

## PROCESS DEVELOPMENT FOR *IN SITU* REMEDIATION OF A HIGHLY CONTAMINATED GROUNDWATER PLUME\*

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### Summary

Over two decades, a chemical processing waste liquor which contained high concentrations of both ammonium sulfate and organic species (up to 85 000 mg/l sulfate and 38 000 mg/l total organic carbon [TOC]), was discharged into surficial trenches, adjacent to a manufacturing facility. Waste deposits have migrated and reacted in the underlying aquifer. A multi-phase contaminant plume has resulted.

*In situ* treatment has been investigated to contain groundwater and treat the contaminants. An appropriate system must arrange process components to effectively eliminate organic and inorganic species. Several process scenarios have been considered. *In situ* precipitation of sulfate to form a groundwater flow barrier, followed by an anaerobic denitrification step appears to be a promising process. Results of laboratory-scale experiments indicate that the combined sequence can reduce total dissolved solids by over 75%, and TOC by nearly 90%. A demonstration of the process at pilot-scale is under consideration.

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### Introduction

For an extended period of time, manufacturing waste liquor was neutralized and disposed of via direct land application. Although this practice was ceased in the early 1970's, existing waste deposits have migrated and reacted in the subsurface domain. An extended area of soil and groundwater contamination has resulted. Groundwater moves across the site, and several distinct zones of groundwater contamination have been identified. Contaminant depths vary with the profile of a hydrogeologic confining layer located at approximately 50 feet below the surface. Currently, one plume has potential for subsurface movement off-site.

Over a two year period beginning in February, 1987, 8 monitoring wells at the site were sampled. These wells were chosen so that distinct levels of con-

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tamination were obtained while providing for definition of the aerial extent of the groundwater plume. Monitoring wells, 3, 17, 32, 34, and 103 were chosen as marginally contaminated groundwater sources. In the moderate concentration region, wells 16 and 35 were sampled. Lastly, a monitoring well close to the disposal area, 28, was chosen to provide high-strength groundwater contamination. Characterization of the groundwater samples is presented in Table 1.

The primary goal of subsequent study was to develop a process to immobilize, eliminate or attenuate ammonium sulfate (AS) and organic contaminants

TABLE 1

Summary of chemical analysis of groundwater samples taken on February 16, 1987

Assay (@ 60°F)	Well number		
	35	16	28
pH	7.4	8.2	7.3
Specific gravity	1.02	1.03	1.13
Viscosity (cP or mPas)	1.001	1.1003	1.3476
Suspended solids (mg/l) (0.45 $\mu$ m, 105C, 24 h)	2 500	250	2 400
Total Dissolved Solids (0.45 $\mu$ m, 105C, 24 h, mg/l)	14 100	24 100	255 000
Cl <sup>-</sup> (mg/l)	2 000	6 150	20 100
Sulfate analysis (mg SO <sub>4</sub> <sup>2-</sup> /l) (HPLC)	6 500	9 500	85 700
Total Organic Carbon (mg/l)	1 780	2 800	38 000
Chemical Oxygen Demand (mg O <sub>2</sub> /l)	8 200	10 300	190 000
Nitrogen analysis (mg N/l):			
Ammonia nitrogen	4 500	6 700	43 900
Organic nitrogen	200	290	24 600
Total Kjeldahl nitrogen	4 750	6 950	68 500
Metals (mg/l):			
Na	387	300	155
Ca	18	2	83
Mg	36	36	34
Mn	1	ND	14
Fe	4	4	126
K	117	60	15
Cr	ND	20	ND
Pb	ND	1	1
Cd	ND	ND	1
Zn	ND	ND	ND
Ag	ND	ND	ND
Cu	ND	ND	ND
Ni	ND	ND	ND

ND = Not detected, 0.1 mg/l detection limit employed.

from the groundwater at the leading edge of the plume. Emphasis has been placed on options which would provide either *in situ* or on-site management. The general approach has included assessment of specific unit processes, such as sulfate precipitation, aerobic microbial mineralization and anaerobic degradation of groundwater contaminants for eventual integration into a comprehensive treatment process. The current study does not consider a long term scenario for source renovation; however, it does provide for development of a process preventing further plume migration. Different treatment scenarios for the grossly contaminated source are under consideration.

### **Experimental approach**

The primary thrust of the investigation has been to assess diverse treatment methods and determine the applicability of each to the system of interest. The first step involved identification of a number of unit processes which had a reasonable chance of fulfilling the goals of the project. After this, batch experiments were conducted to determine relative feasibility of each unit operation. Processes which showed promise in batch studies were scaled up to laboratory continuous flow systems, where appropriate. Data from such flow systems were interpreted and led to additional laboratory-scale studies which were aimed at sequencing specific treatment steps into an integrated process train. Results of laboratory studies led to the development and preliminary design of a field pilot-scale demonstration.

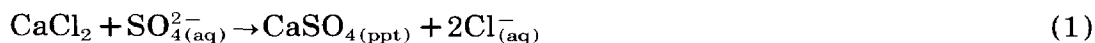
### **Process analysis**

The first step necessary for a remediation process is the removal of sulfate to avoid  $H_2S$  production from subsequent biological process steps. Precipitation of sulfate ion from groundwater using calcium can be carried out in a number of ways, depending on whether or not pH adjustment is desired. Calcium hydroxide ( $Ca(OH)_2$  (lime)) can precipitate out calcium sulfate, with the resulting increase in pH liberating free ammonia. Use of calcium chloride ( $CaCl_2$ ) or calcium nitrate ( $Ca(NO_3)_2$ ) can effect the same precipitation while retaining ammonium ion ( $NH_4^+$ ) in solution. An important consideration in an *in situ* sulfate precipitation process involves the potential change in soil permeability cause by interstitial precipitate accumulation [1]. Plugging of the soil to slow migration or contain the groundwater plume would be advantageous.

