Journal of Hazardous Materials, 29 (1992) 97–125
Elsevier Science Publishers B.V., Amsterdam

Process development for remediation of phenolic waste lagoons*

Rolf Arands, David Kuczykowski and David Kosson[1]

Rutgers University, Department of Chemical and Biochemical Engineering, P.O. Box 909, Piscataway, NJ 08855-0909 (USA)

Abstract

Aqueous phenolic wastes from a phenolic resin production process were disposed in lagoons on the production site. Groundwater contamination in the area has exceeded state limits and thus mandated remedial action. Representative core samples from within and around the highly contaminated soil regions were collected. These samples were physically and chemically characterized to better determine the extent and nature of contamination. Both *in situ* and on-site remediation scenarios were considered. The most promising scenario was *in situ* forced leaching with aboveground aerobic microbial treatment of the leachate. The treatment could be carried out with six months operation at a cost of approximately $170 per ton of treated soil, with the capability of reaching a final residual soil phenol concentration less than 20 mg/kg dry soil.

1. Introduction

The historic practice of landfilling industrial wastes into uncontained disposal areas has resulted in numerous waste deposits and areas of contaminated soils. Leachates from these source materials can pose a serious public health threat through migration of toxic constituents and the resulting contamination of groundwater and drinking water supplies. The evaluation of the applicability of several typical remediation alternatives and the preliminary design of a remediation process for a site containing soils contaminated with phenol are presented in this paper.

An undisclosed chemical manufacturer produced various phenolic resins from phenol and formaldehyde. The type of resin produced was dependent upon factors such as the initial ratio of phenol to formaldehyde, the type of catalyst (acid or alkali), and the reaction time. The process resulted in an aqueous distillate waste containing phenol and reaction residues [1]. The manufacturer disposed the aqueous distillate wastes and off-specification resins into on-site lagoons over a period in excess of three decades.

Site investigations indicated that concentrations of phenol in on-site

*Paper presented at the Symposium on Characterization and Cleanup of Chemical Waste Sites, American Chemical Society 200th National Meeting, Division of Industrial & Engineering Chemistry, Washington, DC, August 29, 1990.

[1]To whom correspondence should be addressed.

groundwater were in excess of state groundwater standards. The chemical manufacturer was required to seek and implement a permanent remediation of the source material and groundwater. Alternatives to site remediation by offsite disposal of the contaminated soils were sought to avoid long-term liability associated with excavating the lagoons and landfilling the wastes and to minimize remediation costs.

Development of the remediation process was accomplished in three stages. First, lagoon contents were sampled and characterized to provide a detailed site description. Second, potential process steps for remediation were evaluated as individual unit processes. Processes evaluated included *in situ* soil extraction, *in situ* anaerobic biodegradation and on-site aerobic biodegradation. Third, process steps were integrated into a preliminary remediation design and cost estimates were developed. Both temporary setup and disposal of the remediation process equipment was considered as part of the preliminary process design to reduce the costs of remediation and the shutdown following cleanup.

2. Site description and history

The natural soil overburden at the site consists of sandy loams and sandy clay loams from the ground surface to depths between 10 and 15 feet. This layer is underlain by a layer of dense clay approximately 50 feet thick. The contaminated groundwater is perched above the underlying clay and is generally located from 1 to 3 feet below the ground surface. The groundwater flows along the upper boundary of the underlying clay in a southwesterly direction. Groundwater movement through the clay layer is not significant because of the typically low hydraulic conductivities and permeabilities of the clays [2]. The clay layer is most likely serving as a natural barrier to further migration of the contaminants. An extensive description of the site is provided elsewhere [3].

Lagoon 1 had been used as a phenol distillate settling pond. The pond was backfilled in 1968 with a soil fill. The lagoon is approximately 50 ft $\times$ 50 ft. The bottom of the lagoon was located at a depth between 15 and 20 feet and was in contact with the natural clay layer. Runon/runoff devices previously had been installed on Lagoon 1. In 1977, the ground in the lagoon area was leveled by backfilling with a clean fill soil, graded, and paved. A shallow drainage system (approximately 5 ft depth) was installed hydraulically downgradient from the lagoon to allow collection and removal of contaminated groundwater. A subsurface vertical concrete slurry wall completely enclosing the lagoon was installed in 1981 to minimize groundwater infiltration.

Lagoon 2 also had been used as a phenol distillate settling pond. The pond had been previously backfilled with a soil fill. No runon/runoff containment devices have been installed on this lagoon. The lagoon is approximately 35

ft × 35 ft and is approximately 15 to 20 feet in depth. The bottom of this lagoon also was in contact with the natural clay layer.

3. Review of existing data and applicable unit processes

Prior data on the physical and chemical properties of the soils within the lagoons were limited. Previous sampling work had not examined the fill material within each lagoon area to an extent acceptable to characterize the contents of the lagoon areas. Borings with split-spoon sampling and installation of a monitoring well within each lagoon were carried out to improve characterization.

Both *in situ* extraction and on-site excavation/above-ground extraction were considered. Excavation of the contaminated soils was undesirable due to the generally higher costs of excavation versus *in situ* extraction. Investigations by Evangelista et al. [4] employing soils from a different contaminated site indicated that between 82 and 95% of the phenol was removed by extraction with water from a phenol-contaminated soil during a lab-scale batch extraction. Passive *in situ* leaching of the soil at the site removed 99.9% of the phenol and 99.7% of cresols in contaminated soils. Water was an effective and efficient extractant for phenol, from a site remediation point of view, because of the hydrophilic nature of phenol and the inherent low cost and safety of water. *In situ* extraction utilizing water was preferred. Evaluation of the desorption behavior of phenol from the contaminated soils was needed to develop the *in situ* extraction process for this site.

Several organic destruction methods were initially considered as potentially applicable unit process steps. Anaerobic biodegradations of a variety of aromatic compounds have been studied extensively [5–10]. Removal rates varied between 10 and 20 mg/l [7]. Typical concentrations treated were up to 200 mg/l [9]. Hydrogen peroxide/UV light (H_2O_2/UV) has been shown to have potential for treatment of wastestreams with organic compounds [11]. Many organic compounds have been treated, with fast removal rates [11,12]. Hager et al. degraded a 100 mg/l prepared solution of phenol in 5 minutes (1200 mg phenol/l h) in a specially designed photoreaction chamber [13]. The process is limited to treating relatively dilute and translucent liquids [11–13]. Aerobic microbial treatment has been used to effectively treat wastestreams containing phenol at concentrations up to 20,000 mg/l [14]. Typical removal rates were approximately 100 mg phenol/l h. Removal efficiencies of up to 99.9% have been reported [14–16].

Phenol concentrations in groundwater from the lagoons in this study were up to 3000 mg/l. These concentrations would hinder the effectiveness of H_2O_2/UV treatment. Dilution of groundwater to yield a more treatable wastestream would increase the treated liquid volume 10 to 30-fold. The typical specially designed photoreaction chamber needed for H_2O_2/UV treatment was beyond

the temporary and "throw-away" philosophy of the remediation process design. The hazards of transporting and handling large volumes of H_2O_2 on the site were additional considerations in the decision to seek an alternative destruction step. Both anaerobic and aerobic treatments of the leachate were considered. Contaminant removal rates and maximum treatable phenol concentrations were more favorable for aerobic microbial processes than either soil-based or activated-sludge anaerobic processes. It was anticipated that maintenance of anaerobic conditions would be more difficult than maintenance of aerobic conditions as an above-ground unit process. Thus, the aerobic process was preferred.

The most favorable unit process scenario was *in situ* extraction of the contaminated soils, followed by above-ground aerobic biodegradation of the collected leachate. Further studies were carried out to determine how the soils and leachate would behave when subjected to these treatments.

3. Lagoon sampling and characterization

3.1 Sampling and analytical methods

Boring and well locations for Lagoons 1 and 2 are shown in Figs. 1 and 2.

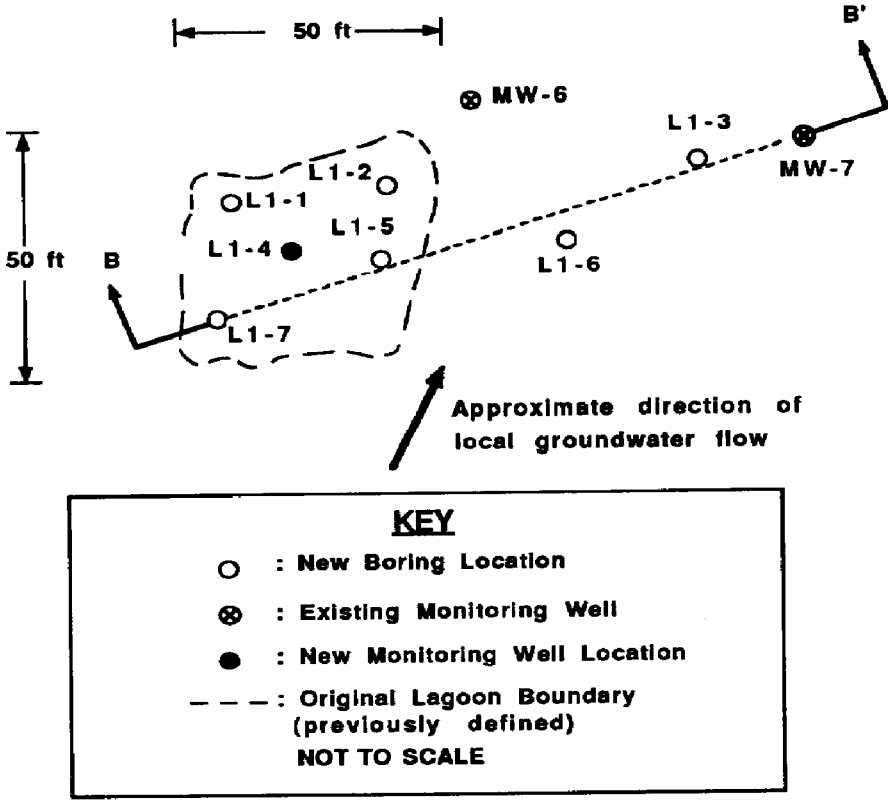

Fig. 1. Lagoon 1—sampling layout.

