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Project Summary

Simulation of Leachate Generation from Municipal Solid Waste

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The modeling of leachate generation from a municipal solid waste (MSW) landfill or landfill simulation should utilize a mechanistic approach which properly accounts for the microbially mediated processes of landfill stabilization. Previous models have been based on the solubility of waste constituents in the water percolating through a landfill. These models, called washout models, provided a reasonable approximation of leachate constituent concentrations after the landfill or landfill simulation had reached a period of relative dormancy, called maturation, but were deficient in predicting leachate constituent concentrations in the early stages of landfill stabilization, and gas production and quality after methane fermentation had been established. These early stages in the life of a landfill are extremely important, because, in most cases, the highest leachate strengths and the most extreme conditions a liner or the surrounding environment would be subjected to occur during this period. Similarly, the methane fermentation stage is important in predicting the potential for gas production, migration and possible utilization.

A mechanistic three-step model, GTLEACH-I, was developed to simulate the microbially mediated processes of landfill stabilization in terms of hydrolysis of substrate, acid formation and methane fermentation. The model was applied to two sets of experimental data and provided a reasonable prediction of volatile acids and gas generation.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The generation of leachate from a landfill is a complex process depending not only on the characteristics of the landfilled wastes, but also on the: (1) interaction of the waste with water percolating through the landfill, (2) operational variables such as waste placement procedures, (3) climatic conditions, (4) landfill design, and (5) potential for interaction of the landfilled waste with ground water. Leachate characterization is further complicated by the effects of microbial activity, which mediates the conversion of both hazardous and nonhazardous wastes and their potential for transport and migration from the landfill site.

Leachate characteristics and the rate of leachate generation are dependent on the time and stage of landfill stabilization. Numerous investigations of the characteristics of leachate generated from municipal solid waste disposal have indicated the highest concentrations of a large number of leachate constituents are generated during the early stages of microbially mediated stabilization. Therefore, if the purpose of a simulation model is to predict changes in chemical concentrations of leachate for assessment of migration potential or liner/leachate compatibility, it is necessary to model the various phases of landfill stabilization.

Landfill Stabilization

The fate of waste constituents disposed in a landfill can be envisioned as a partitioning among the solid, vapor or aqueous phases. Various microbial, chemical, and physical transformations alter the chemical and physical nature of the waste and initiate transfer of reaction products from one phase to another. Likewise, waste constituents are transported from the landfill in aqueous solution and suspension by washout and through the evolution of gases.

Microbially mediated reactions control the landfill environment for some time after initial placement of waste and strongly impact the outcome of other chemical and physical transformations leading to stabilization. Both aerobic and anaerobic microbial processes occur in a landfill; however, free oxygen is typically available only in early stages of landfill stabilization and is often exhausted prior to the appearance of leachate. For this reason, anaerobic activity usually establishes and controls leachate and gas quality during the active life of a landfill.

In a steady-state anaerobic treatment process, three steps occur simultaneously at a rate controlled by the slowest step in the sequence so that there is little accumulation of intermediate products over time. However, in a non-homogeneous, batch-wise system such as a landfill, the activity of acid-forming and methane-forming bacteria may not be in balance at any particular location in the landfill at any one time. As a result, landfills are often characterized by temporal stages governed by the predominance of changing microbial populations in the life of the landfill.

A landfill has been described as evolving through five stages as it becomes stabilized—initial adjustment, transition, acid formation, methane fermentation, and final maturation. Accordingly, microbially mediated reactions first accomplish the transformation and solubilization of waste materials into the aqueous phase. Further transformations into intermediates such as the volatile organic acids, followed by conversion to methane, result in transfer of conversion products to the gas phase. The relative rates of these transformations, combined with the rate of moisture infiltration, determine the concentration and mass flux of the various biochemical intermediates and end-products. Superimposed upon the microbial transformations are solubility, speciation, oxidation-reduction and solid-liquid gas equilibria of both inorganic and organic chemicals. These equilibria establish the partitioning of chemical components among solid, liquid and gas phases.

One of the major difficulties in describing the fate of waste disposed in a landfill stems from uncertainties in the relative impacts of the various transformation and partitioning processes acting on the waste, leachate and gas. Leachate and gas composition and quantity data reveal the net results of the various transformation and partitioning processes but do not necessarily indicate the path taken. Furthermore, data are seldom available and sufficient to describe the composition of the solid phase. Thus, it is difficult to assess the relative impacts of adsorption, complexation and precipitation processes, since they all result in transfer of a component from the aqeuous to the solid phase or *vice versa.* Likewise, assessment of the relative effects of microbial degradation, chemical conversion and sorption on the fate of organic components disposed in a landfill is also exceedingly challenging.