A number of potential treatment pathways for ammonium sulfate waste have been considered. Microbial treatment of organic and nitrogen species, after sulfate removal, has been evaluated. Although the foregoing methods are not all inclusive, they do illustrate a variety of sequences that can incorporate component unit processes into a comprehensive remedial process. Criteria in-

volved in assessing various treatment pathways include efficiency of precipitants of residual ions and effects on subsequent microbial degradation. The feasibility of certain microbial pathways and predicted effluent TDS values were considered. Both above ground and *in situ* treatments have been taken into consideration; however, the restraints for each type of process are considerably different.

The first case considered uses  $\text{CaCl}_2$  for sulfate removal. The stoichiometry for this process is defined as:

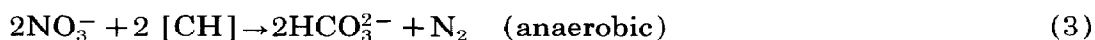
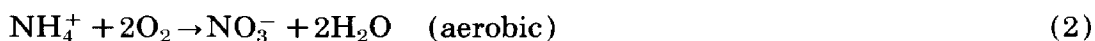


One of the immediately detectable disadvantages of  $\text{CaCl}_2$  precipitation is the potential for high chloride concentrations, which may be inhibitory to microbial populations and pose discharge permit difficulties.

A process sequence employing aerobic degradation followed by anaerobic treatment is advantageous because it allows concurrent conversion of  $\text{NH}_4^+$  to  $\text{NO}_3^-$  (aerobically),  $\text{NO}_3^-$  to  $\text{N}_2$  (anaerobically) and organic species to  $\text{CO}_2$  (both).

Another process sequence considered utilizes three separate microbial steps. The first step anaerobically degrades organic species and nitrate. This, in turn, is followed by an aerobic process in which the ammonium is converted to nitrate with some carbon mineralization. This second step is followed by another anaerobic step in which additional carbon is metabolized, and nitrate is converted to free nitrogen ( $\text{N}_2$ ).

The second precipitant evaluated was  $\text{Ca}(\text{NO}_3)_2$ . Nitrate ion has the advantage of being metabolizable by microorganisms [2]. Pertinent stoichiometry (simplified) in this case is:



One of the process sequences considered includes using calcium nitrate as a precipitant followed by either aerobic or anaerobic degradation; another uses the same precipitation step, with sequential anaerobic/aerobic/anaerobic microbial treatment following.

Process sequences utilizing lime ( $\text{CaO}$ ) for sulfate precipitation were also evaluated. Lime has low solubility in water [3]. Hence, its use was not considered for *in situ* precipitation studies because of anticipated problems with delivery and transport through the soil.  $\text{CaO}$  was considered for surface treatment systems, especially for the lower contaminant level found at the fringe of the ammonium sulfate plume.

The last process sequence considered incorporates mixed chloride and nitrate precipitants for sulfate removal. This step would be followed by anaerobic treatment, where some mineralization of organic species is expected. Subse-

quently, base is added and the resulting free ammonia is stripped from the system. Recarbonation or acid addition reduces pH for aerobic treatment [3].

### Analytical methods

Total Organic Carbon (TOC) assays were carried out using an OI Corporation Model 700 TOC analyzer. Anion analysis entailed the use of a Hamilton anion column with a Perkin-Elmer HPLC. Gas-phase analyses were performed on a HP 5880A chromatograph equipped with a thermal conductivity detector. All other assays were performed in accordance with *Standard Methods* [4].

### Sulfate precipitation studies

#### *Batch experiments*

The floc settling rate of calcium sulfate precipitate formation in groundwater samples from monitoring well 16 has been studied. To simulate contaminant levels between well 16 and the plume fringe, dilution of groundwater with an equal quantity of deionized (DI) water was employed. A 50 ml volume of groundwater or groundwater/DI water mixture was placed in erlenmeyer flasks to which fixed amounts of calcium chloride solution were added. The samples were vacuum filtered through 0.7  $\mu\text{m}$  glass fiber filters after 15, 30, 45 and 60 minutes and, subsequently, after 3 and 24 hours (Table 2).

The majority of precipitation occurred within 30 to 60 minutes after calcium addition; complete precipitation required approximately 24 hours. Precipitation rates were heavily influenced by other groundwater constituents. Ionic polymer shards, either dissolved or in colloidal suspension, most likely acted

TABLE 2

Sulfate precipitation kinetics

Undiluted groundwater				1:1Dilution of groundwater		
Time (h)	Sulfate conc. change (g/l)	Rate of PPT (g/l h)	Cumulative sulfate conc. change (g/l)	Sulfate conc. change (g/l)	Rate of PPT (g/l h)	Cumulative sulfate conc. change (g/l)
0	0.00	-	0.00	0.00	-	0.00
0.25	4.69	18.77	4.69	2.44	9.77	2.44
0.50	0.53	2.10	5.22	0.29	1.16	2.73
0.75	0.32	1.29	5.54	0.23	0.90	2.96
1.00	0.25	0.99	5.79	0.22	0.87	3.17
3.00	0.28	0.14	6.07	0.29	0.15	3.47
24	2.26	0.11	8.32	2.17	0.10	5.63

as flocculation aids. Alternatively, other organic species may have provided nucleation sites for calcium sulfate crystallization. This conclusion was substantiated by experiments with pure aqueous ammonium sulfate solutions. Precipitate resulting from AS solutions formed crystals which grew on any available surface, the glassware in this case, while that from groundwater yielded solids which were best described as a floc. Many small crystals were quickly formed in the solution itself. External seeds for crystal formation were not needed.

### Continuous flow experiments

Additional studies have examined *in situ* precipitation utilizing a packed soil channel designed to simulate field conditions. A 4 ft × 4 ft × 4 in, plexiglass channel was constructed; this channel had provisions for continuous flow of groundwater and subsurface injection of calcium precipitant solution. The channel experiments have allowed the effects of *in situ* calcium sulfate formation on the hydrology of the soil system to be evaluated.