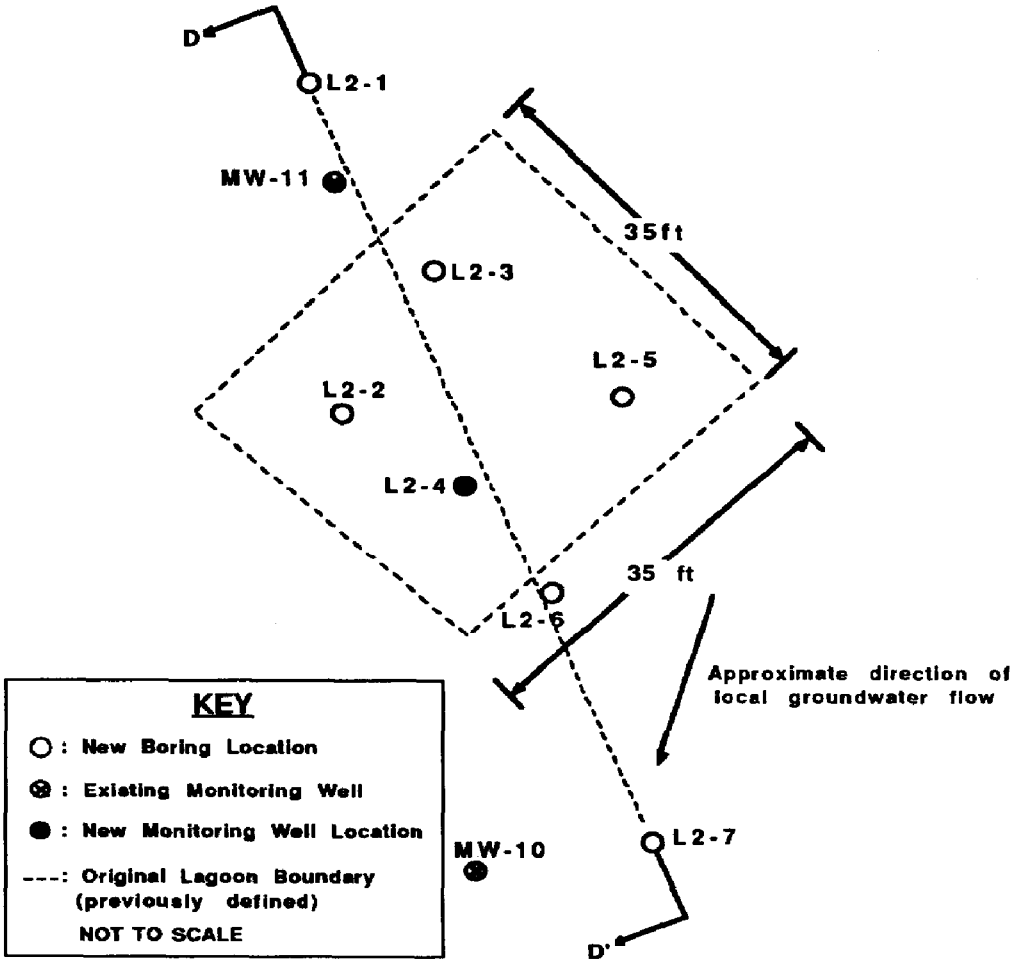

Fig. 2. Lagoon 2—sampling layout.

Boring locations were selected to develop reasonably representative horizontal and vertical profiles without analyzing an excessive number of samples. One boring location was in presumably clean soil hydraulically isolated from each lagoon to provide data on the natural surrounding soil. Borings within the lagoons were arranged such that the lines formed by the borings were either parallel or perpendicular to the groundwater flow. In addition, one boring location for each lagoon was chosen in an area presumably contaminated by migration of groundwater downgradient from the source material.

A portable photoionization detector (PID, 10.6 eV lamp, model TIP II, Photovac Inc., Ontario) was used as a preliminary test for highly contaminated samples during split-spoon sampling. The instrument was calibrated with a 100 ppm (volumetric) isobutylene gas standard. Observations were made about sample consistency, color, and texture. Samples were sealed in glass jars with Teflon-lined lids, iced during transport and stored at 4 °C until analysis. Phenol concentration, total organic carbon (TOC), anions, cations, and pH assays

were carried out as soon as possible following soil sampling to minimize distortion of assays by volatilization or degradation.

Soil extracts were prepared by serial batch extractions with deionized (DI) water. Two successive extractions were used with a liquid to solid ratio of 20:1. The two extracts were combined and quantitatively diluted to 250 ml with deionized water.

All phenol concentrations were quantified by HPLC (5 cm Supelco LC-8 column, 40 deg C, 1.0 ml/min 60:40 methanol:water, 270 nm UV wavelength). A Perkin Elmer (PE) Series 4 HPLC Pump and PE LC-95 UV Detector were used. The typical detection limit was approximately 1 mg/l at a 20 μl injection size. TOC analyses were carried out using an O.I. Corporation Model 700 Total Organic Carbon analyzer. A minimum of two 50 μl injections of each extract were analyzed. Anions were assayed by HPLC (25 cm Hamilton PRP-X100 Ion Exchange column, 50°C, 1.0 ml/min aqueous potassium hydrogen phthalate, 280 nm UV vacancy detection). Cations were assayed using standard atomic absorption (AA) methods on a PE Model 3030 AA System. Soil pH was carried out on unadulterated soil samples using the standard method for soil pH [17].

3.2 Results

Lagoon 1 sampling indicated PID readings up to 1800 ppm between the depths of 0 and 2 feet. Only asphalt and an apparent preparative fill for the asphalt paving were observed between these depths. A heterogeneous region consisting mainly of a gray brown sandy clay was encountered between the depths of 2 to approximately 12 feet. The PID readings were as high as 500 ppm from samples in this region. Alternating layers of a red-brown hard material and a brown sandy material were evident within the lagoon boundaries, suggesting alternating periods of waste disposal and coverings with fill material. The underlying clay layer began at a depth of approximately 11 feet. The PID readings over samples of the clay dropped to near zero within the first several feet, suggesting that vertical migration of the contaminants into the clay had been limited. The heterogeneous region depicted in Cross Section B-B′ (Fig. 3) most likely represents the soil region affected directly by the waste disposal.

Chemical assays of the soils from Lagoon 1 indicated that soil phenol concentrations ranged from below the detection limit (0.5 mg phenol/kg dry soil) to 13,300 mg phenol/kg dry soil (Fig. 4). The installation of clean fill and the continual flushing of the soils between the surface and a depth of 5 feet corroborated with the absence of phenol contamination observed in samples from these depths. Virtually no phenol contamination was observed in samples from Borings L1-1, L1-3, L1-6, and L1-7. Significant phenol contamination was observed in samples taken between the depths of 5 and 17 feet in the remaining borings L1-2, L1-4, and L1-5, suggesting that the main area of contamination was centered on these borings. The improved definition of the boundaries of the highly contaminated region allowed the size, and thus both the complexity

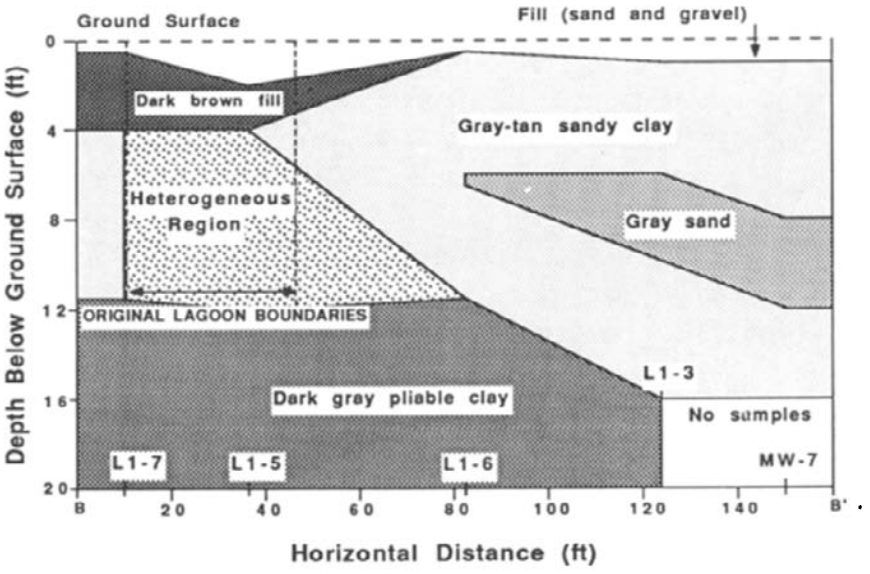

Fig. 3. Lagoon 1—cross section B-B′ (in Fig. 2).

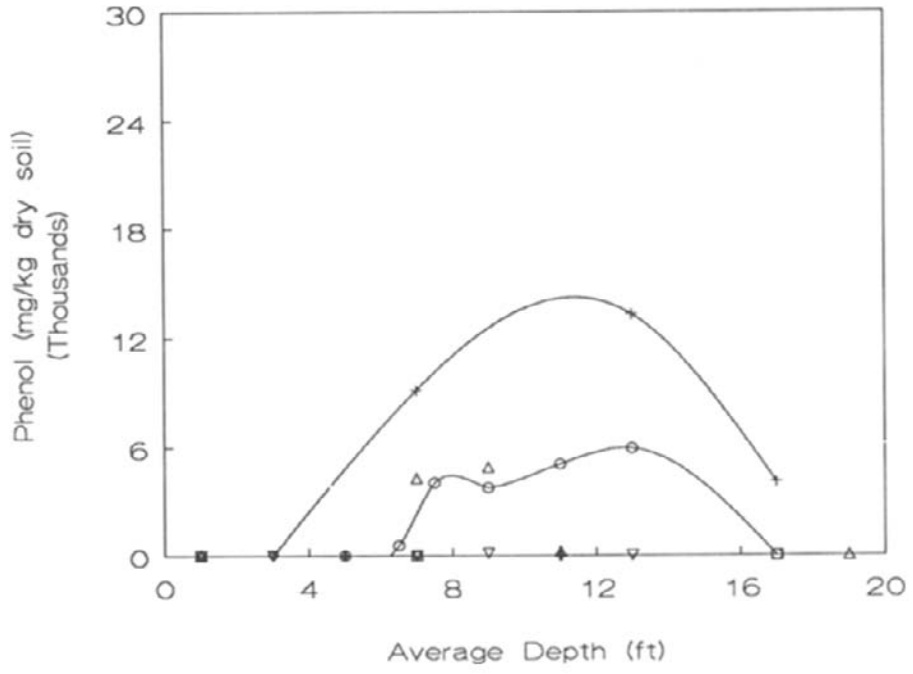

Fig. 4. Lagoon 1—soil phenol concentration: (□) L1-1, (+) L1-2, (◇) L1-3, (△) L1-4, (○) L1-5, (▽) L1-6, and (+) L1-7.

and cost, of the preliminary remediation process to be reduced without reducing its the effectiveness. The calculated soil TOC (based on extract concentration) varied from 6,510 to 26,200 mg TOC/kg dry soil. The average TOC of the samples from the highly phenol-contaminated Borings L1-2, L1-4, and L1-5

was not significantly different (using two-tailed Student t-test, $p < 0.01$) from the measured TOC of the samples from the relatively clean Borings L1-1, L1-3, L1-6, and L1-7. This indicated that TOC concentration was not a useful surrogate for phenol concentration. No anions were detected in the soil extracts. Only one cation, iron, was detected in the soil samples at concentrations up to 5,740 mg/kg dry soil. Soil pH as a function of depth is presented in Fig. 5. The pH was approximately 7.0 at the ground surface and decreased with depth until approximately 10 to 12 feet, where the pH reached its lowest value of 3.66. The soil pH remained fairly constant to a depth of 32 feet, below which the pH rose to nearly 7.0.