GTLEACH-I Model

Since the microbially mediated processes of landfill stabilization control the rate of generation and constituent concentrations of leachate and gas produced from an MSW landfill or landfill simulation, it is necessary to use a mechanistic model which incorporates the effects of the stabilization process. GTLEACH-I is a three-phase mechanistic model capable of simultating changes in leachate volatile acid concentrations and methane gas emerging from the landfill over time. The model is composed of hydrogeologic and biologic modules and is written for a single lift of a landfill or a landfill simulation. Additional effort will be required for application to full-scale landfills.

Hydrogeologic Module

The rate and quantity of water flowing through waste materials can be correlated to the quantity and, to some extent, the characteristics of leachate produced in landfills. This is not to imply that a simple washout model adequately predicts leachate characteristics. Stated very simply, the characteristics of the leachate depend primarily on the adsorption, solution, movement and microbially mediated hydrolysis/conversion of waste materials described by gravity flow models and by biological waste conversion models.

The latter microbially mediated stabilization processes are dependent on many parameters, among which are the water content, porosity, and distribution of water in the waste, the contact time between water percolating through the landfill and the waste materials, and changes in waste surface area, composition and porosity with time. These parameters either affect or are dependent upon the quantity and rate of water flowing into and through the waste materials.

The hydrogeologic module must account for all flow into and out of the landfill and its constituent cells. Therefore, a quasi two-dimensional, deterministic model similar to the HELP model could be incorporated into the hydrogeologic module of GTLEACH-I. The HELP model performs a sequential, time-based water budget for a landfill cell. The water budget is based on soil and waste characteristics, climatological data and landfill design parameters. The model can be described as a component, semi-empirical numerical model which evaluates and effects and interaction of runoff, evapotranspiration, percolation and lateral drainage.

To provide the data required to evaluate the time-dependent progression of microbially mediated stabilization, several modifications of the HELP model were made that yielded unrealistically high flow rates through the waste materials. Therefore, it is anticipated that the vertical flow model will be replaced by a model that provides more realistic flow rates and distribution of moisture content as a function of depth and time in the waste material. In addition, surface run-on interaction with the site hydrology and short-circuiting have been considered necessary components.

Biologic Module

Based on observed landfill stabilization trends it is evident that the appearance and eventual disappearance of volatile acids in leachate are primary indicators of processes responsible for changes in COD, pH, and oxidation-reduction potential within the landfill. Thus, a module which is capable of simulating the changes in volatile acid concentrations in leachate over time could ultimately form the foundation for simulation of other indicator parameters such as pH and oxidation-reduction potential (ORP) along with corresponding changes in the mobility of hazardous constituents disposed in a landfill.

The three-step processes of hydrolysis/solubilization, acid formation and methane fermentation were logical choices on which to base the development of GTLEACH-I. Since it has been applied successfully in the design and operation of other anaerobic processes, it was reasonable to assume that the three-step process would also be successful in modeling anaerobic stabilization in landfill systems. Furthermore, such a mechanistic model could predict the concentration of volatile acid intermediates as a function of time as well as the rate of conversion of leachate COD to methane.

Hydrolysis/solubilization is an important process in the degradation of organic matter, and it is often considered to be the rate-limiting step in the acid phase of anaerobic digestion. The rate of hydrolysis is affected by many factors including pH, temperature, microbial biomass and associated substrate, the remaining concentration of particulate substrate, and hydrolysis product concentration. It is evident that any one or all of these factors may change with time in a batch-wise operation such as a landfill.

At constant temperature and pH, hydrolysis may be approximated as first-order with respect to particulate or solid organic substrate concentration. Therefore, this approach was used to model hydrolysis/solubilization in GTLEACH-I as expressed by the equation:

$$\frac{dM}{dt} = -K_H M$$

where,

- M = solid substrate concentration expressed as if it were suspended in landfill moisture, and
- K_H = hydrolysis/solubilization rate constant.

While the approximation of first-order kinetics for hydrolysis is reasonable when considering the acid formation and methane fermentation phases of landfill stabilization separately, difficulty is expected in modeling the transition between the two phases when pH and other leachate characteristics change dramatically. Additionally, as relatively easily hydrolyzed substrates are exhausted and more refractory substrates begin to be utilized, a corresponding change in the rate of hydrolysis should be manifested. Production of volatile acids was represented in GTLEACH-I by a single group of acid-forming bacteria rather than a more complicated set of equations for multiple populations of bacteria.