The present flow system was operated at three different groundwater velocities: 10, 5, and 2.5 in. per day. Times of transition were determined when the soil bed became impermeable to a given linear velocity; flow was then stepped down to the next increment. Hydraulic gradient, TOC, anion concentrations, and pH were monitored daily.

Hydraulic gradient (difference in static head between inlet and outlet) was measured with a vernier scale cathetometer. Sulfate ion removal levels were often close to the solubility limit of calcium sulfate.

The channel became unable to accommodate flow of 10 inches per day after approximately 16 days. Reductions in sulfate ion concentrations averaged 20 to 30% during this time period. TDS reductions were inconsistent because the system was still in the breakthrough phase of transient operation. The flow was reduced by half and the experiment continued. The soil systems became relatively impermeable to this flow after 18 more days. Performance was not very different from the first phase of operation.

The flow velocity was halved once again and the experiment continued. Hydraulic gradient tended to become relatively stable once the static-head difference approached 55 cm, or approximately 75% reduction in permeability (Fig. 1). In this stage of operation, sulfate ion removal was between 70 and 90%; TDS reduction ranged from approximately 50–70%. Steady-state results were variable; these were likely dependent on ambient temperature and distribution of the precipitant solution within the channel. On a relative basis, the mass flux of sulfate ion leaving the soil channel was less than 5% of influent (Fig. 2).

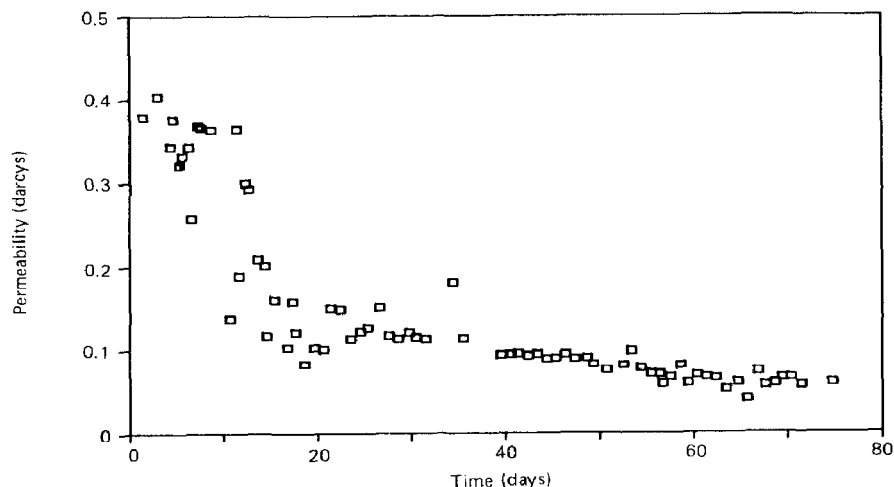


Fig. 1. Precipitation effects on permeability: soil channel experiment.

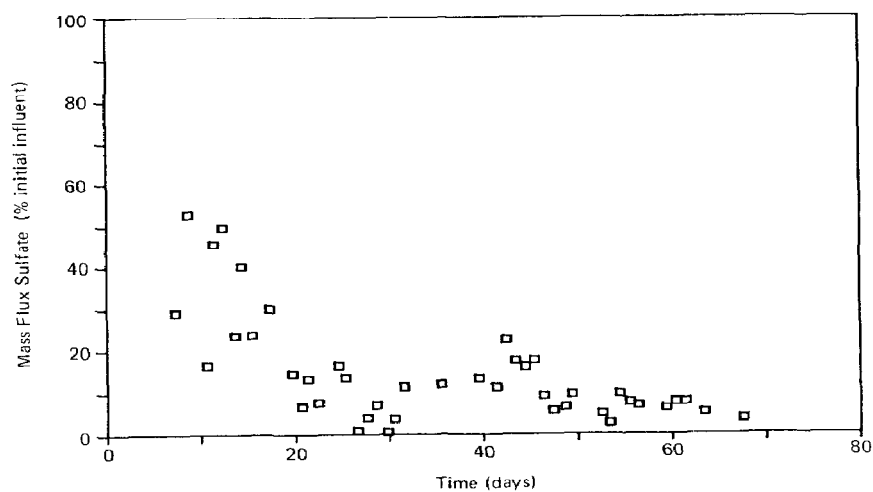


Fig. 2. Relative mass flux of sulfate: soil channel experiment.

### Batch aerobic microbial degradation studies

Shake-flask experiments were developed to assess the extent of total organic carbon removal and nitrification by aerobic bacteria under batch conditions [5,6]. Hence, a factorial arrangement allowing use of standard statistical methods, such as analysis of variance and residuals, was developed to isolate sources of error.

The first set of experiments (AE102887) was designed to assess the effects of overall organic and ammonia species loadings on the degree of TOC removal

by a mixed microbial population. In addition, the experimental design allowed observation of potential co-metabolic processes by using different ratios of organic carbon from groundwater (LOC) to organic carbon from sucrose (SOC). Five different loadings (100 to 1500 mg/l TOC) and five different SOC:LOC ratios (ranging from all sucrose to all groundwater) were considered, creating 25 different experimental conditions.

Each reactor was comprised of a 250 ml erlenmeyer flask with foam stoppers; a 100 ml total fluid volume was used. The flasks were inoculated with 20 ml of seed culture obtained from Somerset-Raritan Valley Sewage Treatment Authority (SRVSA), grown on sucrose for 24 hr in a 3 l fermentor prior to use; 20 ml of nutrient medium/buffer also were added. The remaining 60 ml of reactor volume was a substrate mixture of groundwater from well 16 (Table 1), sucrose, and deionized water, the exact amounts of which were determined by the loading and ratio selected.