Lagoon 2 sampling indicated a layer of medium- to dark-brown topsoil in all borings from 0 to 1 feet. Photoionozation detector readings from the samples reached a maximum of 45 ppm. No consistent layer could be found in the samples between the depths of 1 to 4 feet. Materials observed included a sandy light brown material, a red-brown taffy-like material and a brown sandy layer with pieces of wood evident. Photo-ionization detector readings from these samples were higher than the readings over the samples from the topsoil layer, reaching a maximum of 650 ppm. An extremely hard mottled layer was encountered in all borings except L2-1 (hydraulically upgradient) between the depths of 4 and 10 feet. The typical material encountered was crumbly, dry, and mottled black, grey, brown, and rust. The mottled layer did not appear to

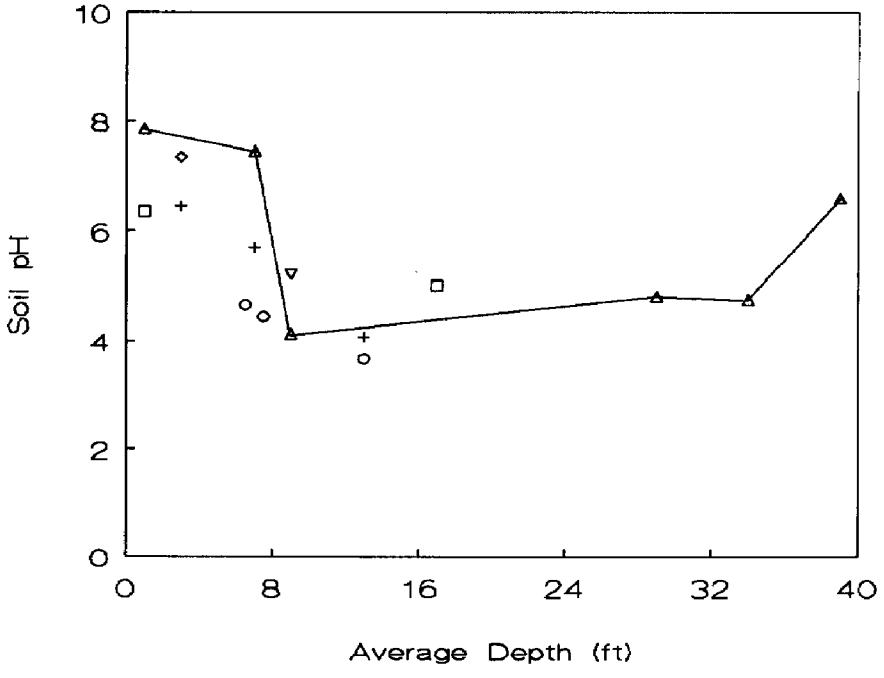

Fig. 5. Lagoon 1—soil pH: (□) L1-1, (+) L1-2, (◇) L1-3, (△) L1-4, (○) L1-5, and (▽) L1-6.

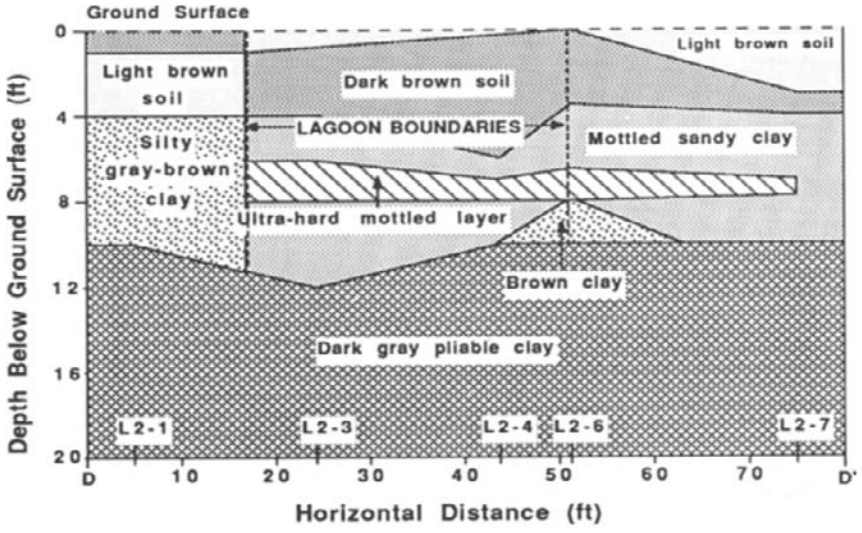

Fig. 6. Lagoon 2—cross section D-D′ (in Fig. 1).

be a natural soil layer but more like a settled residue from the disposed wastes. Detector readings (PID) over samples from this layer were up to 500 ppm. Heterogeneous layers were found between the depths of 8 to approximately 12 feet. Detector readings from these samples were up to 300 ppm. Materials observed in this region included the hard, mottled material previously observed, a pliable grey clay, a mottled hard, dry clay, and a grey brown clay. The underlying clay began at a depth of approximately 10 feet and continued to the bottom of the borings. Detector readings decreased to zero within the first several feet of the clay, again suggesting that contaminant penetration into the clay was limited. The region between the depths of 1 and 10 feet within the lagoon boundaries depicted in Cross Section D-D′ (Fig. 6) most likely represents the soil region affected directly by the waste disposal.

Chemical assays of the soils from Lagoon 2 indicated that soil phenol concentrations varied from below detection limits to 24,500 mg/kg dry soil (Fig. 7). The contaminated soils were distributed more uniformly over the lagoon area than observed for Lagoon 1. High concentrations of phenol were found across the entire lagoon between the depths of 0 and 12 feet. The calculated soil TOC (based on extract concentration) varied from 7,620 to 38,000 mg TOC/kg dry soil. The average TOC of the samples from Borings L2-2, L2-3, L2-4, and L2-5 was not significantly different (using two-tailed Student t-test, $p < 0.01$) from the measured TOC of the samples from Borings L2-1, L2-6, and L2-7. As before, this indicated that TOC was not a useful surrogate for phenol concentration. No anions were detected in any of the soil samples. As before, only iron was detected at concentrations up to 4,620 mg/kg dry soil. Soil pH as a function of depth for Lagoon 2 is presented in Fig. 8. Effective remediation

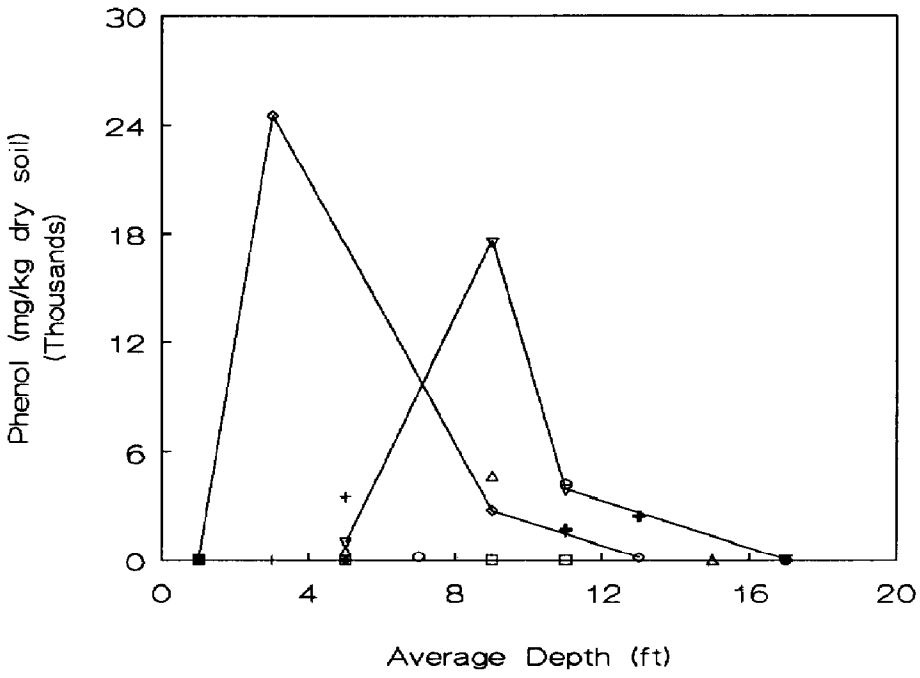

Fig. 7. Lagoon 2—soil phenol concentration: (□) L2-1, (+) L2-2, (◇) L2-3, (△) L2-4, (○) L2-5, (▽) L206, and (+) L2-7.

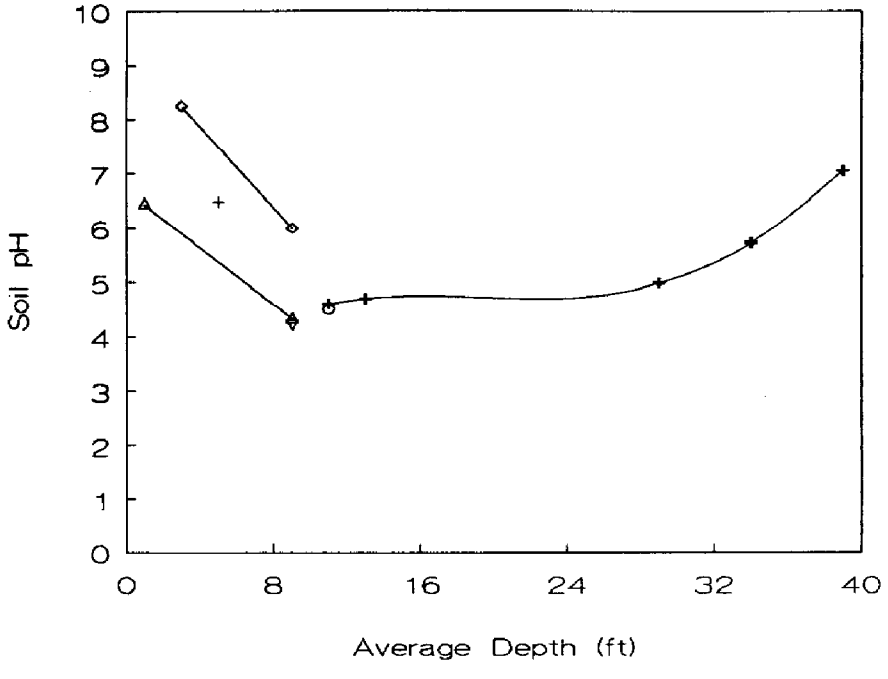

Fig. 8. Lagoon 2—soil pH: (+) L2-2, (◇) L2-3, (△) L2-4, (○) L2-5, (▽) L2-6, and (+) L2-7.

of Lagoon 2 would require that the soils contained within the entire lagoon area, as originally defined, be treated.

3.3 Groundwater collection and analyses

Groundwater was sampled from the new monitoring wells installed in the lagoons during this study. The monitoring well in Lagoon 1 was typically slow to recharge, indicating that the groundwater containment devices had reduced groundwater flow. Standing water in the Lagoon 1 monitoring well was collected. Three well volumes were pumped from the Lagoon 2 monitoring well prior to sampling. Groundwater samples were pumped directly from the wells into amber storage bottles, sealed with Teflon-lined lids and refrigerated until analysis.

Standard methods for the analysis of total Kjeldahl nitrogen (TKN) and total dissolved solids (TDS) were used [18,19]. Unadulterated groundwater was used for both assays. The pH of the groundwater was measured as soon as possible after sampling. For both the phenol and TOC assays, the groundwater was quantitatively diluted to 1 part in 10 to stay within the linear ranges of the instruments.

The TKN of groundwater from Lagoons 1 and 2 was 22 and 57 mg N/l, respectively. The pH of the groundwater from both wells was consistently between approximately 4.5 to 5.0. The acidic pH of the groundwater from both lagoons was consistent with the acidity of the soil samples taken at the well screen depths. The groundwater phenol concentrations varied between 2500 and 3200 mg/l for Lagoon 1 and between 900 and 1100 mg/l for Lagoon 2. The groundwater TOC concentrations were assayed once during the sampling and were 3400 and 1500 mg TOC/l for Lagoons 1 and 2, respectively. Phenol accounted for 68% and 47% of the TOC for Lagoons 1 and 2, respectively.