The major reason for selecting a single equation to model behavior of a group of microorganisms is that the relative activities of the various populations of microorganisms were assumed constant with respect to each other, so that the net reaction follows Monod kinetics. While the validity of this assumption may be questioned when applied to landfills, the single-equation Monod model of acidogenesis was selected to allow application of the model to the database currently available and to minimize the number of input parameters to the model.

One other aspect of methanogenesis to be considered is that methanogen growth and concurrent methane production can be suppressed at pH levels below the range of 6.8 to 7.5. This explains the virtual absence of methane production observed during the acid phase of landfill stabilization when the pH of landfill moisture can be well below pH 6. That methanogenesis is established at all is attributed to the heterogeneous nature of landfills which allows methanogens to begin to grow in small pockets of the landfill not completely saturated with volatile acids. Methanogen growth gradually spreads out from these pockets until a methanogen population is established sufficient to reduce the concentrations of volatile acids in the landfill moisture and increase the pH, thereby allowing unsuppressed methanogen growth throughout.

As a first attempt at modeling landfill processes, it was decided to provide for suppression of methanogenesis during the acid phase by simply delaying initiation of methanogenesis for a specified period of time in GTLEACH-I. An extension of this approach will require development of a pH-inhibition term for methanogenesis which allows for methanogen growth at a suppressed rate during periods of low leachate pH.

Diffusional resistance to reactions in a dense matrix such as a microbial film or aggregate may have significant influence on reaction kinetics by reducing the efficiency of the microbial mass. Due to difficulties encountered in evaluating the total microbial mass, the thickness of biofilms or aggregates, and due to heterogeneities in landfill environments, diffusional resistances were not explicitly treated in GTLEACH-I. Instead, they were subsumed in the fitting of the Monod rate constant to experimental data.

Evaluation of Model

The initial values of the kinetic growth constants for acidogenic and methanogenic bacteria were selected based on compiled data. The parametric analysis indicated that the GTLEACH-I model provided a reasonable approximation of the quantities of volatile acids and methane gas with time. Using the values of the parameters which provided the best fit of the data in the parametric analysis, the model was used to predict the quantities of volatile acids and methane gas for the boundary conditions of selected landfill simulation studies.

A major accomplishment of the model was the application of kinetic constants for hydrolysis/solubilization and acidogenesis in the simulation of two sets of experimental data having substantially different moisture application rates. The model was also a useful diagnostic tool for examining differences in microbial populations resulting from different leachate management options.

Conclusions

A useful interpretation of leachate generation and leachate characteristics is a highly complex and difficult undertaking, primarily because landfill disposal of waste is site specific. The local hydrogeology and landfill design and operation all influence the potential for infiltration and percolation and the rate of saturation of the waste materials. Therefore, leachate characteristics and opportunity for migration will vary in accordance with these factors.

Numerous evaluations and simulations of landfill performance have been conducted to characterize leachate generation patterns. Some of the data from these studies have been used to develop numerical predictive models descriptive of leachate generation as a function of time. A review and further development of these models led to the following conclusions.

1. Data descriptive of microbially mediated processes of landfill stabilization are necessary components of an effective numerical landfill simulation model and are influenced by waste type, availa-

bility of nutrients, moisture content, and opportunity for biological or physical/chemical conversion.

2. Comprehensive analysis of waste characteristics and waste constituent distribution must be available as input data for predicting leachate constituent concentration changes as a function of time, to indicate substrates susceptible to conversion, to help assess any delays in the progress of landfill stabilization, and to appropriately distinguish microbial mediation from simple washout.

3. There are no established techniques to yield data sufficient to accurately predict hydraulic conductivity at landfills. Data from simulation studies performed to date are presumptive of flow conditions and generally ignore nonhomogeneity of the leaching matrix.

4. The GTLEACH-I model has been developed to simulate the microbially mediated process of landfill stabilization in terms of hydrolysis of waste substrate, acid formation and methane formation.

5. GTLEACH-I provides reasonable predictions of volatile acid and gas generation during landfill stabilization and may be expanded to predict variations of pH, pE, and ORP as functions of time. These latter relationships again require a comprehensive database which must include acid-base and oxidation-reduction equilibria not usually present in existing compilations of landfill analyses.

6. Calibration of the GTLEACH-I model has been limited by a general lack of substrate specificity, the uncertainty of flow distribution and short-circuiting, particularly during the early stages of landfill stabilization, the possibility of retardation of microbial mediation, the influences of population dynamics as substrate conversion proceeds and the waste mass is engulfed, and the potential for containment or release of the liquid and gas transport phases.