The flasks were prepared and placed on gyratory shakers at 175 rpm and 25°C. At 12 h intervals, the pH of each flask was measured and adjusted to between 7.0 and 7.2 with 6N HCl or 6N NaOH as necessary. The experiment was carried out for 6 days or until three consecutive equal pH measurements were obtained. The flasks were removed from the shaker, filtered, and analyzed for TIC, TOC and ammonia.

Figure 3 illustrates the variation of percent LOC removal with total loading and SOC:LOC (S:L) ratio. Removal of ammonia compounds ranged from nil to nearly 100%; lower TOC loadings tended to favor higher removal. Symbols listed as "LOC" on the figures indicate substrate source was groundwater only. At higher levels of organic carbon, the degree of ammonia removal decreased sharply. Replication within a given case was quite good for the most part. Dis-

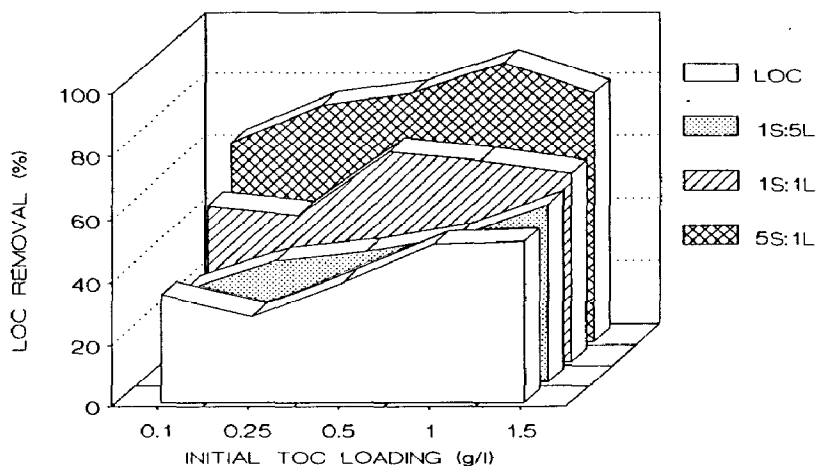


Fig. 3. Aerobic batch study: ammonia present (AE102887).



parities are likely because of pH fluctuations in the flasks. Unfortunately, the large number of test cases did not permit the use of automated pH controllers. The following conclusions were based on statistical analysis:

#### LOC removal

- A 5:1 ratio of SOC to groundwater appeared to work best.
- A SOC:LOC ratio of 1:1 and LOC only were not statistically different in terms of overall LOC removal.
- A SOC:LOC ratio of 1:5 performed most poorly.
- A mass fraction of SOC smaller than 0.5 had little impact on LOC removal.
- The 1500 mg/l total loading was statistically better than the rest.
- TOC loadings of 1000, 500, and 250 mg/l did not exhibit statistically significant differences in either TOC or LOC removal.
- LOC removal averaged over 65% at total loadings higher than 500 mg/l.

#### Ammonia species removal

- Minimal at total organic carbon loadings greater than 250 mg/l.
- Averaged 54 and 90% for 250 mg/l and 100 mg/l total loadings, respectively.

The second set of aerobic batch experiments (AE112887) was designed to determine whether the presence of ammonia compounds enhances or hinders the microbial degradation process. This set of experiments employed a similar format to the initial set. The major differences between the two matrix experiments were the pretreatment of the groundwater and the types of assays performed.

Waste material from well 16 (Table 1) was treated with sufficient dried lime (CaO) to raise the pH to approximately 12, evolving free ammonia while precipitating calcium sulfate (CaSO<sub>4</sub>). Subsequently, the groundwater was filtered, and the pH adjusted to approximately 5 with concentrated hydrochloric

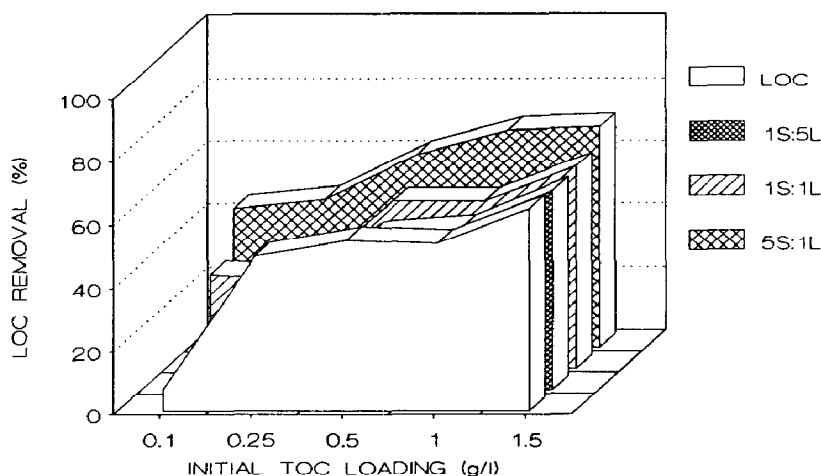


Fig. 4. Aerobic batch study: ammonia absent (AE112887).

acid, transforming carbonates and bicarbonates to gaseous carbon dioxide. The liquid was sparged with nitrogen to free entrained and dissolved gases. The resulting groundwater had a TOC of 3000 mg/l, a TIC of 20 mg/l and an ammonium content of 4 mg/l. The preparation of nutrient/buffer medium, sucrose co-substrate solution, and the seed culture was carried out as described earlier. Maintenance of pH at 12 h intervals was also carried out as before, employing 6N HCl or 6N NaOH as needed. The ambient conditions during this study were the same as the previous set.

Removal of total organic carbon ranged from approximately 10 to 90% and, as in the last experiment, tended to be favored by high loadings and high SOC:LOC ratios (Fig. 4). Removal of groundwater organic species ranged between 10 and 65%, with the highest removals occurring at high overall loadings. Poor results at low TOC loadings are likely a consequence of microbial starvation. However, it appeared the removal of LOC was independent of the SOC loading when the overall loading was greater than or equal to 500 mg/l. The same statistical tests were performed as in Experiment AE102887, and yielded the following conclusions.