4. Evaluation of phenol desorption behavior

The objective of this phase of the study was to investigate phenol release from the contaminated soil during continuous extraction. Soil column experiments were employed to simulate *in situ* extraction conditions (Fig. 9). Two 24-inch long by 3-inch diameter glass columns were packed with a known mass of homogenized composited soil from Lagoon 2. The moisture content and phenol concentration of the packed soil were 22.5% and 1410 mg/kg dry soil, respectively. Extract solution was prepared as needed during the experiment. An alkali extractant was used to offset the acidity of the packed soil.

Removal of divalent cations from soils results in the disaggregation of clay particles within the soil and subsequent clogging of the soil pores. Divalent cations also can be displaced from the soil particles by direct ion exchange with monovalent cations, such as sodium, or from the continual stripping of the divalent cations into the cation-free aqueous phase. This effect is important

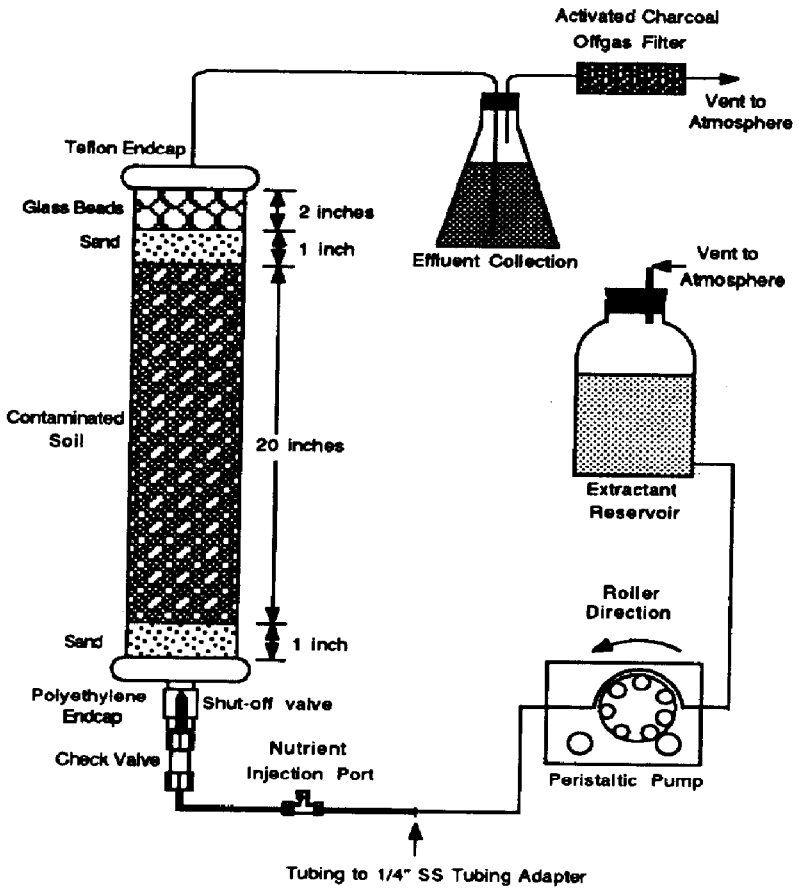

Fig. 9. Soil column design.

in the design of an *in situ* extraction process, which must be developed to prevent the collapse of the soil bed and the resulting loss of extraction efficiency. Removal by continual stripping into the aqueous phase was the most likely means of divalent cation loss in this experiment. Divalent cations were added in the influent stream to effectively flood the soil with divalent cations and prevent the stripping. This same approach could be employed in an *in situ* extraction process. The extract solution was prepared by adjusting the pH of a 0.01 *M* magnesium (from magnesium chloride) to 9 with calcium oxide. Magnesium was used because of the more favourable aqueous solubilities of magnesium salts than calcium salts. Calcium oxide was added for pH adjustment in lieu of adding sodium hydroxide and less soluble magnesium oxide. A peristaltic cassette pump was used to deliver extractant to the columns in an upflow direction to maintain uniform flow. Flow rates were maintained between 200 to 250 ml/day. Excess effluent from the columns was used in aerobic degradation experiments. The effluent from the columns was sampled once every two days. The accumulated volume, phenol and TOC concentrations of the

effluent were determined at each sampling. Effluent phenol and TOC concentrations were assayed as previously described.

4.1 Results and discussion

The extraction ratio was taken as the total accumulated liquid volume passed through the column at a given sampling point divided by the soil mass packed into the column. The effluent phenol concentrations as a function of the extraction ratio for both columns are presented in Fig. 10. The effluent concentrations initially peaked at 2600 mg/l and 3600 mg/l. Between the extraction ratios of approximately 0.0 and 2.0, the effluent phenol decreased rapidly to concentrations between 50 and 100 mg/l, while the effluent TOC decreased from approximately 3700 to 90 mg/l. Between the extraction ratios of 2.0 and approximately 5.0, the effluent phenol decreased slowly to concentrations between approximately 3 and 15 mg/l, while the TOC fell to concentrations of approximately 20 mg/l.

The accumulated mass of phenol removed was calculated by summing the products of the incremental effluent volumes and measured phenol concentrations for each column. Concentrations of phenol in the effluent collected on non-sampling days were estimated by linear interpolation between the nearest sampling days. The fraction of phenol removed was taken as the accumulated mass removed divided by the mass of phenol originally contained in the contaminated soil. The fractions of phenol removed as a function of the extraction

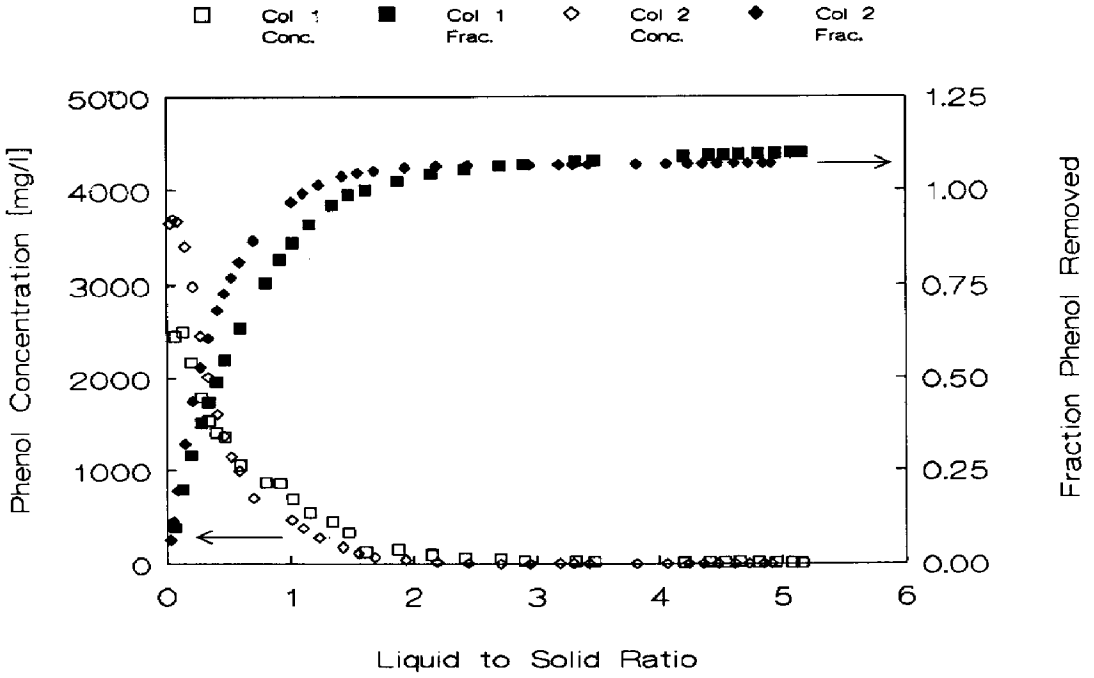

Fig. 10. Phenol desorption study.

ratio were presented in Fig. 10. The phenol removal rate decreased after an extraction ratio of approximately 2 for both columns. From 94 to 99% of the extractable phenol was removed at the extraction ratio of 2.0. A separate batch distribution study indicated a linear distribution coefficient of 1.80 (C_l/C_s). Clean soil from the site was contacted with aqueous solutions containing phenol at known concentrations. Soil concentrations were determined by a mass balance on phenol in the liquid phase. Experimental phenol losses were accounted for by controls at each concentration level.

Acceptable residual phenol concentrations in the soils and groundwater following remediation (cleanup criteria) have not been defined by the appropriate regulatory agency. The current state limit on phenol in groundwater and the detection limit of the phenol assay used were both coincidentally 1 mg/l. The column experiment was carried out until effluent phenol concentrations fell below 1 mg/l. The results of this study were utilized in the design of the remediation process, as the partitioning study modeled the extent of extraction at given liquid-to-solid ratios and allowed calculation of total extractant volumes, and both the flow and infiltration rates, for any desired residual phenol concentration.

Upon completion of soil column operation, the residual phenol concentration within the soil bed was assayed. A thin-walled pipe (1″ ID) with a sharpened end was used as a coring device to obtain 4-inch incremental samples of the packed soils. Soil extractions were carried out on the samples using the extraction method previously described. Extracts were assayed for phenol as previously described.

The residual phenol concentrations in the extracted soil was between 0.5 mg/kg dry soil (detection limit) and 4 mg/kg dry soil at the extractant entrance, and increased with length to between 13 and 17 mg/kg dry soil at the extractant exit from the column. The moisture content of the soil samples was assumed to be 20% because an insufficient amount of soil was recovered on which to determine moisture. The slight increase in residual phenol concentration from the extractant entrance to exit within the column was expected, as the bottom of the column was continuously contacted with fresh influent, while the top of the column was contacted with previously equilibrated liquid.

5. Aerobic microbial degradation of phenol and soil extracts

5.1 Reactor operating method

The objectives of this phase of the investigation were to determine the start-up, operating, and remediation process design parameters of the reactor needed to treat recovered extract. Approximately 2 l of non-acclimated mixed microbes were obtained from a secondary aerobic mixed liquor tank from Somerset Raritan Valley Sewage Authority (Bound Brook, NJ). Microbes were acclimated to phenol as the sole substrate carbon source over three feeding cycles.

During the first feeding, 1500 mg of sucrose were added as a cosubstrate along with 300 mg phenol. During the second feeding, 750 mg sucrose were added with 450 mg phenol. No sucrose and 300 mg phenol were added to the reactor for the third feeding. Groundwater from the site, a prepared concentrated solution of phenol and effluent from the soil column extractions were used as the substrate source for the microbial reactor. A supplemental nutrient solution, containing nitrogen from ammonium sulfate and phosphorous from potassium phosphate (monobasic), was employed to enhance metabolism.

Reactor feeding was on a draw-and-add basis. One-third of the mixed reactor liquid contents was drained. An equivalent volume containing the desired mixture of substrates and nutrient solution was prepared and added to the reactor. The drained reactor liquid was used to investigate the settling behavior of the solids.