Recommendations

Based on the insights obtained from the review and utilization of available data, the following recommendations for future research are proposed:

1. Develop implementation strategies for any future research on landfill stabilization to assure that sufficient data are generated to support the further development and verification of predictive models capable of more accurately modeling both short-term and long-term variations in leachate quality and quantity.

2. Initiate a field study that provides sufficient data to support the refinement and verification of the numerical model.

3. Initiate complementary studies to measure hydraulic conductivity of landfilled wastes to variable physical and chemical characteristics in a temporally and spatially distributed fashion. The study should provide data and information regarding spatial variation of hydraulic conductivity and time related changes in hydraulic conductivity.

4. Refine and expand the GTLEACH-I model to predict pH, pE, and ORP as a function of time, to incorporate more realistic descriptions of flow retardation or inhibition, and to allow prediction of selected inorganic and organic constituent concentrations as population dynamics affect the overall processes of landfill stabilization.

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The complete report, entitled "Simulation of Leachate Generation from Municipal Solid Waste," (Order No. PB 87-227 005/AS; Cost: $18.95, subject to change) will be available only from:
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Project Summary

Novel Vapor-Deposited Lubricants for Metal-Forming Processes

J. J. Mills

This report gives results of a laboratory study of the feasibility of using vapor-phase lubrication to lubricate industrial metal forging dies. It gives results of six tasks conducted during the study and discusses the potential production and environmental impact of the process. If a vapor lubrication system can be developed for general industrial use it can significantly reduce the volume of forging lubricants required by present industrial forging operations. The laboratory results indicate that it may be possible to reduce potential air pollution emissions from forging using vapor lubrication by as much as 85%. This would be accomplished by using 85% less lubricant volume during metal forging.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The forging and shaping of metal parts is one of many metal fabricating processes that may generate emissions of volatile organic compounds (VOCs) and hydrocarbons. In typical metal forming operations hot metal is squeezed in dies to produce metal shapes in the form of the die cavity. This process may require many intermediate forming and shaping steps using successively more accurate dies to reach the finished product. A key aspect of these shaping steps is the lubrication of the dies and metal parts to allow easy release of the part from the die. The used lubricants frequently result in emissions containing VOCs and potentially toxic metal to the atmosphere.

This report presents the results of a Phase I study that investigated the feasibility of using vapor-phase lubrication for industrial metal forging dies. It presents the results of six tasks conducted during the study and discusses the potential production and environmental impact of the effectiveness of the process. A vapor lubrication system developed for general industrial use could significantly reduce the volume of forging lubricants required by present industrial forging operations.

The project proposes to use a vapor-phase polymer film to lubricate forging dies in their closed position. An injection device allows lubricant vapor to be applied automatically through passages in the flange areas of the die. This eliminates large volumes of liquid die lubricants and the resulting emissions typically generated during this operation.

Project Plan

Six tasks were performed during the project. Each was designed to produce vital elements and data for a future pilot scale unit. The six tasks were to:

- Establish a fully operational, laboratory scale vapor-phase lubricant delivery system (LDS).
- Formulate lubricants and evaluate the lubricity of the vapor-deposited polymers using the ring compression test.
- Forge parts using conventional lubricants to provide baseline data.
- Modify the forging die to permit vapor-phase lubrication.
- Forge five parts using vapor-phase lubrication in a modified die.
- Quantitatively compare the emissions from vapor-deposited lubrication with those from the conventional oil-based lubrication system.

Emission Results

The volume of lubricant used during each experiment was determined qualitatively by the metal flow and release properties exhibited by each technique. Metal flow is defined by the interface friction factor (m value) which is a measure of metal flow within the die. Release properties are defined by the relative ease with which the part can be removed from the die. It was assumed that all lubricant used during each experiment was volatilized to the atmosphere. This represents the worst case scenario for the process. Table 1 summarizes the results.

Conclusion

Although this project included a limited number of experiments, it did show that vapor-phase lubrication is feasible for metal forging. It can also result in a significant reduction of potential emissions to the atmosphere. The process could reduce emissions from forging and casting operations by as much as 85%.

The project represents only the first step, laboratory feasibility, of the development program for vapor-phase lubrication. Significant research and development still remains, including die lubrication system design and lubricant formulation development.

Table 1. *Average Emissions and Forging Parameters*

	Conventional Lubrication	*Vapor-Phase Lubrication*
Average block and finish per part, ml	76	11.3
Average forging force, ton (kN)	75 (667)	75 (667)
Average forging time, sec	60	60

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The complete report, entitled "Novel Vapor-Deposited Lubricants for Metal-Forming Processes," (Order No. PB 87-227 351/AS; Cost: $11.95, subject to change) will be available only from:
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