LOC removal was

- between 45 and 65% at loadings higher than 500 mg/l;
- independent of SOC;
- on comparison to matrix experiment one, LOC percent removal appeared to be independent of ammonia load at high initial TOC loadings, at other loadings, performance seemed slightly poorer;
- very poor at low overall loadings.

The third experimental set (AE011088) utilized shake flasks operated in a semi-continuous manner, acclimating a mixed microbial culture to enhance LOC reductions. The method chosen for this experiment employed the addition of a small amount of SOC to reactors at 2-day intervals. This technique allows maintenance of the culture on SOC while acclimation takes place. Once the SOC is fully metabolized, further adaptation to LOC can occur [7]. Groundwater from well 16 (Table 1) was prepared in the same manner as for experimental sets 1 and 2. The pH of the sulfate-free groundwater was adjusted to 7.0 before the beginning of study. There were six different experimental conditions, three of which used groundwater free of ammonium and carbonate, while the remainder had both species present. Three replicates totaling 18 flasks were used.

The reactor size was twice that used in the other aerobic studies, with a total volume of 200 ml. Each flask contained 50 ml of a nutrient/buffer solution of the same type as used earlier and 20 ml of seed culture from SRVSA; the remaining 130 ml was a mixture of groundwater and sucrose co-substrate solution. The experiment had a 6-day duration, with pH correction every 12 h. In addition, each flask was sampled at 2-day intervals, with the addition of 50 mg sucrose in a volume of deionized water sufficient to make up for any loss in

total volume. Samples collected were filtered and assayed for total organic and inorganic as well as for ammonia nitrogen.

Results were very positive. LOC removal ranged from 77% for cases with no initial sucrose or ammonia nitrogen to 79% for initial sucrose and no ammonia nitrogen. SOC controls showed TOC removal in excess of 90%. The 1:5 SOC:LOC ratio reactors worked well both with and without ammonia species present. The all LOC cases, while not performing as well as the 1:5 SOC:LOC ratio cases, also enjoyed favorable results in the presence and absence of ammonia nitrogen. The results indicated that acclimation of a microbial population suitable for degrading LOC could be developed in semi-continuous operation, although upon comparison with the earlier studies, acclimation does not appear to be a requirement to attain reasonable removals. This experiment was repeated as AE022588; similar results were obtained.

### **Anaerobic batch degradation studies**

This study addressed anaerobic degradation of organic species in the ammonia sulfate waste plume. In this case, there were four total loadings and five ratios of leachate organic carbon (LOC) to organic carbon as ethanol (EOC) in duplicate.

Each shake was assembled using a 60 ml amber crimp top bottle with re-sealing Hycar septa. An anaerobic seed culture was obtained as digester sludge from the Berkeley Heights Sewage Treatment Facility; industrial wastes are not treated at this plant.

The sludge was filtered through cheese cloth (approximate 1 mm mesh) under carbon dioxide to remove large particulates. A crimp-top bottle was purged with carbon dioxide for 15 s, after which 10 ml of filtered seed culture and 10 ml of nutrient were added. The septum was quickly put in place and crimped shut. Organic carbon as ethanol, in appropriate concentration was used as cosubstrate.

LOC was provided as groundwater from well 16, and was pretreated with a 50:50 mixture of calcium as  $\text{CaCl}_2$  and  $\text{Ca}(\text{NO}_3)_2$  to remove sulfates. After filtration, the material was sparged with nitrogen gas to remove any entrained and dissolved air. The resulting groundwater mixture had 6700 mg/l ammonia nitrogen and 140 mg/l  $\text{NO}_3^-$ , with a TIC and TOC of 700 and 1900 mg/l, respectively. The mixture of ethanol and groundwater substrates was prepared such that the total volume was 20 ml. The substrate mixture was injected through the septum; the shake flask was placed on a gyratory shaker, at 150 rpm and 30°C, for 3 weeks.

Analyses carried out on the anaerobic shake flasks included pH, TOC and

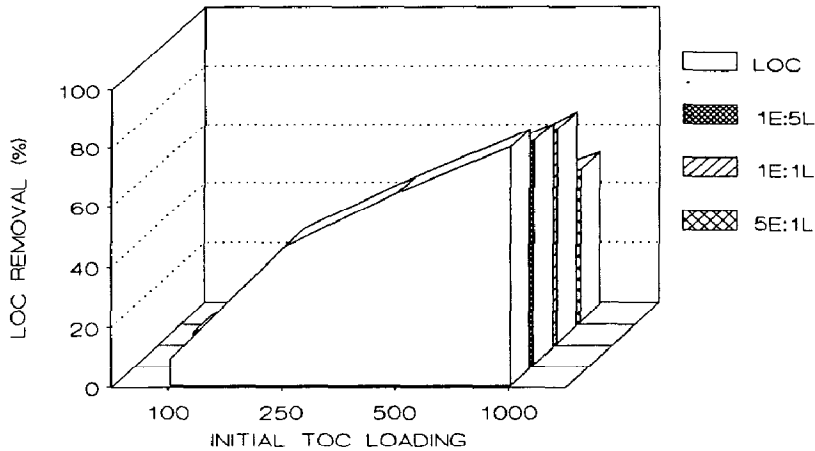


Fig. 5. Anaerobic batch study (AN120987).

TIC. Ammonia assays were carried out on random samples, as reduced nitrogen was not expected to be metabolized during this experiment.