The pH of the reactor was monitored and controlled continuously by an automatic pH controller delivering 0.25 *N* sodium hydroxide as required. Offgas from the reactor was passed through a refluxing condenser maintained at 10°C to remove water from the offgas and reduce volatile losses of phenol. Condensate was recycled back into the reactor. The low vapor pressure of pure phenol (1 mmHg at 41°C) suggested that volatile losses would be minimal. A separate volatilization study carried out in open shake flasks for one week with site groundwater and a 1000 mg/l aqueous phenol standard indicated that 5% of the original phenol mass was lost. Offgas CO_2 concentration was monitored continuously with an on-line CO_2 monitor. The instrument was used to monitor changes in the offgas CO_2 concentration as an indicator of microbial activity and was not used to close a mass balance on the reactor during this study.

The maximum treatable phenol concentration was determined by continuously increasing the initial reactor phenol concentration as presented in Fig. 11. The cell density in the reactor was not monitored or manipulated. The maximum anticipated phenol concentration expected in the remediation process after reactor dilution was 1000 mg/l, based upon the phenol concentrations observed in both on-site groundwater and soil column effluent. The reactor successfully degraded phenol at initial reactor concentrations up to nearly 3000 mg/l, allowing a safety factor in maximum treatable phenol concentration of approximately 3.

The treatment cycle times as a function of initial reactor phenol concentrations were investigated by varying the initial concentrations as presented in Fig. 11 and observing the treatment cycle times. The apparent removal rate was taken as the total mass of phenol fed divided by the product of the reactor working volume and feeding cycle time.

Treatment cycle times and apparent removal rates as functions of initial phenol concentrations are presented in Figs. 12 and 13, respectively. The apparent removal rates were between 60 and 100 mg/l h overall, with one outlying observation at 30 mg/l h.

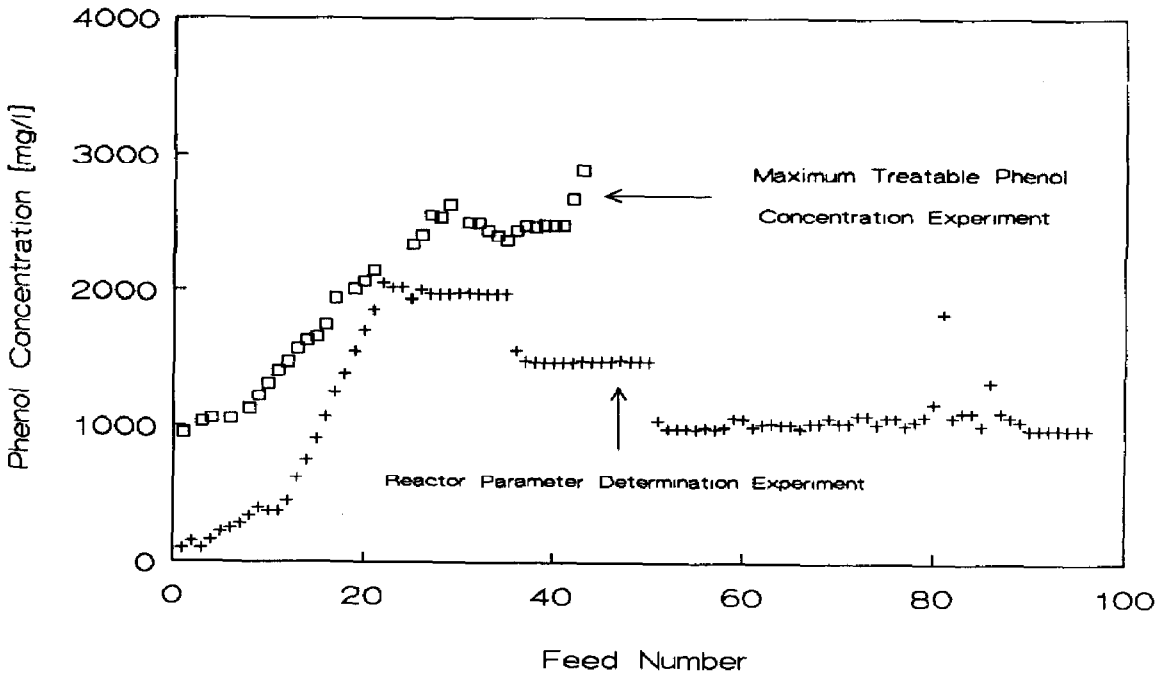

Fig. 11. Aerobic degradation study—initial reactor phenol concentrations.

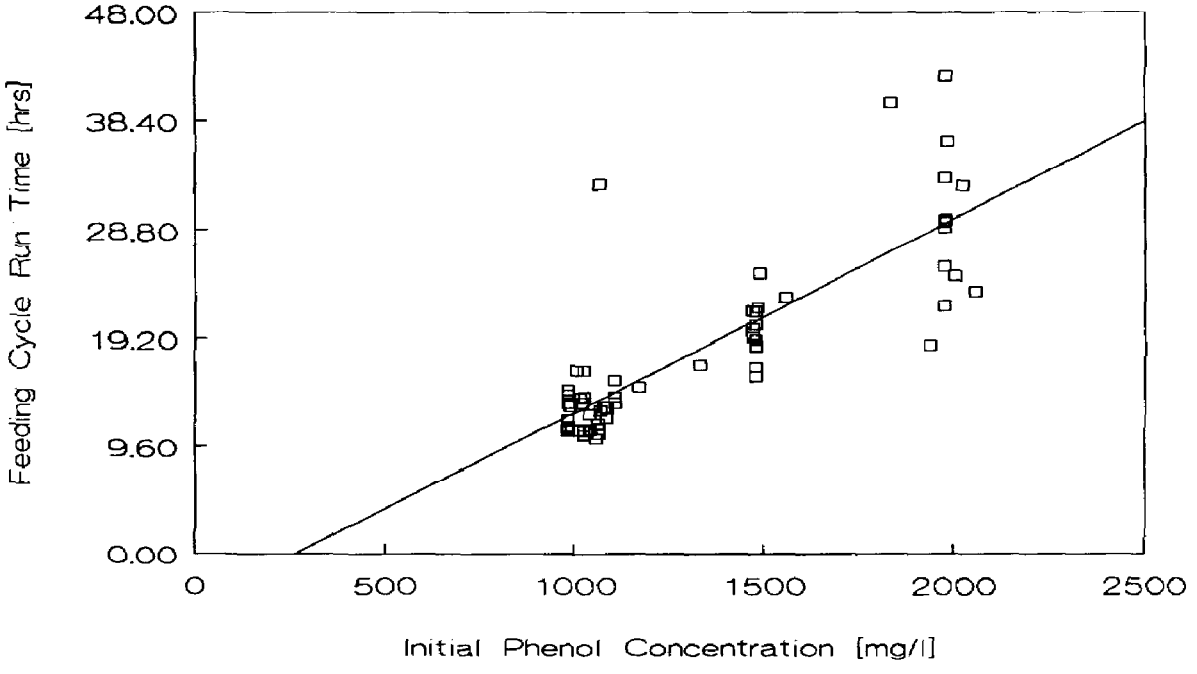

Fig. 12. Treatment cycle times.

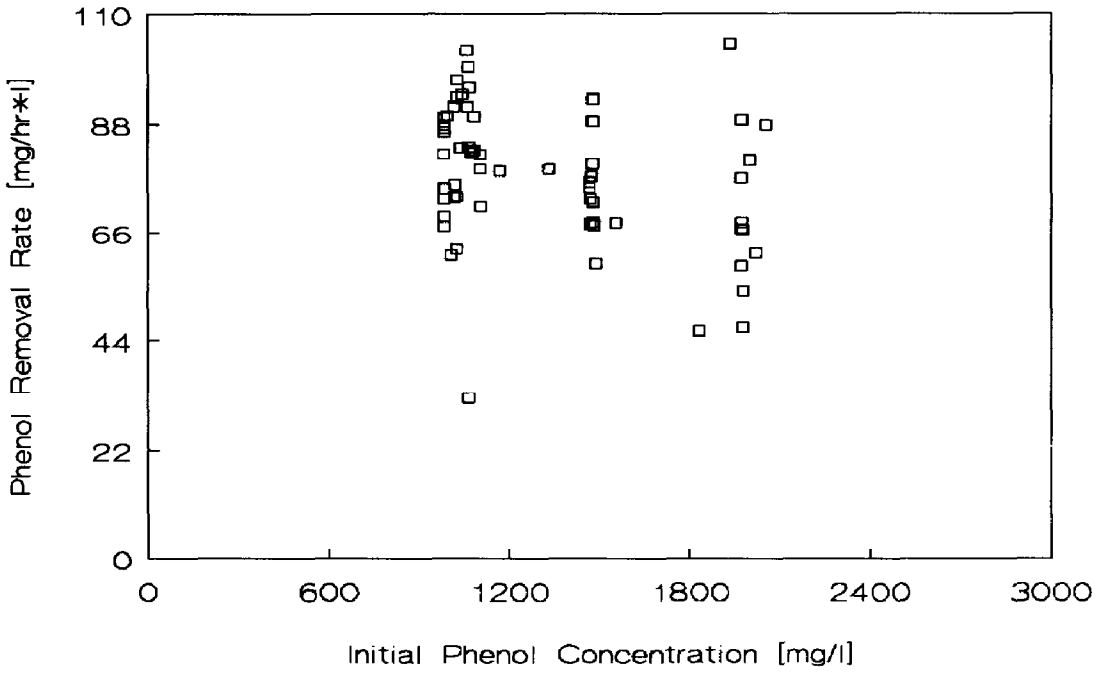

Fig. 13. Apparent phenol removal rates.

Temperature-controlled experiments were carried out to investigate time-dependent variables. The initial reactor concentration in the remediation process was expected to reach a maximum of 1000 mg/l as previously stated. The reactor was maintained at an initial reactor phenol concentration of 1000 mg/l for 45 feeding cycles prior to the temperature-controlled experiments to demonstrate reactor stability. The reactor liquid slurry was maintained at 21 °C during four of these feeding cycles. The reactor phenol concentration was monitored during two of the temperature-controlled cycles. Samples of the reactor liquid were filtered through 0.2 μm syringe filters prior to analysis for phenol and TOC as previously described. Minimal time was allowed between feeding and withdrawal of the initial sample and between sampling and assays to minimize further degradation and volatility losses. The removal rates were determined by calculating the change in phenol concentration between two sampling points and dividing this difference by the time increment.

The measured phenol concentrations and incremental phenol removal rates as functions of time are presented in Figs. 14 and 15, respectively. The discrepancy between the actual and calculated initial phenol concentration was most likely due to initial adsorption and uptake of free phenol into the biomass during the time between feeding and sampling. The phenol concentration in the last samples from both feed cycles fell below the detection limit of the HPLC phenol assay method, 1 mg/l. Removal rates varied between 0 and 140 mg/l h.

