heated to obtain a 0.90 product-to-feed ratio.

The single-stage flash with recycle (Table 5) had a similar performance ratio as the four-stage flash process with recycle. But, the single-stage flash process with recycle requires preheating over 3.5 times the volume of leachate than the multi-stage flash process with recycle. The single-stage flash process with recycle requires the temperature of the concentrate to be raised approximately 20 degrees to reach 97 C, while the four-stage process with recycle must raise the recirculated concentrate approximately 60 C. As a result of the temperature difference and preheat requirements, the four-stage recycle process without heat recovery uses approximately the same amount of steam to produce the same amount of evaporate as the single-stage recycle process, although the latter requires greater volumetric throughput.

Recovered Heat from Condensation

The actual amount of steam required to preheat the feed leachate depends on whether the condensation heat is recovered. The heat from condensing flash vapors can be recovered by using the incoming feed leachate as cooling fluid for condensing the flash vapors. The recovered heat can provide a large percentage of the total energy necessary to preheat the feed leachate to its highest temperature. All the energy, theoretically, cannot be transferred and the amount of heat transfer will depend on the size and design of the heat exchanger. In the case of the full-scale Swiss facility, it is estimated that about 65 percent of the heat from condensing the vapors is available to preheat the leachate. The energy from the last stage cannot be used to preheat the concentrate stream since its vapors are at the same temperature as the recirculating concentrate. By using the heat of condensation, the multi-stage flash evaporation process with recirculation can produce 1 kg of evaporate per 1 kg of steam used in the pre-heater. Increasing the number of stages increases the amount of heat recovery from condensing vapors and increases the performance ratio. In desalination processes, the performance ratio can reach as high as 14 although the number of stages may be over 25 with increased capital cost. The number of stages for a process should be selected with respect to energy costs and capital costs. This comparison has shown that multi-stage flash with recirculation and condensation heat recovery maximizes the amount of evaporate produced and minimizes the steam and pumping energy requirements.

Multi-effect Flash Evaporation

External heat can be added to the leachate by installing submerged heating coils in the flash chambers to vaporize a larger percentage of feed. The resulting process is referred to as multi-effect flash evaporation. To compare multi-effect, multi-stage flash evaporation with multi-stage flash with recirculation, a multi-effect, four-stage flash process was simulated where enough heat was added to vaporize about 60

Table 6 Multi-effect and Multi-stage Comparison of Performance Ratios for Flash Evaporation with 65% Condensation Heat Recovery

Process Description	Product-to-feed Ratio	Performance Ratio with 65% Condensation Heat Recovery
Multi-effect	0.58	1.7
Four-stage Flash		
Four-stage Flash with Recirculation	0.90	1.0

percent of the leachate using the composition reported for the Swiss facility. In the simulation, the initial leachate was adjusted to pH 4, pre-heated to 97 C, and a 605 mm Hg pressure drop was divided between four stages. Table 6 shows a comparison of the product-to-feed ratio and the performance ratio for the multi-effect, four-stage flash process and the four-stage flash process with recirculation. This comparison shows that multi-effect, multi-stage flash is 70 percent more energy efficient than multi-stage flash evaporation. Thus, external heat could be added to obtain the best product-to-feed ratio and performance ratio. However, the addition of multi-effect flash evaporation can cause problems with leachate. Submerged coils need to be installed into the flash chambers to supply the external heat to each stage. Solids such as calcium carbonate and magnesium hydroxide can precipitate, which may cause scaling on the coils and reduce the heat transfer efficiency resulting in increased operating and maintenance costs. Multi-effect flash vaporization eliminates the advantages of pure flash vaporization by introducing a heat transfer surface that is in contact with the leachate during phase separation. Thus, multi-effect flash evaporation of leachate may be beneficial only if scale-forming compounds such as calcium, magnesium, sulfate, phosphate, and organic residues are at low concentrations. Otherwise, multi-effect flash evaporation of leachate may create scaling and deposition problems on heat transfer surfaces.

APPLIED LEACHATE EVAPORATION SIMULATIONS

The treatment of leachate was simulated using two published leachate compositions and a two-step, four-stage, acidic/basic flash vaporization process with recirculation. The leachate feed compositions (Table 1) were the average values reported for a western Pennsylvania facility (PA), and the yearly average values reported by the Delaware Solid Waste Authority (DSWA). These two feed compositions were chosen because they represent a diverse range of leachate strengths and because they reported many similar species that were in REQEM's data base. The DSWA leachate contained almost ten times the amount of acetic acid and twice the amount of ammonia reported in the PA leachate. It was assumed that VOAs or COD values reported for these leachates were present as acetic acid equivalent.