The extent of anaerobic degradation varied with initial loading in the same manner as the analogous aerobic batch studies (Fig. 5). In this case, the difference in removal levels between the highest and lowest loadings encountered was much greater. In addition, it appears that EOC-only cases (controls) did not perform as well as those with solely LOC. This result can be attributed to the high buffering capacity of the LOC substrate, which allowed acid production processes to operate longer than the essentially neutral EOC substrate. Another factor may be the significantly higher nitrate load from groundwater pretreatment; this would enhance gas production as well as allow the process to move further towards completion.

The removal of LOC was independent of EOC in all cases. The statistical tests performed on the similar aerobic batch studies were repeated, with the following results:

#### LOC removal

- is between 40 and 80% at loadings greater than or equal to 500 mg/l;
- decreases sharply at total loadings below 500 mg/l;
- is independent of EOC;
- is independent of ammonia load;
- is close to zero at very low loadings;
- disparity between low and high EOC:LOC ratios increases towards higher initial loadings;
- spread between highest and lowest removals increases at higher mass fractions LOC.

#### TOC removal

- parallels LOC removal;

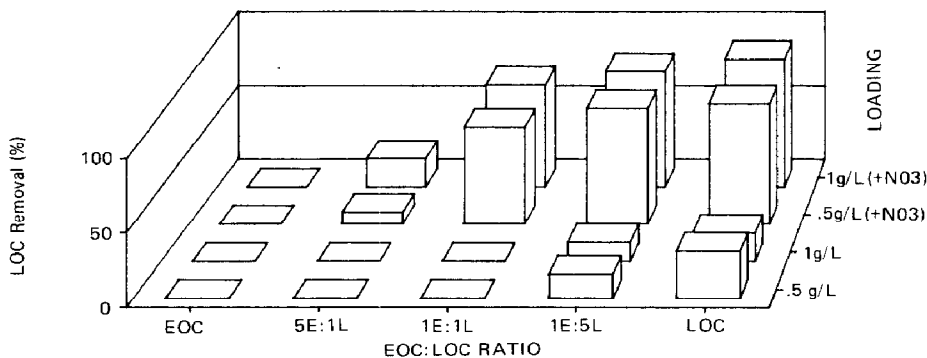


Fig. 6. Anaerobic batch studies three and four: AN030488 - no nitrate, AN040888 - excess nitrate.

- disparity becomes greater at higher mass fractions of LOC.

Later studies (AN030488 and AN040888) were aimed at determining whether denitrification was the dominant metabolic pathway for the anaerobic microorganisms. Experiment AN030488 used sufficient nitrate for nutrient purposes. Results indicated LOC removals of approximately 20%. The experimental design was repeated (AN040888) using excess nitrate as  $\text{Ca}(\text{NO}_3)_2$ . LOC removals of 85 to 90% were observed. Higher LOC conversion was favored by higher initial TOC loading (Fig. 6).

### Anaerobic soil columns

#### *Experimental and mechanical design*

Soil based studies of anaerobic degradation have been conducted in parallel with other studies. Four 3 in. diameter, 2 ft long columns have been packed with clean soil from the disposal area in an upflow configuration. Columns were wrapped with blackout cloth to control photosynthesis. Two substrate concentration regimes have been considered: groundwater from wells 32 and 16.

As in the other anaerobic experiments, the column studies have been carried out using sulfate-free groundwater sparged with nitrogen. Seed cultures were obtained from the Berkeley Heights Sewage Authority; they were filtered prior to introduction to the columns. Acclimation was allowed to proceed naturally within the soil matrix. Bulk influent composition consisted of 200 ml of contaminated groundwater daily with a 30 ml aliquot of nutrient solution added via injection every three days.

The head gas from each column was sampled and measured by gas chromatography. The liquid effluent was assayed for pH, ammonia nitrogen, total organic and inorganic carbon (TOC/TIC).

### Columns fed with well 16

Considerable gas production and declines in total organic carbon were evident for the columns operating on groundwater from well 16. Fig. 7 shows the TOC/TIC data; replication among a given feed level was excellent. Results from effluent TOC assays indicate the typical breakthrough response, followed by a steady decline to concentrations between 250 and 300 mg/l with removal of over 90%. Gas production was high and relatively constant; however, no significant methane production had occurred, indicating little methanogenic activity. Headspace analysis indicates that the bulk of the gas phase was comprised of carbon dioxide and nitrogen. Effluent pH, for the most part, has been between 7.4 and 7.9 for both columns.

The effluent total organic carbon in columns 5 and 6 (Fig. 7) showed a marked increase during week eleven, preceded by a rise in pH to approximately 8.9 and a drastic decrease in gas production. It is suspected that the increase in pH may have caused production of gaseous ammonia, which is highly toxic to the microbes. Another possible explanation involves a shift in the microbial population. The pH of the influent groundwater was adjusted downward to 6.95 to control free ammonia production. After adjustment, gas production rose dramatically and pH fell to reasonable levels, accompanied by a decline in effluent TOC, indicating slow recovery of the microbial population.