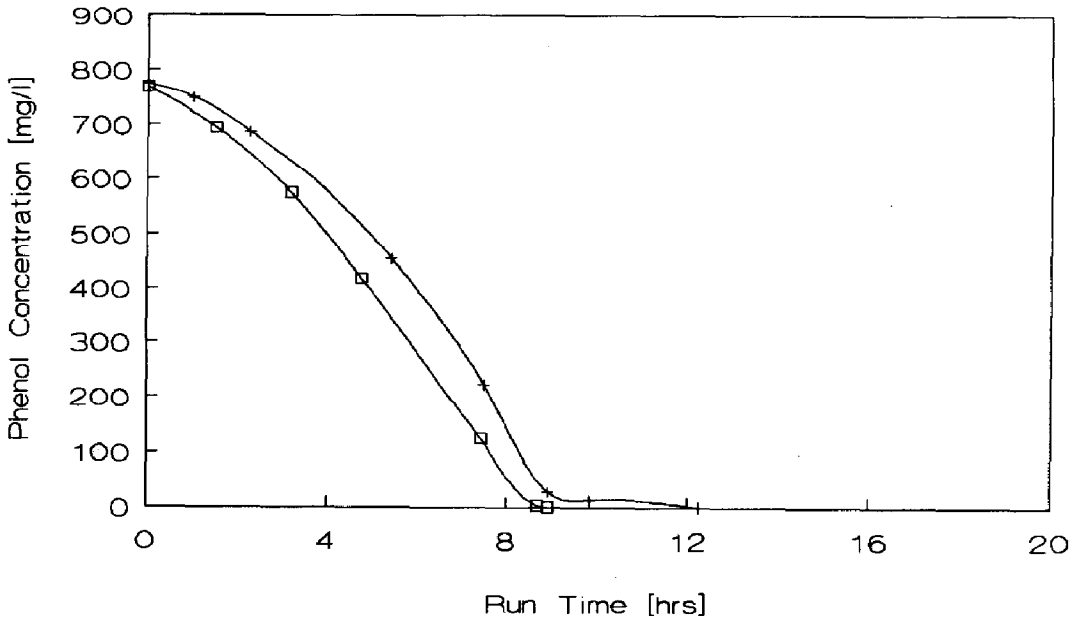

Fig. 14. Measured phenol concentrations: (□) Feed 94, and (+) Feed 96.

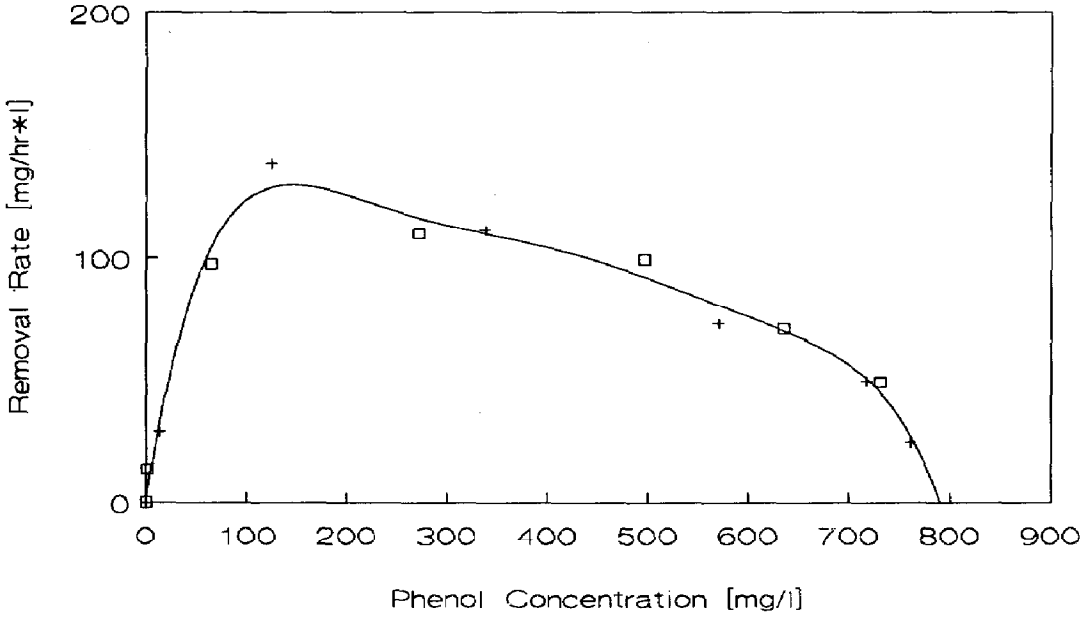

Fig. 15. Calculated phenol removal rates: (□) Feed 94, and (+) Feed 96.

Reductions in chemical oxygen demand (COD) and TOC of the reactor liquid were investigated during the temperature-controlled treatment cycles. All samples were filtered through 0.7 μm (GF/F) glass filter paper to remove particulates and biomass. The standard method for COD analysis in open reflux was used [20]. TOC was assayed as previously described. The observed reduc-

tions in dissolved COD and TOC were 90% and 90%, respectively. The solution COD after treatment was approximately 220 mg O_2/l, which was above the state discharge limit of 100 mg O_2/l. The remediation process design (to be discussed) incorporated 100% recycle of extracting water to minimize or eliminate the discharge of treated water. If treated water were discharged, it could be passed through an activated carbon filter to further reduce COD if necessary. Further experiments were not carried out during this study.

The cell yield was investigated during the temperature-controlled feeding cycles. The cell yield on phenol was taken as the difference in initial and final total suspended solids (TSS) divided by the mass of phenol fed. The standard method for TSS analysis was used [21]. The average cell yield on phenol was 0.6 g dry cell mass/g phenol fed (sample standard deviation = 0.17, CV = 29%). Some discrepancy in the initial cell densities was observed and was most likely due to the difficulty in consistently resuspending the wall growth into solution between the different feeding cycles. This data allowed estimation of the amounts of biomass to be discarded in the remediation process.

A typical CO_2 production curve is presented in Fig. 16. It was observed during all feeding cycles that the typical sudden decrease in CO_2 production occurred with a simultaneous rise in liquid pH. Samples were taken immediately before and after the sharp decrease in CO_2 evolution. The observed decrease in CO_2 production and increase in reactor pH coincided with depletion of phenol from the reactor liquid. The microbes were most likely utilizing degradable

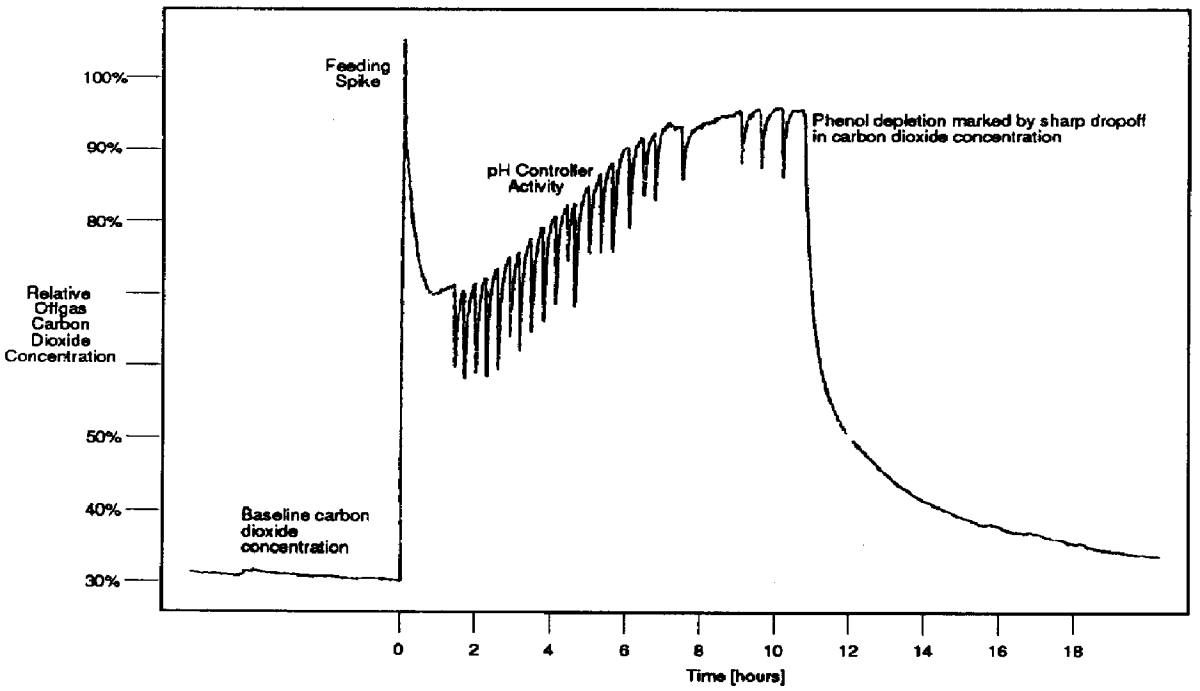

Fig. 16. Carbon dioxide evolution.

acids in solution as substrate upon phenol depletion, resulting in the increasing pH. These data indicated that these changes in solution pH and CO_2 production could be utilized as both an indicator of the end of the treatment cycle and an input to the reactor control system.

State regulations limit the total suspended solids of discharged treated waters to less than 100 mg/l. Clarification and settling rates of reactor effluent were examined using gravimetric settling of solids followed by sand filtration. The effluent from the reactor was allowed to settle undisturbed in a graduated cylinder. The supernatant was siphoned to a separate container. The supernatant was assayed for TSS according to Standard Methods [21]. The settled effluents had TSS between 114 and 140 mg/l. This was slightly above state regulations and further filtration would be necessary.

The philosophy of the remediation process design called for a temporary installation of the process. Sand filtration appeared to be the best compromise between maintaining the design philosophy and still meeting state requirements. An investigation of sand filtration was carried out. The supernatant was filtered through a 7-inch thick sand filter and then assayed for TSS. The sand was rinsed before each use to remove fines and particulates. Sand filtration resulted in a clear, colorless and transparent effluent with a TSS less than the detection limit of approximately 10 mg/l.

The settling rates and total settleable solids were investigated to provide data for the solids settling step in the remediation process. The most desirable characteristics were fast settling rates for an increased throughput of material and minimal final volume of settled solids for decreased solids handling downstream. The standard methods for evaluation of these parameters were used [22].

The pH of the feed mixture to the reactor tended to be acidic because of the low pH of the groundwater and soil extracts. The groundwater and extracts were neutralized with sodium hydroxide prior to feeding the bioreactor for approximately the second half of the 45 feeding cycles at 1000 mg phenol/l. A noticeable precipitate formed and settled rapidly in the neutralized liquids. The precipitate was removed by filtration through Whatman GF/F filter paper. Analysis of the groundwater by atomic absorption spectrophotometry indicated that the iron concentration in the groundwater from Lagoon 1 was reduced from approximately 190 mg/l to 4 mg/l during the precipitation.