In the simulation, the feed leachate was first adjusted to pH 4, pre-heated to 97 C, flashed in the final stage at 40 C, and recirculated until approximately 95 percent of the original volume was obtained. In the second step, the feed leachate was adjusted to pH 11, pre-heated to 97 C, flashed at the final stage at 40 C, and recirculated until approximately 98 percent of the feed volume was obtained. The 0.95 product-to-feed ratio was chosen for the first step of the process because the remaining 5 percent was sufficient volume to contain all the nonvolatile contaminants such as metals and simple salts without creating appreciable precipitated solids in the effluent stream. Also, the ionic strength of the solution was not so

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Species
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Acetic Ac
Phenolate
Phenol
Toluene

Environm

Table 7 Predicted Evaporate and Concentrate Effluent Concentrations for a Two-step, Four-stage Flash Evaporation using DSWA Feed Leachate

Species	Concentrate 1 Molarity	Concentrate 2 Molarity	Evaporate Molarity
H	1.1E-04	4.1E-12	---
NH ₄	4.9E-01	5.1E-31	---
NH ₄ OH	6.3E-05	5.1E-31	7.7E-05
Acetate	7.1E-02	3.2E+00	---
Acetic Acid	3.3E-01	5.0E-07	1.4E-07
Phenolate	4.4E-10	1.7E-03	---
Phenol	3.1E-05	4.3E-06	2.9E-06
Toluene	6.4E-06	5.1E-31	6.0E-06

strong as to introduce errors in computing activity coefficients. The product-to-feed ratio in the second step was larger since the stream would not contain solid forming constituents.

The predicted molarities of the two concentrate streams and the evaporate stream from the DSWA and PA leachates are presented in Tables 7 and 8, respectively, for selected species. Many of the compounds formed were only present in the concentrate and are not included in these tables. As expected, less than 1 percent of ammonia and acetic acid, and less than 7 percent of phenol remained in the final evaporate for either leachate. Toluene did carry over to the final evaporate. Separate treatment would be necessary to remove the remaining toluene. Steam-stripping pre-treatment, as in the German evaporation facility, or air stripping pre-treatment, as provided in the Swiss evaporation facility, are two possible alternatives to remove nonionic, volatile organic compounds.

For the DSWA leachate, a two-step pH adjustment process is necessary to remove ammonia, acetic acid and phenol to acceptable levels. In the simulation, 3300 mg/L of hydrochloric acid was added to achieve a pH value of 4, and an additional 500 mg/L was added to maintain the pH of 4 through out the evaporation. For the basic pH adjustment, 7700 mg/L of sodium hydroxide was added initially, and no additional base was necessary during the run to maintain the pH above 11. The feed leachate was predicted to recycle 25 times in the first step and 38 times in the second step. The calculated performance ratio for the two-step process was 0.5 kg evaporate/kg steam. The performance ratio was low because the evaporate had to be vaporized twice to remove both ammonia and acetic acid. As a result, twice the amount of steam had to be used to produce roughly the same quantity of evaporate as in a one-step flash vaporization. The second concentrate effluent stream contains significant acetate and small amounts of phenolate. In practice, it may be possible to dispose such concentrate to a sewer system without further treatment other than pH adjustment.

For the western PA leachate, the simulations show that a single-step, four-stage flash vaporization process may be suf-

Table 8 Predicted Evaporate and Concentrate Effluent Concentrations for a Two-step, Four-stage Flash Evaporation using Western PA Feed Leachate

Species	Concentrate 1 Molarity	Concentrate 2 Molarity	Evaporate Molarity
H	1.7E-04	2.4E-12	---
NH ₄	4.4E-01	6.6E-30	---
NH ₄ OH	8.6E-05	9.6E-31	5.4E-05
Acetate	9.2E-03	1.8E-01	---
Acetic Acid	5.3E-02	3.8E-08	1.5E-08
Phenolate	1.5E-12	5.1E-06	---
Phenol	1.8E-07	1.8E-08	1.4E-08
Toluene	5.2E-06	9.6E-31	3.3E-06

Table 9 Predicted Evaporate Concentrations for a One-step, Four-stage Flash Evaporation Process using Western PA Feed Leachate and for a Two-step, Four-stage Flash Evaporation Process using DSWA Feed Leachate