The column experiment was repeated. As in the earlier study, ammonia tox-

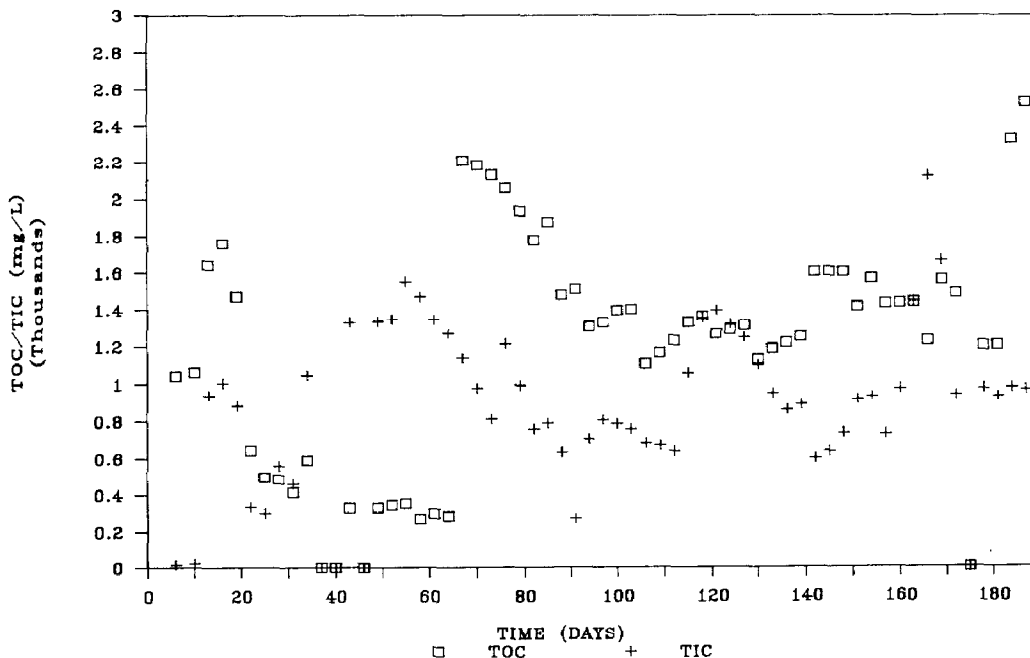


Fig. 7. Soil column experiment: TOC and TIC in effluent from column 5 fed with groundwater from well 16.

icity tended to play a role in column failure. In each case, an ammonia event was preceded by a rise in pH. The increase in alkalinity is inherent in denitrifying processes, as depletion of nitrate ion effectively removes nitric acid from the system, which, in turn, causes pH to increase. Coupled with the strong inorganic carbon load in the water, the two factors which place an upward pressure on pH have had negative ramifications for the microbial population.

The precise pH control necessary to implement soil based treatment makes an *in situ* application unlikely. An alternative scenario which has greater promise would be an above ground denitrification process.

### Conceptual process design

#### *Process flow diagram*

The experiments conducted to date have pointed to a number of potential treatment processes. Of these, the most promising seems to be a sequence which includes sulfate precipitation, as the first step, followed by above-ground aerobic treatment or anaerobic denitrification.

The first step in this process pathway would be a sulfate removal step. The preferred calcium precipitant is calcium nitrate, because it does not cause problems on injection into a soil system, and residual nitrate can be metabolized in subsequent microbial processes.

The next process step is recovery of low-sulfate groundwater via pumping, after which organic species in the AS waste may be treated above ground. Both aerobic and anaerobic batch studies have given promising results.

#### *Location of pilot facility*

The selection of proposed pilot process placement was based on a number of important factors. First, relatively high sulfate ion concentrations in contaminated groundwater are required to achieve *in situ* precipitation of calcium sulfate. This factor restricts placement to a concentrated portion of the plume, as shown in Fig. 8.

Another important consideration is the method of hydraulic control. At depth, physical separation of the study area from the plume is not possible. The most practical method, therefore, is flow control via limited pumping.

It also was determined that the study area should be placed such that the plume concentration vector is aligned with the velocity vector to avoid potentially confounding crossflows. The dimensions of the pilot study area were chosen as 50 ft by 35 ft. Care had to be taken to make the operating area large enough to yield statistically valid results, yet small enough to be controlled reasonably with a minimum of maintenance and analytical effort. With these issues addressed, it was possible to select a physical location for the pilot facility.

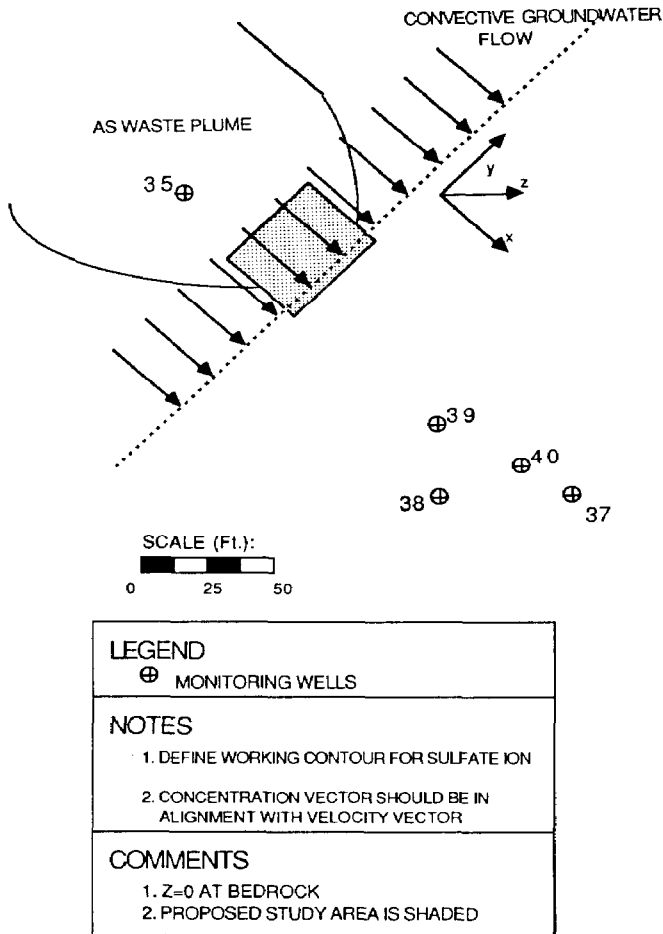


Fig. 8. Location of proposed pilot study site.

### Conceptual operation

A sample configuration for pilot-scale evaluation is shown in Fig. 9. The sulfate removal area consists of injection points for calcium nitrate precipitant solution, and wells designed to increase the effective linear velocity of the groundwater are provided for recovery. A number of well points would be distributed throughout the area for sampling purposes to define process performance. The injection points at the opposite ends of the study area would feed precipitant at a high rate; this permits infiltration-limiting mounding to occur. The inner points would inject  $\text{Ca}(\text{NO}_3)_2$  at a lower rate.