Prior to feeding with a neutralized groundwater, the final settled solids volume attained was between 10 and 13% of the initial total liquid volume. After feeding with a neutralized groundwater commenced and progressed, the final settled solids volume increased from the initial value of 13% to 40% of the initial total liquid volume. This represented a significant deterioration of settleability, as maximum compaction of the solids was desired to reduce the total volume of solids to be handled. The settled fractions of the activated sludge as a function of time for four feeding cycles are presented in Fig. 17. The settling

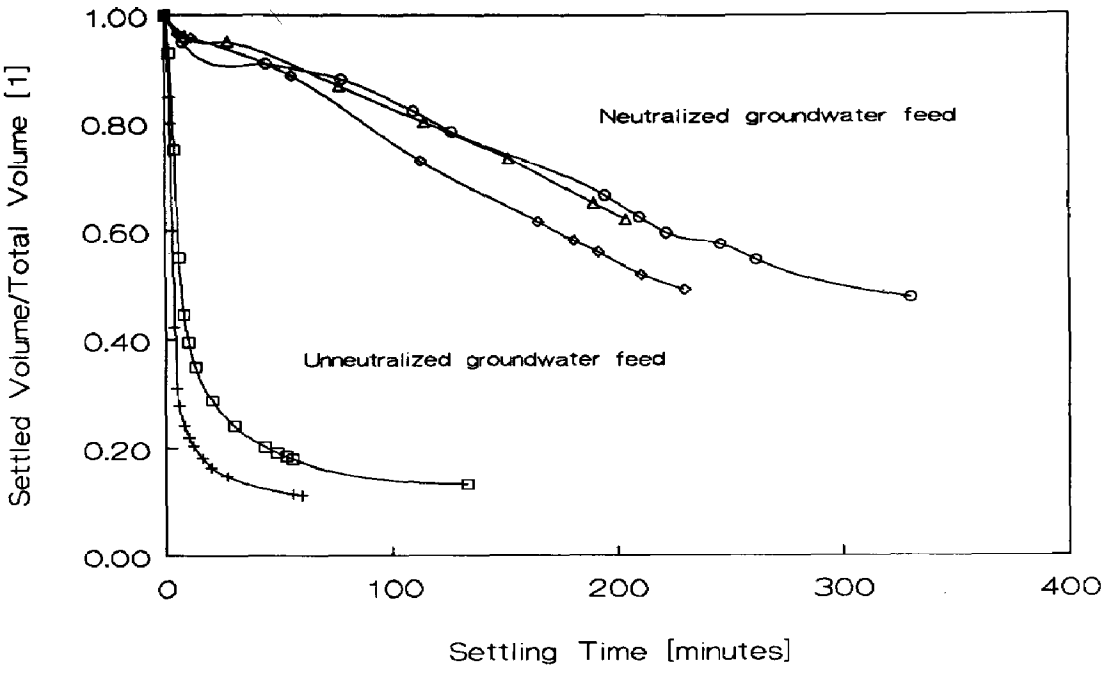

Fig. 17. Aerobic reactor solids settling study.

behavior for the two treatment cycles utilizing an unneutralized groundwater feed were characterized by fast settling of solids. The presence of the iron in the reactor feed appeared to improve the settling behavior of the reactor solids.

6. Remediation process design

The remediation process was designed to be a temporary treatment facility. Disposal of both remediation process materials and equipment was simplified by anticipating in the original design the disposal of the process equipment at plant shutdown. A reduced capital investment was implicit in the temporary design of the plant and explicit in minimizing the negative return on investment. Usable and existing on-site equipment and facilities were incorporated into the design as much as possible. Existing and relatively standard equipment was used in the design of the process steps. Complex equipment was avoided to simplify process set up and operation. The entire process was designed to be a stand-alone treatment with minimal inputs and outputs, other than utilities, nutrients, and sludge disposal. Flexibility was incorporated during equipment sizing to allow the treatment process to be coupled to an extraction process on either lagoon or both lagoons simultaneously.

The flow diagram for the remediation process is presented in Fig. 18. The most promising scenario was *in situ* forced leaching of soil contaminants combined with above-ground aerobic microbial treatment of the collected leachate.

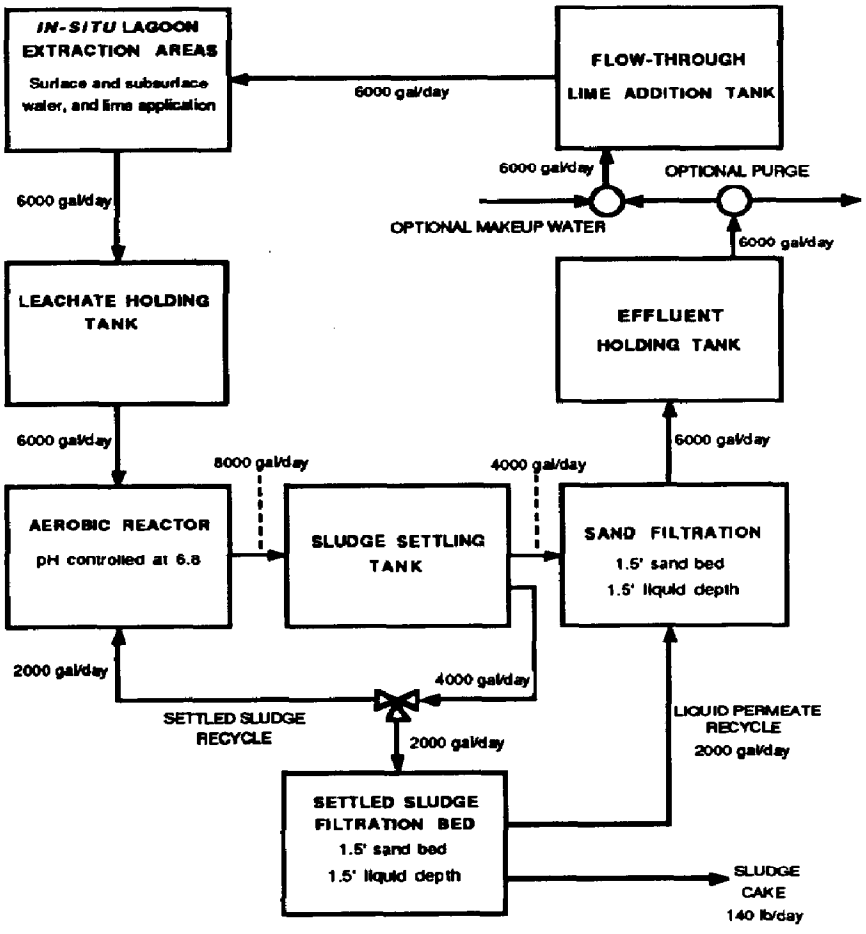

Fig. 18. Preliminary process flow diagram.

The *in situ* extraction process would include both surface and subsurface application of water across the treated area. Surface application of extractant would be delivered by either perforated pipe or standard irrigation drip tubing. Subsurface application of extractant would be provided by installing well points into the soil at various depths and locations. Positive pressure would be applied to the injected extractant by pump or gravity-feed to force infiltration. The use of well points would allow adjustment of well point locations by simply pulling the point out of the ground and hammering it into a new location. Well point location adjustment would improve coverage of the soils by the extracting water. Leachate would be collected by either an intercepting collection trench and sump installed downgradient from the lagoon or via a series of recovery wells.

The application rates of extracting water for both lagoons are presented in Table 1. The average lagoon properties were determined by averaging all values at each given depth in the borings within the area to be treated, and then

TABLE 1

Process design calculations

Parameter	Lagoon 1	Lagoon 2
Lagoon parameters		
Dimensions (L×W×H, ft)	60×53×12	40×43×10
Average density (kg/m^3)	1 400	1 640
Average moisture (wt%)	22.4	23.4
Average phenol (mg/kg dry soil)	2 090	2 930
L:S ratio (l water/kg wet soil)	2:1	2:1
Treatment time (months)	6	6
Calculated parameters		
Treated soil volume (m^3)	960	450
Treated soil mass (kg dry soil)	1.04×10^6	0.57×10^6
Extractant volume (m^3 water)	2.69×10^6	1.49×10^6
Extractant flow rate (gal/h)	164	90
Infiltration rate (in/day)	2.24	2.20
Aerobic reactor parameters		
Phenol mass removed (kg)	2,200	1,670
Sludge mass produced (kg dry)	1,300	990
Sludge production rate (kg/day, 80% water)	36	28

averaging over the entire depth of the lagoon. For Lagoon 1, the averages were computed across Borings L1-2, L1-4, and L1-5. For Lagoon 2, the averages were computed across Borings L2-2, L2-3, L2-4, and L2-5. An extracting water volume to soil mass ratio of 2 to 1 was assumed to be sufficient to extract the phenol, based on the results of the soil column experiments. A treatment time of 6 months of continuous remediation process operation was assumed.

The extraction system for Lagoon 1 was estimated assuming that the existing slurry wall, surficial containment wall, and cistern drainage system would provide adequate containment of the leachate. Infiltration of groundwater into the lagoon area would be minimal, due to the slurry wall. Rainwater would augment the applied flow through the treated area. Leachate was assumed to be recovered in a series of monitoring wells arranged around the perimeter of the treated area. Further sizing of the collection system was not carried out for Lagoon 1.

Both rainwater and natural groundwater flow would augment the flow through the treated soil in Lagoon 2. Leachate would be recovered using a trench draining groundwater to a central sump pit. The downgradient side of the trench would be sealed with an impermeable material to minimize infiltration of downgradient water. A surficial containment berm would be installed around the surface perimeter of the treated area to reduce rainwater runon and leachate runoff.

A hydraulic conductivity of 1.11 in/h (determined previously) and the calculated extractant flow rate of 164.0 gal/h were used to estimate the surface area of the collection system. The surface area of the collection system was calculated to be 240 ft^2. For this preliminary design only, a trench of 25 ft length located 10 feet downgradient was assumed to be sufficient. The base of the trench was assumed to extend to the underlying clay to minimize bypass underneath the trench.

The extraction progress could be monitored most directly throughout the remediation by retrieving and extracting samples from different regions of the treated soils. However, this approach is not practical because manual sampling and extraction of samples would be too expensive and time-consuming to carry out several times on soil regions of this relatively small size. Alternatively, residual phenol concentrations may be monitored based on observed phenol concentrations in recovered extract during operation. Dilution effects, possibly resulting from high extractant fluxes through the soils, can be minimized by allowing a quiescent period without extractant injection prior to monitoring well sampling.

Standard circular design above-ground swimming pools (4 ft wall height) were incorporated into the remediation process design for the aerobic reactor, settling basin, and the sand filtration steps. Swimming pools were chosen as the best available compromise between safety, reduced capital investment, and reduced difficulty in equipment disposal. The swimming pools were sized based upon a maximum allowable height of all contained materials of 3 feet, allowing a safety margin of 25% in the contained volume for process flow variation.

The leachate would be pumped to and stored in an existing above-ground holding tank available on-site. Leachata and nutrients would be charged to an aerated and agitated batch aerobic microbial reactor. The activated sludge from the reactor would be transferred to a settling basin at the end of the feeding cycle. Half of the settled solids was assumed to be recycled back into the reactor with the remaining half being filtered and disposed. The supernatant from the settling basin would be passed through a clarifying sand filter basin. Both the liquid stream from the settled solids filtration and the clarified supernatant stream would be recycled back into the extraction process, reducing both the fresh water input and discharge demand.

The feeding cycle time for an initial reactor phenol concentration of 1000 mg/l observed in the aerobic microbial degradation study was between 10 and 15 h. The residence time of the aerobic reactor at the 8000 gal/day combined fresh leachate and recycle flow rate would be 1.6 days, or approximately three times the anticipated feeding cycle time.

The maximum residence time of liquid in the sludge settling basin would be 1.0 days. Based upon the settling rates observed during the aerobic microbial degradation study, one to two hours would be sufficient to achieve the maximum attainable solids settling.