Species	One-step, Western PA Predicted Evaporate Molarity	Two-step, DSWA Predicted Evaporate Molarity
	NH ₄ OH	5.0E-05
Acetic Acid	1.3E-02	1.4E-07
Phenol	3.8E-07	2.9E-06
Toluene	2.6E-06	6.0E-05

ficient to obtain acceptable evaporate quality, since initial acetic acid and phenol concentrations are low. The predicted evaporate molarities for single-step treatment of the western PA leachate and the two-step treatment of DSWA leachate are shown in Table 9. The predicted composition from the first step with the PA leachate was similar to the evaporate concentration from the second step with the DSWA leachate except for the acetic acid concentration. The acetic acid concentration in the evaporate from the first step is predicted to be about 0.013 M (about 800 mg/L as COD) for the PA leachate. For simulation purposes, all the COD was assigned as acetic acid, although most of the COD in leachate from older landfills would be comprised of nonvolatile components (Birchler *et al.*, 1994). Thus, depending on the COD composition, a single-step evaporate process may produce acceptable evaporate. For the first step acidic evaporation simulation, 730 mg/L of hydrochloric acid was initially added to the feed to achieve a pH value of 4, and an additional 120 mg/L of hydrochloric acid was added during the recirculation to maintain the recycled concentrate at a pH of 4. The PA leachate feed was predicted to recycle 26 times to vaporize 95 percent of the original feed using the single-step, four-stage flash. The computed performance ratio was approximately 1.0 kg evaporate/kg steam for the one-step process.

ECONOMIC ISSUES

The results from model simulations suggest that the evaporate composition from a two-step leachate vaporization treatment process may be high quality with respect to conventional pollutants. The major operating costs of evaporative leachate treatment are the large amounts of energy required to vaporize water and costs for disposal of the effluent streams. If landfill gas can be used as the energy source for the process, the operating costs are greatly reduced. The concentrate from the second evaporation step may contain mainly VOAs and could be easily biotreated or disposed to a sewer system. The disposal of the concentrate or sludge from the first evaporation step may be a principal operating cost. As with some conventional biological and chemical leachate treatment processes, the resulting sludge may be characterized as hazardous waste. The disposal of the sludge back into the landfill, as at the Swiss facility, may not be possible due to more stringent regulations in the United States. Additional treatment for the sludge, and other disposal options, would increase the total operating costs.

The number of evaporation stages and the size of the heat exchangers would affect the total cost. Many stages and large heat transfer areas would reduce steam consumption and operating costs, but increase capital costs. The capital cost should not be greatly influenced by the need for a two-step pH adjustment process versus a one-step process, since the same equipment could be used for both steps with suitable holding vessels. The capital costs are influenced also by the need to protect against the corrosive nature of the solutions.

CONCLUSION

Only limited published information is available on evaporation of landfill leachate. The Reaction EQUilibrium Evaporation Model (REQEM) was developed to evaluate the use of evaporation processes to treat leachate. REQEM was designed to: i) simulate different flash vaporization processes, ii) predict the effluent stream compositions and quantities, and iii) compute the energy requirements.

Simulations have shown a one-step evaporation process may be sufficient for obtaining adequate evaporate quality with respect to ammonia or acetic acid for low concentrations of either contaminant. However, it is evident that a two-step evaporation process, such as an acidic/basic evaporation process or equivalent technology, would be needed to obtain satisfactory evaporate quality for a strong leachate having high concentrations of ammonia and volatile organic acids (VOAs). If nonionic, volatile organic compounds (VOCs) are present in appreciable amounts in leachate, then pre- or post-treatment may be necessary to obtain adequate evaporate quality.

The resulting evaporate from leachate treatment, which will be mostly water, may be easier to dispose than effluent streams produced by conventional treatment processes. The concentrate streams will be a small fraction of the original leachate volume. The first concentrate stream of a two-step vaporization process may be characterized as a hazardous waste depending on the initial concentration of constituents in leachate and the vaporized fraction, particularly with respect to concentrating heavy metals. The concentrate stream from the second flash vaporization is predicted to contain only residual ionic volatile organic compounds, e.g., VOAs, and may be suitable for discharge to a sewer system. Alternatively, biological treatment could be used to effectively treat the VOAs in the evaporate from a single stage process in lieu of second stage evaporation. Simulations have shown that using HCl instead of H₂SO₄ to control the pH of leachate decreases the likelihood of scaling during flash evaporation. The adjustment of pH in the leachate feed will have no direct effect on the product-to-feed ratio, the performance ratio, or the evaporate quality with respect to either nonionic VOCs, or nonvolatile compounds such as metals and simple salts.