Data of interest should include static water level and cumulative volume yield from the recovery wells, as well as TOC, TDS, ammonia-nitrogen, and anion concentrations.



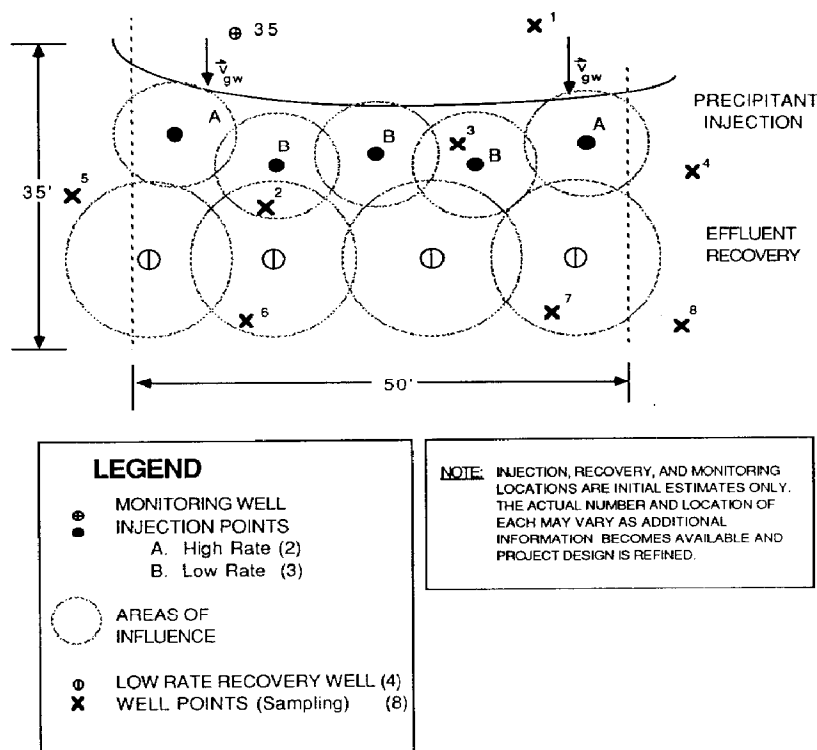


Fig. 9. Potential pilot plant layout.

## Conclusions

The experimental effort has yielded a number of important observations. Sulfate precipitation studies, have shown that batch precipitation of groundwater occurs in the expected manner. The exact calcium solution used has little effect on the kinetics of sulfate precipitation. The crystal-size and floc-settling characteristics of  $\text{CaSO}_4$  precipitation from groundwater indicate that *in situ* application is feasible. Soil-based precipitation studies have supported this hypothesis.

Aerobic batch studies have shown that substantial removal of organic carbon in AS waste-contaminated groundwater is possible. It appears that co-substrate is not a requirement for practical operation. In addition, the presence of ammonium ion and inorganic carbon has minimal impact on the ability of microbial processes to degrade the organic groundwater contaminants. An acclimated culture can be developed for treatment of contaminated groundwater.

Anaerobic batch studies indicated that LOC is readily degradable by anaerobic microorganisms, without a need for co-substrate. LOC removals of up to 90% were attained in a three week study at 30°C.

Anaerobic laboratory soil columns operated on high strength groundwater had very promising results; however, column failure was likely if pH rose sufficiently to produce free ammonia. The degree of pH control necessary to successful treatment is not practical for *in situ* application.

Process design considerations tend to favor an *in situ* process, although a surface treatment scenario is also possible. It appears that sulfate removal for these processes is a successful preliminary step and can be followed by microbial treatment. The precise order of microbial treatment appears to be independent of LOC removal efficiency; good results have been obtained both aerobically and anaerobically. With further optimization, only one microbial treatment step may be necessary. For an *in situ* application, sulfate precipitation, followed by groundwater recovery and above-ground microbial treatment appears most reasonable.

### Notation

AS	Ammonium sulfate
COD	Chemical oxygen demand (mg/l)
EOC	Organic carbon as ethanol (mg/l)
E:L	EOC:LOC ratio
LOC	Organic carbon in groundwater (mg/l)
SOC	Organic carbon as sucrose (mg/l)
S:L	SOC:LOC ratio
TDS	Total dissolved solids (mg/l)
TIC	Total inorganic carbon (mg/l)
TKN	Total Kjeldahl nitrogen (mg/l)
TOC	Total organic carbon (mg/l)
TSS	Total suspended solids (mg/l)

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### References

- 1 R.E. Olson and D.E. Daniel, Measurement of the hydraulic conductivity of fine grained soils, In: Permeability and Groundwater Contaminant Transport, ASTM Special Technical Publication 746, Philadelphia, PA, 1981, p. 18.
- 2 T.D. Brock and M.T. Madigan, Biology of Microorganisms, Prentice Hall, Englewood Cliffs, NJ, 1988.

- 3 R.C. Weast (Ed.), CRC Handbook of Chemistry and Physics 60th edn., CRC Press, Boca Raton, FL, 1980.
- 4 A.G. Greenberg, R.R. Trussel and L.S. Clesceri, Standard Methods for the Examination of Water and Wastewater, Port City Press, Baltimore, MD, 1985.
- 5 D.S. Kosson, I.A. Legiec, E.A. Dienemann and R.C. Ahlert, Operation and control of a soil-based microbial treatment system, AIChE Summer National Meeting, Boston, MA, August 1986.
- 6 E.S. Venkatarami and R.C. Ahlert, Acclimated mixed microbial responses to organic species in industrial landfill leachate, J. Hazardous Materials, 10 (1985) 1.
- 7 E.S. Venkatarami and R.C. Ahlert, Role of cometabolism in biological oxidation of synthetic compounds, Biotechnol. Bioeng., 27 (1985) 1306.