The filtering media in the sludge filtration step was assumed to be sand to a depth of 1.5 feet. Harris et al. [23] found the optimum hydraulic loading rates on intermittent sand filters to be between 3700 and 5600 m^3/ha day, equal to infiltration rates between 0.37 and 0.56 m/day. The infiltration rate for the circular sand filter (15 ft diameter) with a 2000 gallon/day (gpd) loading was calculated to be 0.46 m/day. Removal of accumulated sludge was assumed to be carried out manually. Filtered water would be pumped from underneath the sand bed by a sump pump.

The infiltration rate on the supernatant sand filter would be 0.47 m/day. The TSS of the supernatant observed from the settling experiments in the aerobic microbial degradation study was approximately 110 mg/l, or 0.011% by weight. The expected daily total suspended solids loading rate on the filter (based upon 4000 gpd flow rate) was 1.7 kg TSS/day. Limited cleaning of the clarifying filter was expected at this loading rate. Filtered liquid would be pumped from the bottom of the filter by a sump pump.

An optional continuous-flow lime addition tank was incorporated into the design to increase the pH of the recycled liquid to reduce the acidity of both the soil and recovered leachate. A reduction in the acidity would reduce corrosion of pumps and increase the likelihood that an *in situ* microbial population would become established from natural soil microbes and carry-over inoculum from the reactor.

6.1 Process cost estimate

All equipment was sized based on the flow rates as indicated in Fig. 18. Equipment and supply costs were determined by direct quotes from vendors when possible. Installation costs of the trench and recovery wells were determined by an estimate from the drilling firm that was contracted for previous on-site work. Operating costs were estimated by calculating electric utility, nutrient, and sodium hydroxide for the pH control system. Construction and installation costs were assumed. Costs not included were manpower costs during steady-state operation, disposal costs of the sludge, and water utility costs. One cubic yard of soil was assumed to be approximately one ton.

The cost (per ton) to treat each lagoon independently (independent treatment) was estimated by assuming that the purchase of the equipment and the setup of the remediation process facility was carried out separately for each lagoon. All capital costs, other than equipment, were assumed to be equal for both lagoons.

The cost (per ton) to treat Lagoons 1 and 2 in sequence (sequential treatment) were estimated by assuming that all equipment was purchased and the remediation process facility was set up to treat Lagoon 2 first. Upon completion of the treatment of Lagoon 2, as much of the existing process equipment as possible was assumed to be transferred to and used to treat Lagoon 1. The

additional piping and equipment rental costs for Lagoon 1 were assumed to be equal to Lagoon 2.

The majority of the control, labor, and electrical costs were invested in the aerobic treatment process. The additional costs for the controls, labor, and electrical work for Lagoon 1 reflect the biasing of capital investment towards the initial installation. The additional costs for piping and equipment rental reflect costs for the extraction process.

The cost (per ton) to treat both lagoons simultaneously (parallel treatment) were also estimated. All necessary equipment and facility setup was assumed to be purchased at one time. Additional capital costs for Lagoon 1, other than equipment, were estimated by multiplying the corresponding capital cost for Lagoon 2 by 1.5, thus assuming that the additional capital costs to treat the second lagoon were proportionally less than the costs for treating each lagoon independently.

The results of the three estimation scenarios are presented in Table 2. The independent treatment scenario resulted in per ton treatment costs of $170 and $344 for Lagoons 1 and 2, respectively, accomplished in one year. The capital and operating costs for each lagoon were not strongly dependent upon the amount of soil to be treated. The significantly higher per ton cost for Lagoon 2 reflected the smaller treated soil volume.

The sequential treatment scenario resulted in a combined per ton treatment cost for both lagoons of $170, accomplished in one year. The parallel treatment scenario resulted in a combined per ton treatment cost of $164 for both lagoons, accomplished in 6 months. The sequential treatment scenario offered the advantage over the parallel treatment scenario of a reduced complexity of setup and operation of the process equipment at the expense of an increased treatment time. The parallel treatment scenario offered a slightly lower per ton cost, and required only one-half of the treatment time.

TABLE 2

Process cost estimate ($)

Cost	Independent treatment		Sequential treatment	Parallel treatment
	Lagoon 1	Lagoon 2		
Capital	136,000	123,000	170,000	165,000
Operating	9,000	8,000	18,000	12,000
Analytical	75,000	75,000	135,000	135,000
Final	220,000	206,000	323,000	312,000
Per ton	170	340	170	164

7. Summary and conclusions

The main area of phenol contamination for Lagoon 1 was centered around Borings L1-2, L1-4, and L1-5. The vertical extent of contamination was between the depths of 5 and 13 feet, with the exception of L1-2 where phenol was found to a depth of 17 feet. The phenol contamination in Lagoon 2 was more widespread throughout all of the borings except L2-1. Significant concentrations of phenol were found hydraulically downgradient from the lagoon in borings L2-6 and L2-7. Phenol penetration into the clay was not observed beyond the depth of 14 feet.

Since groundwater flow through the clay would be minimal due to the low hydraulic conductivities of clays, no significant leaching of phenol from contaminated clay after remediation of the overlying soils was expected. The usefulness of assaying for soil TOC was limited. High phenol concentrations, depressed soil pH and nutrient deficiency (nitrogen, phosphorous, and trace metals) within the lagoon areas would hinder any natural microbial activity within the soil matrix. Microbial treatment of recovered contaminated groundwater or leachate would require addition of essential nutrients. Neutralization of the acidic groundwater would be necessary to maintain an active microbial population and minimize equipment corrosion.

The phenol was observed to partition readily and favorably into an aqueous phase. The phenol was observed not to be bound tightly to any fraction of the soil. *In situ* removal of the phenol from the soil was not expected to be hindered by tight binding of the phenol to the soil. A liquid-to-mass ratio of 2.0 was expected to be sufficient to remove 94 to 99% of the extractable phenol from the lagoon soils in an *in situ* extraction. Raising the extraction ratio would further remove residual phenol, but marginal increases in the total phenol removed would most likely not justify the additional time and expense of prolonged operation of the remediation process.

The aerobic microbial treatment of groundwater and aqueous soil extracts readily removed phenol at reactor concentrations up to three times the maximum anticipated field reactor concentration of 1000 mg/l. Removal rates up to 140 mg/l h were achieved with an acclimated microbial population. Monitoring and control of the reactor pH appeared to be the most convenient method of evaluating the progress of the degradation reaction and controlling microbial activity by alkali additions.

The sludge filtration step included an intermittent sand filter as the means of sludge/liquid separation. This approach presented both a simple process design and reduced capital investment, at the expense of the increased manpower required to remove accumulated material from the sand. A continuous belt press filter or similar design would reduce the manpower required, at the expense of increased capital investment. Further remediation process design will determine which is the preferred approach.

It was recommended that both lagoons be treated simultaneously with a parallel treatment approach. The increased remediation process complexity of a parallel treatment approach over the independent and sequential treatment approaches would most likely be more than offset by the reduction in the per ton treated costs and the reduction in overall treatment time that would be accomplished by this approach. A parallel treatment approach would also provide two substrate sources, as opposed to only one source in both an independent and sequential treatment approaches, thus reducing the likelihood of process failure due to loss of substrate.

References

1 F. Billmeyer, Textbook of Polymer Science, Interscience Publ., New York, NY, 1962, pp. 463–469.
2 R. Bowen, Groundwater, 2nd edn., Elsevier, London, 1986.
3 R. Arands, Development of an In-situ and On-site Remediation Process for Phenol Distillate Lagoons, thesis presented to Rutgers - The State University, at New Brunswick, New Jersey, in 1990, in partial fulfillment of the requirements for the degree of Master of Science.
4 R.A. Evangelista, H.L. Allen and R.M. Mandel, Treatment of phenol and cresol contaminated soil, J. Hazardous Mater., 25 (1990) 343–360.
5 W. Evans, Anaerobic degradation of aromatic compounds, Annu. Rev. Microbiol., 42 (1988) 289–317.
6 S. Hrudey, E. Knettig, S. Daignault and P. Fedorak, Anaerobic biodegradation of monochlorophenols, Environ. Technol. Lett., 8(2) (1987) 65–76.
7 G. Bakker, Anaerobic degradation of aromatic compounds in the presence of nitrate, FEMS Microbiol. Lett., 1 (1977) 103–108.
8 D. Dobbins, J. Thornton-Manning, D. Jones and T. Federle, Mineralization potential for phenol in subsurface soils, J. Environ. Qual., 16 (1987) 54–58.
9 J. Smith and J. Novak, Biodegradation of chlorinated phenols in subsurface soils, Water Air Soil Pollut., 33(3) (1987) 29–42.
10 G. Cenci, G. Caldini and G. Morozzi, Chlorinated phenol toxicity by bacterial and biochemical tests, Bull. Environ. Contam. Toxicol., 38(5) (1987) 868–875.
11 M. Borup and E. Middlebrooks, Photocatalyzed oxidation of organic wastestreams, In: G.D. Boardman (Ed.), Toxic and Hazardous Wastes, Proc. 18th Mid-Atlantic Industrial Waste Conf., June 29–July 1, 1986, Technomic Publ., Lancaster, PA, 1986, pp. 554–568.
12 M. Mansour, Photolysis of aromatic compounds in water in the presence of hydrogen peroxide, Bull. Environ. Contam. Toxicol., 34 (1985) 89–95.
13 D. Hager and C. Loven, On-site destruction of organic contaminants in water, paper presented at HWHM Natl. Conf. and Exhibition, Washington, DC, March 16–18, 1987.
14 W. Ying and J. Duffy, Biological treatment of phenolic wastewaters, Paper presented at 197th ACS National Meeting, Dallas, TX, April 9–14, 1989.
15 M. Hamoda, A. Al-Haddad and M. Abd-El-Bary, Treatment of phenolic wastes in an aerated submerged fixed-film (ASFF) reactor, J. Biotechnol., 5(5) (1987) 279–282.
16 W. Ng, Biodegradation of phenols in integrated activated carbon bed and suspended biological growth reactor, Agric. Wastes, 18(2) (1986) 163–170.
17 Methods of Soil Analyses, Part 2 - Chemical and Microbiological Properties, 2nd edn., American Society of Agronomy, Inc. and Soil Science Society of America, Madison, WI, 1982, pp. 203–209.

18 Standard Methods for the Examination of Water and Wastewater, 16th edn., M.A. Franson (Ed.), American Public Health Association, Port City Press, Baltimore, MD, 1985, pp. 411–412 (Method 420-B. Semi-micro-Kjeldahl method).
19 Standard Methods, Port City Press, Baltimore, MD, 1985, pp. 93–94 (Method 209-A. Total solids dried at 103–105°C).
20 Standard Methods, Port City Press, Baltimore, MD., 185, pp. 533–535 (Oxygen Demand (Chemical)–Method 508-A. Open reflux method).
21 Standard Methods, Port City Press, Baltimore, MD, 1985, pp. 96–97 (Method 209-C. Total Suspended Solids Dried at 103–105°C).
22 Standard Methods, Port City Press, Baltimore, MD, 1985, pp. 129–131 (Methods 213-B, 213-C, and 213-D).
23 S. Harris, J. Reynolds and D. Hill, Intermittent sand filtration for upgrading waste stabilization pond effluents, J. Water Pollut. Control Fed., 49(1) (1977) 83–102.