In the evaluation of different process configurations, the multi-stage flash process with recirculation and condensation heat recovery maximized the amount of evaporate produced and minimized the steam and pumping energy requirements. The number of stages for a process should be selected with respect to balancing energy costs and capital costs. Multi-effect, multi-stage flash evaporation of leachate may be more energy efficient than multi-stage flash with recirculation, but feasible only if scale-forming compounds are at low levels. In general, multi-stage flash evaporation with recirculation and heat recovery appears to be the preferred process.

It appears that flash vaporization may have many benefits which merit further investigation. Flash vaporization systems can be evaluated by computer simulation to anticipate the best operating conditions for a particular leachate feed composition. Flash vaporization can be operated in batch (or semi-continuous) mode as needed to handle varying leachate compositions. Startup and shutdown of an evaporation system is not subject to acclimation or recovery that are key factors for biological systems. The evaporation system is constrained by problems associated with the handling and disposal of the concentrate waste stream. These limitations are mostly regulatory and not operational problems.

Future work on modeling leachate treatment by evaporation should address integrating models to simulate additional technologies with the flash vaporization model, such as batch distillation, air stripping, or biological treatment to assess combined strategies for the removal of VOCs and VOAs. Other compounds, such as heavy metals and additional volatile organic compounds, should be added into the data bank to allow

a greater variety of leachate stream compositions to be simulated. A process economic evaluation needs to be performed for flash evaporation to determine trade offs between operating and capital costs, and for comparing costs for handling/disposing of the residual streams from leachate evaporation processes with those from conventional treatment technologies.

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LITERATURE CITED

1. Amsonleit, N., "Evaporation of Problematic Landfill Leachates," *Wasser, Luft, und Betrieb*, 29, pp. 63-66 (1985).
2. Birchler, D. R., M. W. Milke, A. L. Marks, and R. G. Luthy, "Landfill Leachate Treatment by Evaporation," to appear, *J. Env. Engng.*, ASCE, Sept/Oct (1994).
3. Boston, J. F., and H. I. Britt, "A Radically Different Formulation and Solution of the Single-Stage Flash Problem," *Comput. Chem. Engng.*, 2, pp. 109-122 (1978).
4. Bromley, L. A., "Thermodynamic Properties of Strong Electrolytes in Aqueous Solutions," *AIChE J.*, 19, No. 2, pp. 313-320 (1973).
5. Buhler, R., Hofstetter Company, Personal Communications, Hindelbank, Switzerland (1991).
6. Cavallotti, P., G. Celeri, and B. Leonardis, "Calculation of Multicomponent Multiphase Equilibria," *Chem. Engng. Sci.*, 35, pp. 2297-2304 (1980).
7. Delaware Solid Waste Authority, October, "Request for Proposal, Testing, Design, Construction, and Operation of a Leachate Evaporation/Incineration Facility at the Central Solid Waste Management Center, Contract DSWA-223," Appendix A (1990).
8. Diwekar, U. M., and K. P. Madhavan, "Batch-Dist: A Comprehensive Package for Simulation, Design, Optimization and Optimal Control of Multicomponents, Multifraction Batch Distillation Columns," *Comput. Chem. Engng.*, 15, No. 12, pp. 883-892 (1991).
9. Diwekar, U. M., "An Efficient Design Method for Binary, Azeotropic, Batch Distillation Columns," *AIChE J.*, 37, No. 10, pp. 1571-1578 (1991).
10. Gmehling, J., *Vapor-Liquid Equilibrium Data Collection*, Dechema-Schollum International, Flushing, NY (1977).
11. Henley, E. J., *Equilibrium-Stage Separation Operations in Chemical Engineering*, Wiley Publishers, New York, (1981).
12. Hofstetter, U., B. Hausherr, W. Wehrli, M. Posnansky, and M. Bichsel, "Leachate Treatment: Autoflash-Multistage-Evaporator," Hofstetter Company, Hindelbank, Switzerland (1991).
13. Kahn, A. H., *Desalination Processes and Multi-stage Flash Distillation Practice*, Elsevier, New York (1986).
14. Konrad, L., "Process-Technical Principles of the Evaporation of Leachates," *Ber. Wasserqueleewirtsch. Gesundheitsingenieurwes.*, Tech Univ., Muenchen, 86, pp. 257-277 (1989).
15. Marquardt, D. W., "An Algorithm for Least-Squares Estimation of Nonlinear Parameters," *J. Soc. Indust. Appl. Math.*, 11, No. 2, pp. 431-441 (1963).
16. Meissner, H. P., C. L. Kusik, and J. W. Tester, "Activity